COORDINATION CHEMISTRY OF THE CYANATE, THIOCYANATE, AND SELENOCYANATE IONS

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I. Introduction

The cyanate, thiocyanate, and selenocyanate ions are pseudohalides (*106*) and have also been called *chalcogenocyanates.* They have the general formula NCX^- ($X = O, S, Se$, or Te) and they are all potentially ambidentate, that is, they can form a coordinate bond to a Lewis acid through either N or X. Thus, the thiocyanate ion, for example, will form either N- or S-bonded complexes depending on the nature of the metal, and this preference may be modified by the presence of other ligands or by whether the complex is in the solid state or in solution. The chalcogenocyanates can also be present in a variety of bridging modes. There are many examples of such varied coordination behavior of the thiocyanate ion, and several different, sometimes conflicting, explanations have been put forward. The remaining chalcogenocyanates have not been studied to the same extent but they also show similar characteristics and have attracted a largely similar set of explanations. It has recently become apparent that kinetic factors (i.e., through which of the available atoms does the chalcogenocyanate act as a nucleophile?) as well as the thermodynamic stability of the final product need to be considered in providing a reasoned account of the coordination chemistry of these ions.

This review, therefore, is concerned with the structural information in the literature relating to complexes formed between these ions and transition metal ions, with the similar kinetic data where these relate to a known mode of coordination, and, finally, with assessing the validity of some of the explanations, initially offered for a select group of complexes, against a broader canvas. The task of reviewing the literature has been complicated by the fact that the thiocyanate ion is stable and is readily available to coordination chemists, so that, of the ions in question, it, in particular, has been widely used as a ligand without the main purpose of the investigation necessarily relating to its mode of coordination. The compilation of material has been therefore somewhat selective, concentrating more on reliable structural data than on the recording of the existence of compounds with unconfirmed bonding modes. For these reasons the extensive literature relating to solvent extraction of thiocyanate complexes has also been ignored.

Previously, reviews have appeared on the crystal chemistry of thiocyanate and selenocyanate coordination compounds (*612*), selenocyanate complexes (*334*), the stability and formation of thiocyanate complexes (*637*), the chalcogenocyanates in coordination chemistry (*474*), and the infrared spectra of thiocyanate and related complexes (*57*). Other reviews that are largely devoted to aspects of the chemistry of the chalcogenocyanates have appeared on organometallic pseudohalides of the main group elements (*479*, *722*), nitrogen-containing pseudohalide ligands (*86*), ambidentate ligands (*140*, *141*, *576*), and linkage isomerism (*303*). Reviews on sulfur-containing ligands (*421*) or ligands containing Group VI donors (*497*) have included sections on thiocyanate and selenocyanate complexes. Intra- and intermolecular bonding and structure in NCO$^-$ and NCS$^-$ compounds, and some related pseudohalides, have been reviewed (*398*).

The reactivity of ambidentate ligands toward organic centers has been reviewed (*679*). The review by Beck and Fehlhammer (*86*) includes a most useful section on methods used for the preparation of these complexes, and this aspect will not be emphasized here. The principles of formation of selenocyanate complexes have been reviewed (*682*).

NOMENCLATURE

An N-bonded thiocyanate or isothiocyanate will be termed an *N*-thiocyanato complex and its formula will be written M—NCS, and an *S*-bonded or normal thiocyanate will be termed an *S*-thiocyanato complex, written M—SCN; the corresponding formalism will apply to the other ions. Where the mode of coordination is not known the complex will be termed thiocyanate and written M—CNS. Beck and Fehlhammer (*86*) have rightly objected to this "atom inversion, against chemical knowledge," but it, nevertheless, remains a convenient shorthand and is not likely to cause confusion in this review which contains few, if any, references to fulminates, thiofulminates, etc.

The following abbreviations for chemical names will be used throughout the text.

acacH	acetylacetone
am	ammonia (or occasionally an amine)
an	aniline
aq	aquated, H_2O
Ar	aryl or arene (ArH)
bipy	2,2′-bipyridyl
bu	butyl (prefix *n*, *i*, or *t* for normal, iso, or tertiary butyl, repectively)
can	chloroaniline
Cp	cyclopentadiene, C_5H_5
Dben	*N*,*N*′-dibenzylethylenediamine
DH_2	dimethylglyoxime
diars	*o*-phenylenebisdimethylarsine, o-$C_6H_4(AsMe_2)_2$
DMA	*N*,*N*-dimethylacetamide, $CH_3CON(CH_3)_2$
DMF	*N*,*N*-dimethylformamide, $HCONMe_2$
DMSO	dimethylsulfoxide, Me_2SO
dpm	diphenylphosphinomethane
en	ethylenediamine, $H_2NCH_2CH_2NH_2$
Et	Ethyl

fan	fluoroaniline
HMPA	hexamethylphosphoramide, $(Me_2N)_3PO$
L	ligand
lut	lutidine
M	central (usually metal) atom in compound
Mben	*N*-benzylethylenediamine
Me	methyl
Me_6tren	tris-(2-dimethylaminoethyl)amine, $N(CH_2CH_2NMe_2)_3$
$NTAH_3$	nitrilotriacetic acid, $N(CH_2COOH)_3$
8-oxH	8-hydroxyquinoline
Ph	phenyl, C_6H_5
phen	1,10-phenanthroline
pic	picoline
pn	propylenediamine (1,2-diaminopropane)
PNP	bis-(2-diphenylphosphinoethyl)amine, $HN(CH_2CH_2PPh_2)_2$
Pr	propyl (prefix *i* for isopropyl)
py	pyridine
QAS	tris-(2-diphenylarsinophenyl)arsine, $As(o\text{-}C_6H_4AsPh_2)_3$
QP	tris-(2-diphenylphosphinophenyl)phosphine, $P(o\text{-}C_6H_4PPh_2)_3$
quin	quinoline
R	alkyl or aryl group
TAN	tris-(2-diphenylarsinoethyl)amine, $N(CH_2CH_2AsPh_2)_3$
TAP	tris-(3-dimethylarsinopropyl)phosphine, $P(CH_2CH_2CH_2AsMe_2)_3$
TAS	bis-(3-dimethylarsinopropyl)methylarsine, $MeAs(CH_2CH_2CH_2AsMe_2)_2$
tet a	*trans*-1,4,8,11-tetraazacyclotetradecane
tet b	*cis*-1,4,8,11-tetraazacyclotetradecane
d tet	3,3-dimethyl-1,5,8,11-tetraazacyclotrideca-1-ene
t tet	2,4,4-trimethyl-1,5,8,11-tetraazacyclotrideca-1-ene
THF	tetrahydrofuran
TMED	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMU	*N*,*N*,*N*′,*N*′-tetramethylurea
tn	1,3-diaminopropane(trimethylenediamine)
tol	toluidine
TPN	tris-(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$
tren	tris-(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$
trien	triethylenetetraamine, $(CH_2NHCH_2CH_2NH_2)_2$
TSN	tris-(2-methylthiomethyl)amine, $N(CH_2CH_2SMe)_3$
TSeP	tris-(2-methylselenophenyl)phosphine, $P(o\text{-}C_6H_4SeMe)_3$
TSP	tris-(2-methylthiophenyl)phosphine, $P(o\text{-}C_6H_4SeMe)_3$
TTA	tenoyltrifluoroacetone, $C_4H_3SCOCH_2COCF_3$
tu	thiourea
urt	urotropine
X	halogen or pseudohalogen

II. The Chalcogenocyanate Ions

A. PREPARATION

The ionic compounds are readily available (except for tellurocyanates) and their preparation will not be reviewed here. They can generally be prepared by the reaction of a cyanide with the appropriate Group VI element. Thus, oxidation of potassium cyanide gives potassium cyanate (*323*), whereas treatment with free sulfur or a polysulfide gives potassium thiocyanate (*323*); potassium selenocyanate is formed from the similar reaction with selenium (*323*). The use of large cations, such as tetraethylammonium (*260*) or tetraphenylarsonium (*44*), is apparently necessary for the reaction between cyanide and tellurium to proceed to completion: attempts to prepare potassium tellurocyanate by the aforementioned reaction were unsuccessful (*347*).

Potassium cyanate is readily hydrolyzed, and, for the stoichiometric reaction,

$$KNCO + 2H^+ + H_2O \longrightarrow K^+ + NH_4^+ + CO_2$$

a hydrogen ion concentration of greater than 0.06 *M* is required to suppress side reactions (*753*). The remaining salts are hydrolyzed to give varying proportions of H_2X or free X (X = S, Se, or Te) depending on X and on the conditions. Acid hydrolysis of potassium thiocyanate can give appreciable quantities of COS. The decomposition of $NCSe^-$ by H^+ to give free Se is hindered in the presence of soft acids [in the Pearson sense (*596*, *597*)] and encouraged by hard acids, and it is suggested that the soft acids compete with H^+ to attack at the selenium (*74*). Lodzinska (*499*) has noted the interdependence of pH and certain cations in affecting the stability of KNCSe. A further indication that the nature of the cation is important in determining the stability of these species is given by Songstad and Stangeland (*695*) who have shown that the ultraviolet spectra of NCS^- and $NCSe^-$ in CH_3CN are very dependent on the cation employed, and that the deselenation reaction with arylphosphines to give the corresponding phosphine selenide, originally reported by Nicpon and Meek (*564*), also goes more readily in the presence of the more electrophilic cations. Hamada (*365*) observed that the standard free energies of formation of NCX^- (X = O, S, Se) increased linearly with the size of X.

B. MOLECULAR GEOMETRY

Details of interatomic distances and bond angles within the ions and in their hydracids are given in Table I. Similar parameters will be given for complexes of these ions in Section IV. Iqbal (*398*) has collated data on the lattice parameters of the ionic cyanates and thiocyanates. The ions are linear, although in many cases this is not confirmed by direct measurement but is assumed for the purposes of the subsequent calculation. Increasingly, thiocyanates of Group I and II metals are

TABLE I

INTERATOMIC DISTANCES AND BOND ANGLES OF CHALCOGENOCYANATE IONS

Compound	N—C (Å)	C—X (Å)	NCX angle	H—NC angle	Method	References
HNCO	1.19 ± 0.03	1.19 ± 0.03	180°	125° (est.)	ED	(*274, 378*)
	1.207 ± 0.01	1.171 ± 0.01	180°	128°5′ ± 30′	Microwave and IR	(*419*)
HNCS	1.216_4 ± 0.007	1.560_5 ± 0.003	180°	134°59′ ± 10′	mm-wave spec.	(*434*)
HSCN	1.21	1.61	180°	145°	Estimated	(*772*)
HNCSe	1.22	1.75	180°	140°	Estimated	(*772*)
NCO^-	1.17	1.23	180°	—	Calc. from force constants	(*512*)
$NCSe^-$	1.16	1.79	180°	—	Calc. from force constants	(*772*)
$NCTe^-$	1.16	2.03	180°	—	Estimated	(*772*)
KNCS	1.149 ± 0.014	1.689 ± 0.013	178.3° ± 1.2	—	X-ray	(*21*)
NH_4NCS	1.15	1.63	180°	—	X-ray	(*792*)
KNCSe	1.17 ± 0.026	1.829 ± 0.025	178.8° ± 2.5	—	X-ray	(*710*)

used in the X-ray study of complexes of cyclic ethers (e.g., *233*) but these results have not been included.

C. MOLECULAR VIBRATIONS AND FORCE CONSTANTS

The chalcogenocyanate ions are linear triatomic species belonging to the point group $C_{\infty v}$. The three normal modes of vibration shown in Fig. 1 are both infrared and Raman active. The vibrations are commonly described as though group frequencies existed unmixed in these ions, even though this is, at best, an approximation. Thus, the pseudoantisymmetric stretching frequency (ν_1) is referred to as the CN stretching frequency (ν_{CN}); the pseudosymmetric stretching frequency (ν_3) is referred to as the CX stretching frequency (ν_{CX}); and ν_2 is the doubly degenerate deformation or bending frequency. The first overtone of ν_2 belongs to the same symmetry species at ν_3 and, in the case of the cyanate ion, these frequencies are sufficiently close for Fermi resonance to occur (*244*, *512*).

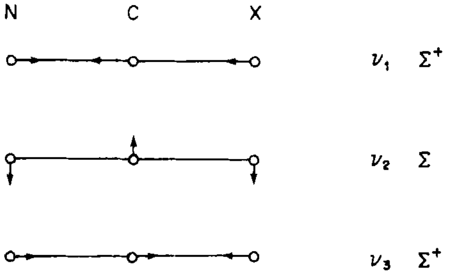


FIG. 1. Normal modes of vibration of NCX^-.

The fundamental vibrations of these ions are listed in Table II. The values cited are those recorded for the potassium salts and anharmonicity corrections have not been applied. Splittings are solid state effects. The vibrational spectra of different isotopic compositions of the cyanate ion have been extensively examined in a number of different host lattices—the results of several different groups of workers are discussed in (*657*, *691*).

The force constants have been calculated for the ions in a number of lattices and for different isotopic compositions for NCO^- (*512*, *657*), NCS^- (*418*), and $NCSe^-$ (*138*, *543*). The results for the solid compounds are summarized in Table III. The effects of different potassium halide matrices on these data are not given here but are listed by Schettino and Hisatsune (*657*).

TABLE II

FUNDAMENTAL VIBRATIONS OF POTASSIUM CHALCOGENOCYANATES

Ion	ν_{CN} (cm^{-1})	ν_{CX} (cm^{-1})	δ_{NCX} (cm^{-1})	References
NCO^-	2165	1254[a]	637,628	(*512*)
	2160	1249[a]	637,625	(*347*)
NCS^-	2053	746	486,471	(*418*)
	2048	747	485,470	(*347*)
$NCSe^-$	2070	558	424,416	(*543*)
	2070	561	426,417	(*347*)
$NCTe^-$[b]	2073	450	366	(*267*)

[a] Calculated on the basis of equal mixing; see, however, Ref. *657*. Peaks were observed at 1301 and 1207 cm^{-1} (*512*) and at 1294 and 1205 cm^{-1} (*347*).

[b] $(CH_3)_4N^+$ salt.

A complete vibrational analysis has been made of the complex anions $[Zn(NCX)_4]^{2-}$ ($X = O$, S, or Se) and the force constants calculated (*301*). These results will be referred to later.

Infrared spectra of a number of single crystals of cyanates and thiocyanates have been recorded and correlations made with the crystal structure. However, these results are not listed here since they have been reviewed recently by Iqbal (*398*).

The mean square amplitude of vibrations have been calculated for these ions (*550*), and Bastiansen-Morino shrinkage effects reported (*767*, *768*).

D. ELECTRONIC STRUCTURE AND ASSOCIATED PROPERTIES

1. *Electronic Structure*

The chalcogenocyanate ions have sixteen outer electrons. The energy levels for such linear triatomic systems have been characterized by Mulliken (*546*, *547*) and discussed by Walsh (*778*); the topic has been recently reviewed (*623*).

The cyanate ion has the ground-state electronic configuration $1\sigma^2$, $2\sigma^2$, $3\sigma^2$, $4\sigma^2$, $5\sigma^2$, $6\sigma^2$, $1\pi^4$; the thiocyanate and subsequent ions are similar unless account is taken of the core electrons or empty d orbitals of sulfur, selenium, or tellurium which increase the complexity of the ground-state description. The most sophisticated calculations that have been carried out on these ions are those of McLean and Yoshimine (*506*) on NCO^- and NCS^-. The calculated orbital energies are given in Table

TABLE III

FORCE CONSTANTS OF SOME POTASSIUM SALTS

Compound	f_{NC}	f_{CX}	f'	f_{α/l_1l_2}	f	References
KNCO in KBr	15.879	11.003	1.422	0.5086	0.7319	*(512)*
KNCS	15.95	5.18	0.9	0.311 0.300	—	*(418)*
KNCSe	15.97 ± 0.30	3.754 ± 0.045	0.88 ± 0.25	0.218 0.228	—	*(138)*

TABLE IV

CALCULATED ORBITAL ENERGIES FOR NCO^- AND NCS^-

Orbital[a]	NCO^- [b] (eV)	NCO^- [c] (eV)	NCS^- [b] (eV)
1σ	-552.85	-549.06	-2495.24
2σ	-415.38	-413.33	-416.64
3σ	-301.26	-301.17	-301.13
4σ	-32.25	-27.51	-236.94
5σ	-26.21	-22.77	-173.88
6σ	-12.77	-7.63	-25.86
7σ	-7.97	-4.25	-21.29
8σ	+16.86	—	-10.62
9σ	—	—	-8.32
10σ	—	—	+13.40
1π	-10.00	-6.56	-173.80
2π	-3.67	-0.43	-7.58
3π	+15.01	—	-3.06
4π	—	—	+12.00

[a] The orbitals are not listed necessarily in order of decreasing energy.

[b] From Ref. *506*.

[c] From Ref. *117*.

IV together with those of comparable calculations; less meticulous calculations will be referred to as appropriate in the following sections. Electronic energy surfaces have been calculated for NCO^- using cuspless wave functions (*789*).

2. *Absorption Spectra*

Bands at 300 nm (4.1 eV) and 190–205 nm (6.5–6.0 eV) have been assigned to the transitions $^3\Sigma^+ \leftarrow {}^1\Sigma^+$ and $^1\Sigma^- \leftarrow {}^1\Sigma^+$, respectively, for the cyanate ion (*621*, *622*), while the corresponding transitions for the thiocyanate ion occur at 340–360 nm (3.6–3.5 eV) and 220–240 nm (5.6–5.2 eV) (*503*). Higher energy transitions have been reported (*503*, *622*) for details of which the reader is referred to the original references. Both the spin-forbidden and the allowed low-energy bands are essentially $\pi \rightarrow \pi^*$ in nature, and the assignments are justified by the authors on the bases of calculations and of analogies with comparable systems. However, Trenin and co-workers have claimed that the bands in question for the cyanate ion (*487*) and for the thiocyanate, selenocyanate, and tellurocyanate ions (*353*) are charge transfer to solvent (CTTS) in character, and support this by demonstrating appropriate solvent shifts and by measurements at variable temperatures. Other workers have argued in favor of the spin-forbidden transition just mentioned and suggest that it may become allowed on coordination (*249*). This point of view has been examined qualitatively by Barnes and Day (*75*) (see Section III, B) who have shown that the nature of the band in question depends on the metal; the same observation applied to cyanate and selenocyanate complexes (*242*). Thus, it appears that internal transitions have been adequately observed and assigned for NCO^- and NCS^-, but that, because of the nature of these ions, the transitions are particularly susceptible to perturbations from neighboring metal ions or solvent molecules.

3. *Nuclear Magnetic Resonance Spectroscopy*

The ^{14}N nuclear magnetic resonances (NMRs) of the chalcogenocyanate ions have been measured by a consistent procedure and compared with the results of previous workers (*431*). The observed chemical shifts for these ions and for some related linear molecules vary linearly over a considerable range of values with π-electron densities calculated by a LCGO—MO method (*431*). The shift values were $NCO^- = 288$, $NCS^- = 165$, and $NCSe^- = 135$ ppm (relative to $NO_3^- = 0$ ppm) (*431*) and have been confirmed by later workers (*192*, *390*). The π-electron charges on the atoms and the π-bond orders that correlate with these results are given in Table V, together with the calculated data for $NCTe^-$ which had not been characterized at that time (*772*). More detailed calculations of the chemical shifts in the cyanate ion have been compared with those in the azide ion, and in the corresponding hydracids (*191*).

The ^{13}C NMRs of aqueous solutions of potassium cyanate and thiocyanate are -1.1 and -5.7 ppm (relative to benzene) (*504*) and comparison of these data with those from related compounds suggests that the ions have a small or zero formal charge on the carbon, in general agreement with the ^{14}N results.

TABLE V

CALCULATED π-ATOMIC CHARGES AND π-BOND ORDERS[a]

NCX^-	Q_N	Q_C	Q_X	π_{NC}	π_{CX}
NCO^-	−0.7712	−0.0442	−0.1846	1.5503	1.2629
NCS^-	−0.4826	+0.1934	−0.7108	1.8243	0.7964
$NCSe^-$	−0.3941	+0.2345	−0.8404	1.8943	0.5973
$NCTe^-$	−0.4919	+0.1859	−0.6940	1.8156	0.8179

[a] Data from Ref. *772*.

4. *Electron Spectroscopy for Chemical Analysis* (*ESCA*)

The N(1s), C(1s), and appropriate X (except Se) binding energies have been measured (*579*) for the series $Ph_4As(NCX)$ (X = O, S, Se, Te) and the results are given in Table VI, together with the previously determined N(1s) binding energies in NCO^- and NCS^- as the potassium (*376*) or bis-(triphenylphosphine)iminium (*711*) salts, and the Se(3p) binding energy in KNCSe (*712*).

Basch (*76*) has suggested that a direct correlation should exist between chemical shifts from NMR measurements and ESCA measurements. On this basis, it is not surprising that, in view of the small ^{13}C shifts observed for NCO^- and NCS^- (*504*) (see preceding section), the C(1s) binding energies of the ions in question should be almost identical. Similarly, the results in Table VI would predict only small changes in ^{14}N NMR measurements for these ions, whereas, in fact, considerable chemical shifts were observed and were correlated with changes in π-electron density at the nitrogen atom (*431*). In many cases binding energies show a linear correlation with the calculated total charge, and extended Hückel calculations give a total charge of -1.572 and -1.672 (-1.711 if d orbitals are included) for the nitrogen atoms in NCO^- and NCS^-, respectively (*376*).

Thus, on the one hand, the ^{14}N chemical shift data and calculated total charges indicate that changing X in NCX^- does alter the electron density on the nitrogen, and, on the other, the ESCA measurements support no such effect. It has been suggested (*579*) that this apparent discrepancy may arise from the importance of a direct electrostatic interaction between the cation and the nitrogen end of chalcogenocyanate ion, which masks any mesomeric or inductive effect of X transmitted through carbon to nitrogen. In support of this hypothesis

TABLE VI

BINDING ENERGIES FOR THE ATOMS IN THE CHALCOGENATOCYANATE IONS

Compound	N(1s) (eV)	C(1s) (eV)	X (eV)	References
Ph_4AsNCO	397.0	291.2	532.0 (1s)	(*579*)
KNCO	398.3	—	—	(*376*)
$(Ph_3P)_2NNCO$	400.5	—	—	(*711*)
Ph_4AsNCS	396.6	291.3	161.8 (2p)	(*579*)
KNCS	398.5	—	—	(*376*)
$(Ph_3P)_2NNCS$	400.2	—	—	(*711*)
$Ph_4AsNCSe$	397.0	291.3	—	(*579*)
KNCSe	—	—	159.3 ($3p_{3/2}$)	(*712*)
			165.1 ($3p_{1/2}$)	(*712*)
$Ph_4AsNCTe$	396.8	—	573.3 ($3d_{5/2}$)	(*579*)
			583.6 ($3d_{3/2}$)	(*579*)

it was pointed out that the N(1s) binding energies for either NCO$^-$ or NCS$^-$ show greater differences due to changing the cation than to changing X (*579*).

There appear to be no examples of the photoelectron spectra of appropriate inorganic molecules containing the chalcogenocyanate group (*788*).

5. *Nuclear Quadrupole Resonance Spectroscopy*

Ab initio calculations of the ^{14}N nuclear quadrupole coupling constant suggest that the cyanate nitrogen atom is more ionic than that of the thiocyanate ion (*118*), but measurements show the latter to be more ionic than that in the selenocyanate ion (*397*).

E. THERMODYNAMIC AND RELATED PROPERTIES

Compounds of these ions do not occur frequently in the lists of thermodynamic data; some of the few results available are given in Table VII. The dissociation constants of hydrocyanic, hydrazoic, cyanic, thiocyanic, and selenocyanic acids are in the approximate ratios $1:10^5:10^6:10^9:10^{10}$ (*123*). Some thermodynamic functions of these acids have been obtained, but no attempt was made to confirm that the latter three acids were indeed the N-bonded compounds and that the X-bonded isomers were absent (*123*). Hydrogen bonding between these acids and various bases has been studied but will not be considered further in this review (see, e.g., Refs. *68* and *362*, and references therein). Some electronegativities are also included in Table VII; of the cases quoted, only Huheey (*394*) considered both possible atoms and he assumed -tri di di hybridization in each case.

Early work by Birckenbach and Kellermann (*106*) established the following order of increasing reducing power of the halide and pseudohalide ions: F^-, NCO^-, Cl^-, N_3^-, Br^-, CN^-, NCS^-, I^-, $SeCN^-$, $TeCN^-$. Few data on the pseudohalides are available to justify this sequence on other than the original chemical grounds.

The activity and osmotic coefficients of sodium thiocyanate in water have been determined (*531*). The solvation number of NCS$^-$ has been reported as zero. (*588*), and the ion tends to be less structure-breaking than most anions (*136*). Its transport number and ionic conductance have been measured in formamide (*581*), and 1:1 solvates have been reported from dimethylformamide solutions of M—NCS (M = NH_4, Na, K) (*595*).

III. Physical Methods for Determining the Mode of Coordination

The determination of the mode of coordination of chalcogenocyanate ligands is fraught with difficulties. Although various techniques have

TABLE VII

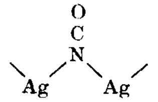
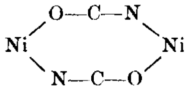
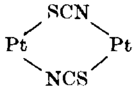
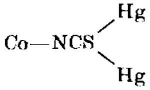
SOME THERMODYNAMIC AND RELATED PROPERTIES OF CHALCOGENOCYANATES

Parameter	Units	NCO^-	NCS^-	$NCSe^-$	Reference
$\Delta H_f\ (X_g^-)$	kcal/mole	-19	-4	—	*(248)*
	kcal/mole	—	-24.3 to -23.0	—	*(544)*
ΔH for $X^-_{(g)} \rightarrow X^-_{(aq)}$	kcal/mole	-93	-74	—	*(761)*
Electron affinity	kcal/mole	—	49.9	—	*(551)*
Gaseous entropy	eu	54.4	56.9	—	*(470)*
	eu	53.0	55.5	—	*(29)*
Ionic entropy	eu	—	34.23	—	*(754)*
Partial molal entropy	eu	31.1	—	—	*(29)*
Entropy of hydration	eu	-15	—	—	*(29)*
Partial molal volume	ml/mole	26.7	41.0	50.3	*(523)*
Electronegativity	Pauling scale	3.52	—	—	*(786)*
	Pauling scale	3.05	2.9	2.6	*(203)*
	Pauling scale	4.46	4.17	—	*(394)*
	Pauling scale	4.66 ($—OCN^-$)	3.91 ($—SCN^-$)	—	*(394)*

been used successfully in many instances, there are a number of cases where the application of these previously satisfactory techniques gives ambiguous answers. Thus, X-ray crystallography remains the most reliable technique. A representative selection of illustrative structures is given in Table VIII; further crystal structures will be given subsequently. In addition to the tabulated types of coordination, *O*-cyanato complexes and various selenocyanate-bridged complexes have been characterized by spectroscopic methods.

TABLE VIII

SOME TYPES OF CHALCOGENOCYANATE COORDINATION CONFIRMED BY X-RAY CRYSTALLOGRAPHY

Compound	Type of coordination	Comments	References
$Ph_4As[Ag(NCO)_2]$	$[OCN—Ag—NCO]^-$	Linear anion	(*1*)
$(\pi\text{-}C_5H_5)Cr(NO)_2NCO$	Cr—NCO		(*165*)
AgNCO			(*125*)
$[Ni_2tren_2(NCO)_2](BPh_4)_2$			(*265*)
$[Co(NH_3)_5NCS]Cl_2$	Co—NCS		(*693*)
$[Co(NH_3)_5SCN]Cl_2$	Co—SCN		(*693*)
$[Ph_2P(CH_2)_3NMe]Pd(CNS)_2$	Pd—NCS | SCN	Both types of monodentate coordination in a single molecule	(*198, 199*)
$[Ph_2P(CH_2)_3PPh_2]Pd(CNS)_2$	Pd—NCS | SCN		(*102*)
$K_2Pd(SCN)_4$	Pd—SCN ↓ Pd	Weak coordinate bond to a second Pd	(*524, 525*)
$Co(NCS)_4Hg$	Co—NCS—Hg		(*407*)
$Pt_2Cl_2(PPr_3)_2(SCN)_2$			(*348*)
$Co(NCS)_6Hg_2 \cdot C_6H_6$			(*351*)
$Ni(DMF)_4(NCSe)_2$	Ni—NCSe		(*736*)
$K[Co(DH)_2(SeCN)_2]$	Co—SeCN		(*8*)

A. INFRARED SPECTROSCOPY

Infrared spectra of thiocyanate and related complexes have been thoroughly reviewed by Bailey *et al.* (*57*). Because of the importance of this technique for structural assignments, a certain amount of repetition of material included in their review is necessary here, although the retabulation of data already collated has been kept to a minimum.

Various criteria have been examined at different times with a view to correlating frequency shifts with the mode of bonding of the thiocyanate group. Chatt *et al.* (*186*, *187*) showed that the CN stretching frequency is found at higher wave numbers in bridging than in terminal complexes. Later it was shown that, for terminal thiocyanate groups, this same frequency often occurred at higher wave numbers for *S*-thiocyanates than for N-bonded complexes; but it was also shown that other structural and electronic factors prevented this criterion from having a general application (*533*, *727*, *728*). The C—S stretching frequency has been considered also, when frequencies near 700 cm^{-1} have been taken to be indicative of S-bonding, whereas those between 800 and 830 cm^{-1} to suggest N-bonding (*489*). As well as being subject to the structural and electronic effects referred to in the foregoing, this frequency occurs in the same region of the spectrum as frequencies associated with other ligands or counterions so that, being only of medium or weak intensity, it is difficult to assign. A further complication is caused by the fact that this frequency can sometimes be confused with the first overtone of the bending frequency (*640*).

A single sharp band at $\sim 480\ \mathrm{cm}^{-1}$ has been assigned to the bending mode in an N-bonded complex, in contrast to the several, low-intensity bands near 420 cm^{-1} observed in *S*-thiocyanates (*489*, *639*).

Many of these frequency changes can be accounted for by taking a simple view of the alternative structures, which can be assumed to be predominantly M—N=C=S and M—S—C≡N, respectively. However, it is not surprising that difficulties are encountered in making the assignments and that the range of frequencies observed for *N*-thiocyanato complexes overlaps with that for S complexes, when the factors affecting frequency shifts are considered. Even in terms of the foregoing model, it is clear that changes in the mass, size, or charge of M can have profound consequences on the position of a given frequency, notwithstanding the further effects due to the size or electronic nature of other ligands.

The views of various authors on the origins of these frequency shifts, and on attempts to assess the relative significance of the different effects, have been summarized by Bailey *et al.* (*57*) and will not be repeated here. The complexity of the system is illustrated by the experimental results in Table IX and by the conclusions reached by Kharitonov *et al.* (*440*), who calculated theoretical changes in the vibrational frequencies with changes in the force constants of M—N and M—S bonds on the assumption that the internal force constants remained unchanged from the free ion values. They considered the systems M—NCS (with $M\hat{N}C = 180°$), M—SCN (with $M\hat{S}C = 180°$, 120°, or 90°), and linear M—NCS—M, and varied the atomic weight of M from 50 to 200. The conclusions of Kharitonov *et al.* have been usefully summarized (*57*) as follows.

For the nitrogen-bound case:

1. The ν_{CN} and ν_{CS} bands should increase in energy with an increase of k_{MN} (metal–nitrogen bond force constant). Hence, ν_{CN} and ν_{CS} increase on coordination.
2. ν_{CN} is almost independent of the mass of the metal ion, and ν_{CS} only slightly more influenced by this; ν_{MN} is mass-dependent.
3. Changes in $k_{MN,CN}$, the interaction force constant, have little effect on ν_{CN} and almost none on ν_{CS} and ν_{MN}.
4. The ν_{CN}, ν_{CS}, and ν_{MN} bands are not pure vibrations; there is mixing in all cases.
5. These effects occur in addition to those due to electron redistribution from coordination, such as changes in the CN and CS force constants. These should be small since the effect of k_{MN} alone gives reasonable correlation with experimental observations.

For the sulfur-bound case:

1. For unchanged force constants, coordination of the SCN^- group through S has no influence on the frequency of ν_{CN}. However, ν_{CS} increases relative to the free ion but to a lesser extent than in the N-bound case.
2. ν_{CN} is almost independent of the mass of atom M, and ν_{CS} and ν_{MS} are only slightly affected by it.
3. ν_{CN} is almost independent of the CSM angle, but ν_{CS} decreases and ν_{MS} increases as the angle decreases from 180° to 90°.
4. ν_{CN} is almost independent of k_{MS}, but ν_{CS} and ν_{MS} increase as k_{MS} increases.
5. In order to fit experimental results, k_{CN} and k_{CS} and, hence, the bond orders must change on coordination (C—S decreasing, C—N increasing).

For the bridged case:

1. The ν_{CN} and ν_{CS} bands increase almost linearly with k_{MN} and k_{SM} (for $k_{MN} = k_{SM}$).

TABLE IX

Infrared Spectra of Some Thiocyanate Complexes[a]

Compound	ν_{CN} (cm^{-1})	ν_{CS} (cm^{-1})	δ_{NCS} (cm^{-1})	A ($\times 10^4$ M^{-1} cm^{-2})	References
π-$C_5H_5Mo(CO)_3NCS$	2099 s[b]	—	—	9.80[b]	*(690)*
π-$C_5H_5Mo(CO)_3SCN$	2114 m[b]	699 w	—	2.19[b]	*(690)*
$(\pi$-$C_5H_5)_2W(NCS)_2$	2199 s 2107 vs	—	—	—	*(344)*
$(\pi$-$C_5H_5)_2W(NCS)(SCN)$	2121 s 2104 s 2094 s	700 w	423	—	*(344)*
$Mn(CO)_5SCN$	2160	676 w	—	—	*(279)*
$Mn(CO)_5NCS$ (in CH_3CN)	2113	813	—	—	*(279)*
$Mn(CO)_3(AsPh_3)_2SCN$	2148 m[b]	—	—	—	*(280)*
$Mn(CO)_3(AsPh_3)_2NCS$	2103 m[b]	814 m	—	—	*(280)*
$Mn(CO)_3(SbPh_3)_2SCN$	2148 m[b]	—	—	—	*(280)*
$Mn(CO)_3(SbPh_3)_2NCS$	2097 m[b]	820 m	—	—	*(280)*
$Mn(CO)_3(PPh_3)_2NCS$	2096 m[b]	820 m	—	—	*(280)*
π-$C_5H_5Fe(CO)_2NCS$	2123 s[b]	830 m	—	6.70	*(690)*
π-$C_5H_5Fe(CO)_2SCN$	2118 m[b]	698 w	—	1.64	*(690)*
$[Ru(NH_3)_5NCS](ClO_4)_2$	2120 s	850	—	—	*(490)*
$[Ru(NH_3)_5SCN](ClO_4)_2$	2065	—	—	—	*(490)*
cis-$Co(DH)_2(H_2O)NCS$	2070	—	—	—	*(3)*
trans-$Co(DH)_2(H_2O)SCN$	2180 2120	—	—	—	*(3)*

trans-Co(DH)$_2$pyNCS	2128 s,sp	837 w	—	10.24	(*574*)
trans-Co(DH)$_2$pySCN	2118 s,sp	—	—	1.2	(*574*)
trans-Co(DH)$_2$4-*t*-bupyNCS	2110 s	—	—	—	(*269*)
trans-Co(DH)$_2$4-*t*-bupySCN	2055 m	—	—	—	(*269*)
[Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$	2125 b	806	—	—	(*134*)
[Co(NH$_3$)$_5$SCN](ClO$_4$)$_2$	2100 sp	710 w	426 m	—	(*134*)
K$_3$[Co(CN)$_5$NCS]	2123 s	812 w	483 w 470 vw	—	(*359*)
(*n*-Bu$_4$N)$_3$[Co(CN)$_5$NCS]	2113 s	—	475 mw	—	(*359*)
[Co(CN)$_5$NCS]$^{3-}$	2137 s^{bc} 2118 s^{bc}	—	—	—	(*359*)
K$_3$[Co(CN)$_5$SCN]	2144 ms^{c} 2134 s^{c} 2110 vs^{c}	718 w	472 w 461 vw 448 w	—	(*359*)
[Co(CN)$_5$SCN]$^{3-}$	2112 s^{cd} 2097 ms^{cd}	—	—	—	(*359*)
[Rh(NH$_3$)$_5$NCS]$^{2+}$	2145 s,b	815 s	—	—	(*659*)
[Rh(NH$_3$)$_5$SCN]$^{2+}$	2115 s,sp	770 w,b	—	—	(*659*)
mer-Rh(PMe$_2$Ph)$_3$Cl$_2$NCS	2122 sh 2113 vs 2113^{b}	809	—	—	(*126*)
mer-Rh(PMe$_2$Ph)$_3$Cl$_2$SCN	2108 vs 2115 ^{b}	—	—	—	(*126*)
mer-Rh(PMe$_2$Ph)$_3$(SCN)$_3$	2126 sh 2106 vs	702	473	—	(*126*)
Rh(PPh$_3$)$_3$NCS	2095	820–810	—	8.5	(*35*)
Rh(PPh$_3$)$_2$pip(NCS)	2090	815	—	6.5	(*35*)
Rh(PPh$_3$)$_2$MeCN (SCN)$_3$	2136	—	—	3.0	(*35*)
[Ir(NH$_3$)$_5$NCS]$^{2+}$	2140 s,b	825	—	—	(*659*)
[Ir(NH$_3$)$_5$SCN]$^{2+}$	2110 s,sp	700 m	—	—	(*659*)

(*continued*)

TABLE IX—*continued*

Compound	ν_{CN} (cm^{-1})	ν_{CS} (cm^{-1})	δ_{CNS} (cm^{-1})	A ($\times 10^4$ M^{-1} cm^{-2})	References
$Pd(AsPh_3)_2(NCS)_2$	2089 s,b	854 m	—	—	(*143*)
$Pd(AsPh_3)_2(SCN)_2$	2119 s,sp	—	—	—	(*143*)
$Pd(bipy)(NCS)_2$	2100 s,b	849 sh 842 m	—	—	(*143*)
$Pd(bipy)(SCN)_2$	2117 m,sp 2108 s,sp	—	—	—	(*143*)
$Pd(4,7\text{-diph-phen})(NCS)_2$	2110 s,b	—	—	—	(*103*)
$Pd(4,7\text{-diph-phen})(SCN)_2$	2120 sh 2113 s,sp	—	419	—	(*103*)
$[Pd(Et_4dien)NCS]^+$	2060	830	—	—	(*78*)
$[Pd(Et_4dien)SCN]^+$	2125	710	—	—	(*78*)
$Pd(4,4'\text{-di-me-bipy})(NCS)(SCN)$	2120 s,sp	—	458 mw	—	(*103*)
	2090 s,b	—	452 mw	—	(*103*)
$Pd[Ph_2As(\text{-}o\text{-}C_6H_4PPh_2)](NSC)(SCN)$	2117 2085	—	—	—	(*526*)
	2118[a]	—	—	4.2	(*526*)
	2085[a]	—	—	8.2	
$Pd(Ph_2P(CH_2)_2NMe_2)(NCS)(SCN)$	2126 2108	—	—	—	(*526*)
	2126[a]	—	—	1.90	(*526*)
	2085[a]	—	—	11.71	

$Pd(Ph_2P(CH_2)_2PPh_2)(NCS)(SCN)$	2118 2095	—	—	—	(*526*)
	2121[d] 2086[d]	— —	— —	2.5 10.7	(*526*)
$Cu(tripyam)(NCS)_2$	2100 s,b 2070 sh,b	—	—	—	(*473*)
Cu(tripyam)(NCS)(SCN)	2128 s,sp 2080 s,b	—	—	—	(*473*)
$Cu(tripyam)(SCN)_2$	2122 s,sp 2100 s,sp	—	—	—	(*473*)
Cu(dppa)(NCS)(SCN)	2128 s,sp 2081 s,b	—	—	—	(*473*)
$Cu(dppa)(SCN)_2$	2122 s,sp 2100 s,sp	—	—	—	(*473*)

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[a] Data are recorded as mull spectra unless otherwise indicated.

[b] In $CHCl_3$.

[c] Includes ν_{CN} for cyano groups.

[d] In CH_2Cl_2.

2. Change in mass of M has almost no effect on ν_{CN} and only a small one on ν_{CS}; the effects appear as increases in k_{MN} and k_{MS}.
3. Constant k_{MS} has almost no effect on ν_{CN}.
4. ν_{MS} depends on both k_{MN} and k_{MS}.
5. The high values of ν_{CN} found experimentally are due to the combination of increase for N bonding and a change in force constants due to S bonding.

An alternative method for attempting to determine the mode of thiocyanate coordination by infrared measurements involves the intensity of the CN stretching frequency. This method was suggested by Fronaeus and Larsson (*305*), and developed by Pecile (*599*). As currently applied, it requires the measurement of the integrated intensity, *A*, (i.e., the area under the absorption peak) of the CN stretching frequency, and Ramsay's method of direct integration (*625*) is often used. The equation is

$$A = (\pi/2Cl)[\log(I_0/I)]\Delta\nu_{1/2}$$

where C = concentration in moles per liter, l = cell thickness, I/I_0 = percentage of transmitted light, and $\Delta\nu_{1/2}$ = apparent width of the absorption band at half the height of its peak.

Values of A in the region $3\text{–}5 \times 10^4\ M^{-1}\mathrm{cm}^{-2}$ are found for the free thiocyanate ion; integrated intensities below this are found for S-thiocyanates, whereas N-bonded complexes have values generally above $9 \times 10^4\ M^{-1}\ \mathrm{cm}^{-2}$. A theoretical justification for these results has been advanced (*305*, *482*), whereby coordination through S would favor an increased contribution from $\mathrm{N{\equiv}C{-}S^-}$ of the three resonance forms of the ions given in Table X, so that the dipole moment of the ion would be decreased; conversely, coordination through N would favor an increase in the contributions of the two other resonance forms, resulting in an increase of the dipole moment of the ion. The whole argument

TABLE X

PERCENTAGE CONTRIBUTIONS OF THE PRINCIPAL RESONANCE FORMS OF THE CHALCOGENOCYANATE IONS

X atom	$\mathrm{N{\equiv}C{-}X^-}$ (%)	$\mathrm{^-N{=}C{=}X}$ (%)	$\mathrm{^{2-}N{-}C{\equiv}X^+}$ (%)	References
O	75	1	24	(*575*)
S	76	5	19	(*575*)
Se	88	0	12	(*568*)
Te	90	4	6	(*568*)

depends on the assumption that a change in the magnitude of the dipole moment causes a corresponding change in the rate of change of the dipole during vibration and, hence, a change in the intensity of the band.

The disadvantage of the method and the need for care in interpreting the results centers around the fact that measurements are made on solutions rather than on solids. As will be discussed in detail later, the nature of the solvent can affect the mode of bonding of the thiocyanate ion, even to the extent of causing isomerization. Dissociation of the coordinated ion is a further chemical possibility, the degree of which will depend on the nature of the solvent. Solvation of the coordinated thiocyanate group itself can also occur and hydrogen bonding solvents can, for example, cause considerable broadening of the vibrational peaks. Thus a variety of factors can affect the integrated intensity and make difficult the interpretation of the results.

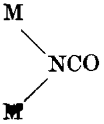
An attempt has been made to extend the intensity criterion to insoluble materials, using KBr disks. Satisfactory results have been obtained enabling N-bonded complexes to be distinguished from S-bonded (*481*). This technique has been further extended by using a suitable internal standard (*60*): the C—O stretching band in salicylic acid (1654 cm^{-1}) has been used, and the ratio of the intensity of ν_{CN} to the intensity of this band has been suggested as a satisfactory criterion to distinguish N- and S-bonded complexes, provided that known complexes are used for calibration.

Whatever the experimental approach, integrated intensities are cited per thiocyanate ion to normalize the results for different stoichiometries. For complexes containing only one thiocyanate group this presents no problems, but let us consider cis and trans isomers of square planar $ML_2(NCS)_2$ and assume that these complexes have the idealized microsymmetries C_{2v} and D_{2h} around the metal. Group theory predicts that both CN stretching frequencies are infrared-active in the former case, but that only one is in the latter case. In some *N*-cyanato complexes of palladium(II) and platinum(II), where an essentially similar problem arises, it was not possible to observe two CN stretching frequencies (*575*) even though subsequent work confirmed the presence of largely *cis*-platinum and *trans*-palladium compounds in the series studied (*578*). Nevertheless, the integrated intensities were expressed per cyanate group and chemically sensible results were obtained. The approach can perhaps be justified since the infrared-active mode in the trans complex is a complex vibration involving both CN-containing groups, so that the two groups both contribute to the intensity of the one band. Similarly, the coupling may be assumed to be proportionally less in the cis compound so that the two bands each contribute to the total intensity.

However, this analysis becomes further complicated in other symmetries, for example, in square planar or tetrahedral $[M(NCS)_4]^{n-}$ or in the corresponding octahedral series. The problem remains unresolved, and casts some doubt on the validity of the use of integrated intensities, notwithstanding the increasing amount of empirical data supporting this method.

TABLE XI

APPROXIMATE FREQUENCY RANGES FOR DIFFERENT TYPES OF CHALCOGENOCYANATE COORDINATION

Compound type	ν_{CN} (cm^{-1})	ν_{CX} (cm^{-1})	δ_{NCX} (cm^{-1})	A (× 10^4 M^{-1} cm^{-2})
NCS^-	2053	746	486, 471	3–5
M—NCS	2100–2050 s,b	870–820 w	485–475	7–11
M—SCN	2130–2085 s,sp	760–700 b	470–430	1–3
M—NCS—M	2165–2065	800–750	470–440	—
$NCSe^-$	2070	558	424, 416	2–3
M—$NCSe^-$	2090–2050 s,b	650–600	460–410	5–12
M—$SeCN^-$	2130–2070 s,sp	550–520	410–370	0.5–1.5
M—NCSe—M	2150–2100	640–550	410–390	—
NCO^-	2165	1254	637, 628	8
M—NCO	2240–2170	1350–1320	640–590	12–20
M—OCN	2240–2200	1320–1070	630–590	9–15[a]
	2210–2150 s	1340–1300 w	660–610 m	—

[a] Organic cyanates ROCN have $A = 1$–$2 \times 10^4\ M^{-1}$ cm^{-2} (35).

Table IX lists the positions of the thiocyanate fundamental frequencies in a representative selection of complexes, with the integrated intensities of ν_{CN}; metal–thiocyanate frequencies are also included and will be discussed later. The complexes are, in most instances, pairs of linkage isomers, and the results indicate the difficulties in drawing conclusions concerning the nature of effects causing vibrational shifts. In view of the difficulties, and because of the doubts expressed previously concerning the use of integrated intensities, great caution should be exercised in assigning the mode of bonding of the thiocyanate group on the basis of infrared data—wherever possible, supplementary measurements should also be made. Table XI summarizes the frequency ranges for different types of thiocyanate coordination.

The previous discussion has been concerned with thiocyanate complexes, but a similar situation obtains with selenocyanates (*437*, *438*). Table XI includes the frequency ranges for different modes of selenocyanate coordination. Kharitonov *et al.* (*439*) obtained similar results for selenocyanate complexes as for thiocyanate complexes in their theoretical treatment outlined previously, and their conclusions are the same in both cases. Thus, frequency shifts can be due to electronic effects or to changes in the bonding mode. The relative contributions of the resonance forms of NCSe$^-$ (Table X) are comparable to those of NCS$^-$ so that integrated intensities can be used in a similar way, and with the same possible dangers. Table XII contains some infrared data for a representative selection of selenocyanate complexes—fewer linkage isomers are known than have been reported for thiocyanate complexes.

TABLE XII

INFRARED SPECTRA OF SOME SELENOCYANATE COMPLEXES[a]

Selenocyanate	ν_{CN} (cm^{-1})	ν_{CSe} (cm^{-1})	δ_{NCSe} (cm^{-1})	A ($\times 10^4$ M^{-1} cm^{-2})	References
π-cpFe(CO)(PPh$_3$)NCSe	2120 m	663 mw	—	—	(*410*)
	2107 m[b]	—	—	5.3	(*410*)
π-cpFe(CO)(PPh$_3$)SeCN	2112 mw	532 w	—	—	(*410*)
	2117 mw[b]	—	—	1.7	(*410*)
cis-Co(DH)$_2$(H$_2$O)NCSe	2075	605	—	—	(*3*)
trans-Co(DH)$_2$(H$_2$O)SeCN	2140	—	—	—	(*3*)
Rh(PPh$_3$)$_2$CO(NCSe)	2094	—	—	7	(*150*)
Rh(PPh$_3$)$_2$MeCN(SeCN)	2135[d]	—	—	2.3	(*36*)
[Pd(Et$_4$dien)NCSe]$^+$	2085 s,br	618	—	—	(*153*)
	2089[c]	—	—	6.6	(*153*)
[Pd(Et$_4$dien)SeCN]$^+$	2121 s,sp	533 w	404 w	—	(*153*)
	2125[c]	—	—	0.63	(*153*)

[a] Data are recorded as mull spectra unless otherwise indicated.

[b] In CHCl$_3$.

[c] In acetone.

[d] KBr disc.

It has been seen that correlations between the bonding modes of NCS$^-$ and NCSe$^-$ and infrared spectral parameters have been established largely on an empirical basis, with only partial theoretical justification. Further, the infrared data for a particular compound apparently may be consistent with either of the main bonding modes or, indeed, with a form of bridging. With these thoughts in mind the use of infrared measurements to determine cyanate-bonding modes becomes even more difficult for two reasons: (*a*) there is more coupling between the cyanate stretching frequencies than is observed for the other ions and this is also observed in complexes, e.g., the force constant calculations on $[Zn(NCX)_4]^{2-}$ (*301*); (*b*) there are very few reported *O*-cyanato complexes, none of which have been confirmed by X-ray crystallography, and only $(C_5H_5)_2Ti(OCN)_2$ has been confirmed by measurements other than infrared (^{14}N NMR; see Ref. *93*). Apart from $Rh(PPh_3)_3NCO$ and its linkage isomer, there are therefore no sets of N- and O-bonded complexes comparable to the compounds in Tables IX (thiocyanate) and XII (selenocyanates) for which measurements can be compared, and from which bonding criteria may be deduced. Analogies with the theoretical justifications for frequency shifts for NCS– and $NCSe^-$ are also risky because of the lack of purity of the vibrational modes of NCO^-.

Kharitonov *et al.* (*742*) have carried out calculations, similar to those described for the thiocyanate and selenocyanate groups, to elucidate the changes in the vibrational frequencies of the cyanate group when it is N- and O-bonded. With similar models to those described previously, they reported the following findings.

For *N*-cyanato complexes:

1. ν_{CN} and ν_{CO} should increase with an increase of k_{MN}, that is, on coordination.
2. On increasing the mass M, ν_{CO} changes slightly, whereas ν_{CN} is hardly altered and ν_{MN} decreases steadily.
3. ν_{MN} increase almost linearly with k_{MN}.
4. ν_{CN}, ν_{CO}, and ν_{MN} are not pure vibrations. There is mixing in every case, which is most pronounced for ν_{CO}.
5. The contribution of the change in vibration mechanics is probably greater than that of any other change (such as that due to electronic effects) in the force constants k_{CN} and k_{CO}.

For *O*-cyanato complexes:

1. ν_{CN} is not affected, and ν_{CO} should increase in energy to a greater extent than the N-bonded case.
2. ν_{CN} is independent of the mass of M, and ν_{CO} is only slightly affected; ν_{MO} varies with M.
3. An increase in k_{MO} does not influence ν_{CN}, increases ν_{CO}, and appreciably increases ν_{MO}.

4. In contrast to the N-bonded case, a redistribution of electron density could outweigh the foregoing predictions which are based on a mechanical model.

It is useful at this stage, to discuss the arguments of Nelson and Nelson (*557*) who have also carried out some calculations on vibrational changes in the cyanate group.

The percentages of the three principal resonance hybrid structures of the cyanate ion are given in Table X. Nelson and Nelson (*557*) studied the effect on ν_{CN} and ν_{CO} as the force constants are altered by including progressively increasing contributions from, first, the resonance form $N{\equiv}C{-}O^-$ and, second, ${}^{2-}N{-}C{\equiv}O^+$; their results in the former case are repeated in Table XIII: The calculations were carried out in order to determine the nature of the bridging cyanate group (M—NCO—M or M—N(CO)—M) and do not include the form ${}^-N{=}C{=}O$ which would be of importance in *N*-cyanato complexes. However, $N{\equiv}C{-}O^-$ is the resonance form most likely to be of importance in *O*-cyanato complexes, in which case the calculations show that ν_{CN} and ν_{CO} will, respectively, increase and decrease relative to the free ion values, in contrast to the prediction for M—OCN based on the mechanical model described previously.

TABLE XIII

EFFECT OF INCREASING THE CONTRIBUTIONS OF $N{\equiv}C{-}O^-$ ON ν_{CN} AND ν_{CO} (RELATIVE TO NCO^-)[a]

Percentage increase in contribution of resonance for $N{\equiv}C{-}O^-$	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})
0 (free ion value)	2183	1254
5	2212	1248
10	2214	1239
30	2217	1191
50	2224	1133
70	2236	1063
100	2257	941

[a] Data from Ref. *557*.

The infrared spectra of a number of cyanato complexes are recorded in Table XIV. One of the compounds $cp_2M(OCN)_2$ (M = Ti,Hf) is incorrectly formulated. The infrared data are as listed, and ^{14}N NMR (*93*) and mass spectral data (*145*) support $cp_2Ti(OCN)_2$. However, the dipole moment ratios of the compounds suggest that they cannot *both* have the same type of coordination (*411*). Most cyanato complexes can

TABLE XIV

Infrared Spectra of Some Cyanate Complexes[a]

Cyanate	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})	δ_{NCO} (cm^{-1})	A ($\times 10^4\ M^{-1}\ cm^{-2}$)	Reference
$(\pi\text{-cp})_3CeNCO$	2145 s	1310	—	—	*(423)*
$(C_9H_7)_2Ce(NCO)_2$	2225 m	1320 m	—	—	*(423)*
$(\pi\text{-cp})_2Ti(OCN)_2$[b]	2235[c] 2196[c]	1132 m	626 m 593 m	13 18	*(145)*
$(\pi\text{-cp})_2TiNCO$	2216[d]	1302 ms	599 m 590 m	—	*(145)*
$(\pi\text{-cp})_2Zr(OCN)_2$[b]	2233[c] 2200[c]	1257 w 1070 sh	631 m 607 m	12 16	*(145)*
$(\pi\text{-cp})_2Hf(OCN)_2$	2246[c] 2211[c]	1257 w 1071 sh	632 m 606 m	12 18	*(145)*
$[Mo(OCN)_6]^{3-}$	2205 s	1296 m	595 m	—	*(56)*
		1104 m	—	—	*(56)*
$[Re(OCN)_6]^{2-}$	2224 s	1306 w	595 m	—	*(56)*
		1138 w	—	—	*(56)*
$[Re(OCN)_6]^{-}$	2220 s	—	—	—	*(56)*

$Pd(py)_2(NCO)_2$	2180S2210 s	1332 m,sp	586 m,sp	—	*(575)*
	2202[e]	—	—	21.4	*(575)*
$Pt(Ph_3P)_2(NCO)_2$	2230 sh 2200 s,sp	1355 vw 1312 m,br	590	—	*(575)*
	2258[f]	—	—	13.0	*(575)*
$Rh(PPh_3)_2CO(NCO)$	2239	—	—	—	*(87)*
$Ph(PPh_3)_3NCO$	2230[g]	—	592	12.7	*(37)*
$Rh(PPh_3)_3OCN$[h]	2215[g]	1318	607 590	9.0	*(37)*
$K[Cu(pic)_2(OCN)]$	2143	1205	630 625	—	*(321)*

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[a] Data are recorded as mull spectra unless otherwise indicated.

[b] One or other of these structures is incorrectly formulated (see text).

[c] In CH_2Cl_2.

[d] In acetone.

[e] In $CHCl_3$.

[f] In CH_3NO_2.

[g] As KBr disk.

[h] ν(Rh—OCN) at 332 cm^{-1} *(37)*.

be assumed to be N-bonded from infrared and other measurements, and it is seen that, in general, the CN stretching frequency increases and the NCO bending frequency decreases (slightly) on coordination, as might be expected from the preceding arguments; $(C_5H_5)_2Ti(OCN)_2$ shows similar changes. The CO stretching frequency does not alter very much in *N*-cyanato complexes. The percentage contributions of the different resonance forms (Table X) are comparable with those of the other ions, and this would appear to indicate that integrated intensity criteria can be used as before. Thus, for a series of palladium(II) and platinum(II) compounds, $ML_2(NCO)_2$, the integrated intensity per cyanate group was in the range 13–23 × 10^{-4} liter $mole^{-1}$ cm^{-2}, and larger than the free ion value of 8.4 × 10^{-4} liter $mole^{-1}$ cm^{-2} (*575*) indicating *N*–cyanato complexes in every case. However, the integrated intensities of $(C_5H_5)_2M(OCN)_2$ are also larger than the free ion values, and it has been suggested that this criterion is inapplicable to cyanate complexes because of the small difference in mass between the nitrogen and oxygen atoms (*145*). The integrated intensities for the linkage isomers $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$ do suggest, however, that values about equal to the free ion value are characteristic of *O*-cyanates (*37*).

The lack of compounds means that generalizations cannot be advanced for cyanates in the same way that they have been developed for the thiocyanate and selenocyanate complexes. Such data as are available suggest that ν_{CN} for *O*-cyanates lie within the range for *N*-cyanates and that the degeneracy of the deformation mode is apparently removed for some *O*-cyanates as well as for some *N*-cyanates.

Because the foregoing criteria all are found wanting, although on the basis of very few data, attention must now be turned to the remaining frequency, namely the CO stretching frequency. Fermi resonance occurs between ν_{CO} and 2δ in the free ion (see Section II, C). On coordination through nitrogen, ν_{CO} generally increases in magnitude and δ decreases. For these or for other reasons, Fermi resonances have not been observed in *N*-cyanato complexes. In *O*-cyanato complexes there is ample opportunity for the phenomenon of Fermi resonance to be maintained, and in $[Re(OCN)_6]^{2-}$ and $[Mo(OCN)_6]^{3-}$ the bands near 1300 and 1140 cm^{-1} (see Table XIV) have been assigned on this basis (*56*). Similarly, Burmeister has argued that the medium strong band at 1132 cm^{-1} in $(\pi\text{–}cp)_2Ti(OCN)_2$ is one component of such a pair of bands (*145*), but later he indicated that he prefers to formulate this compound $cp_2Ti(NCO)_2$ (*411*). The situation is not clarified by the linkage isomers $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$ since the only band observed in this region of the spectrum is at 1318 cm^{-1} in the latter compound, and this has been assigned only tentatively to ν_{CO} (*37*). It is possible that the Fermi resonance which has led to the extensive modification of ν_{CO} in some of the reported *O*-cyanates does not occur in this instance [nor in the case of $cp_2Ti(OCN)_2$?]. In either event, all the assignments for these compounds must be treated with caution pending further data.

The ranges observed for the different modes of coordination of the chalcogenocyanates have been summarized in Table XI. These ranges are based on the data in Bailey's review (*57*) and on the results included in Tables IX (thiocyanate), XII (selenocyanate), and XIV (cyanate). It will be clear from the preceding paragraphs and from these tables that many effects other than isomerization can cause considerable shifts in the frequencies concerned. It follows therefore that great care must be exercised in the application of the data of Table XI, which are not exclusive.

TABLE XV

PALLADIUM–LIGAND STRETCHING FREQUENCIES

Palladium compound	ν_{Pd-X} (cm^{-1})[a]	Reference
trans-$Pd(PPh_3)_2(NCO)_2$	350	(*578*)
trans-$Pd(AsPh_3)_2(NCO)_2$	360	(*578*)
$[PdL(NCO)]^{+b}$	365	(*482*)
cis-$Pd(bipy)(NCO)_2$	389, 374 sh	(*578*)
trans-$Pd(\gamma\text{-pic})_2(NCO)_2$	416	(*578*)
cis-$Pd(bipy)(NCS)_2$	345, 332	(*336*)
$[PdL(NCS)]^+$	365	(*482*)
trans-$Pd(AsPh_3)_2(SCN)_2$	306	(*336*)
cis-$Pd(bipy)(SCN)_2$	316, 304	(*336*)
$[PdL(SCN)]^+$	320	(*482*)
$[PdL(NCSe)]^+$	360	(*482*)
$[PdL(SeCN)]^+$	318	(*482*)

[a] X = anion.
[b] L = Et_4dien.

Far-infrared spectra have also been considered for these complexes, and Bailey *et al.* (*57*) conclude the section in their review on this topic "Indeed, there is little reason to expect this frequency to offer a simple bonding mode criterion." The effect of stereochemistry on ν_{M-L} is particularly marked. Thus, Clark and Williams (*201*) have shown that $\nu_{M-Cl} > \nu_{M-NCS}$ for tetrahedral MX_2L_2 compounds, but $\nu_{M-Cl} < \nu_{M-NCS}$ for most octahedral compounds (see Ref. *57*). The few results for palladium(II) complexes recorded in Table XV show that other factors can have drastic effects also (see Refs. *57* and *578* for discussion).

B. ULTRAVIOLET AND VISIBLE SPECTROSCOPY

In Section II, D, 2 it was concluded that the internal electronic transitions have been adequately assigned for NCO^- and NCS^- and that they are particularly susceptible to perturbations from neighboring metal cations. It has been argued that *S*-thiocyanato complexes have a strong characteristic band at ~30,000 cm^{-1}, and *N*-thiocyanato complexes at ~38,000 cm^{-1} (*585*). However, Barnes and Day (*75*) have discussed the origin of this intense band which lies between 30,000 and 40,000 cm^{-1} in many thiocyanate complexes, and the distinction is not so clear cut. Such bands are not observed with nonreducible ions such as La^{3+}, Gd^{3+}, or Zn^{2+}, and it was concluded that these transitions were associated with a charge transfer to a reducible metal. By considering the nature of the orbitals concerned, Barnes and Day further concluded that the lowest-energy absorption in the free thiocyanate ion results in a net transfer of charge from nitrogen to carbon. In *N*-thiocyanato complexes, therefore, the position of this transition will depend on the oxidizing power of the reducible metal. Similarly, the lowest-energy bands at *N*-cyanato and *N*-selenocyanato complexes of the divalent ions of the first transition series are primarily ligand-to-metal charge transfer spectra (*242*). The spectra of a variety of tetra- and hexacoordinated metal complexes with NCS^- and $NCSe^-$ have been collated and discussed by Schmidtke (*663*), but no simple distinction between the possible modes of coordination is possible. The spectra of some cyanate complexes have been discussed also (*453*).

Transition metal ions with partially filled d orbitals will show the expected d-d spectra which will depend on the degree of perturbation of these orbitals by the coordinating ligand. It has been well established that coordination through sulfur causes less perturbation than coordination through the nitrogen of the thiocyanate ion, or —SCN occurs lower in the spectrochemical series than —NCS (see, e.g., Ref. *664*), and a similar distinction may be made between —SeCN and —NCSe (*663*).

Although the foregoing generalizations can assist in the assignment of the spectrum of a compound of known structure, they are less useful when it comes to determining the mode of coordination of a chalcogenocyanate group unless other known compounds are available for comparative purposes. Thus, the green solution of the unstable $[Cr(H_2O)_5SCN]^{2+}$ was identified by comparing it with the purple solution of $[Cr(H_2O)_5NCS]^{2+}$: the absorption spectra were similar except that the maxima in the former were shifted some 40 nm toward longer wavelengths (*363*). This and some other examples are given in Table XVI where some intraligand bands are also quoted.

TABLE XVI

Electronic Spectra of Some Thiocyanate Complexes

Thiocyanate	ν (cm^{-1})	ε	Assignment[a]	References
$[Cr(NCS)_6]^{3-}$	31,700	27,000	$t_{1u} \rightarrow t_{2g}$	*(663)*
$[Ru(NCS)_6]^{3-}$	18,200	7,850	$t_{1u} \rightarrow t_{2g}$	*(663)*
$[Os(NCS)_6]^{3-}$	22,000	11,370	$t_{1u} \rightarrow t_{2g}$	*(663)*
$[Rh(SCN)_6]^{3-}$	34,800	25,300	$t_{1u} \rightarrow e_g$	*(663)*
$[Pt(SCN)_6]^{2-}$	34,600	44,000	$t_{1u} \rightarrow e_g$	*(663)*
$[Cr(H_2O)_5SCN]^{2+}$	38,200	8,000	C.T.	*(587)*
	22,300	20	—	
	16,100	26	—	
$[Cr(H_2O)_5NCS]^{2+}$	24,400	33.5	—	*(364)*
	17,600	31.4	—	
cis-$[Cr(H_2O)_4(NCS)_2]^+$	23,800	31.6	—	*(388)*
	17,600	28.2	—	
trans-$[Cr(H_2O)_4(NCS)_2]^+$	23,500	25.1	—	*(388)*
	16,900	25.1	—	
$[Cr(H_2O)_4(NCS)(SCN)]^+$	37,700	8,300	C.T.	*(129)*
	22,700	43	—	
	16,500	55	—	
$[Ru(NH_3)_5SCN]^{2+}$	45,000	13,300	$\pi \rightarrow \pi$ (NCS^-)	*(490)*
	36,000	209	$^2E_u \rightarrow {}^2T_{2g}$	
	31,100	407	$^2E_u \rightarrow {}^2T_{1g}$	
	20,200	3,620	$^2E_u \rightarrow {}^2E_u$	
$[Fe(CN)_5NCS]^{3-}$	38,500 sh	2,280	$2\pi(NCS) \rightarrow d\pi(Fe)$	*(360)*
	37,000 sh	2,130	LF	
	33,300 sh	1,360	$\sigma(CN) \rightarrow d\pi(Fe)$	
	31,000 sh	1,090	$\pi(CN) \rightarrow d\pi(Fe)$	
	28,600	995	LF	
	25,300 sh	520	$\pi(CN) \rightarrow d\pi(Fe)$	
	19,200	3,600		

(continued)

TABLE XVI—*continued*

Thiocyanate	ν (cm^{-1})	ε	Assignment[a]	References
$[Co(CN)_5SCN]^{3-}$	50,000	16,700	$(5e, 2b_2) \rightarrow 6e$	*(359)*
	44,000	4,300	$2\pi \rightarrow 3\pi$	
	37,700	17,100	$4e \rightarrow 3a_1$	
	26,500	191	$^1A_1 \rightarrow {}^1E\ (^1A_2?)$	
$[Co(CN)_5NCS]^{3-}$	49,500	28,100	$(5e, 2b_2) \rightarrow 6e$	*(359)*
	37,700	2,340	$4e \rightarrow 3a_1$	
	27,600	500	$^1A_1 \rightarrow {}^1E\ (^1A_2)$	
$[Co(DH)_2py(SCN)]$	40,000	—	—	*(574)*
	33,500	—	—	
$[Co(DH)_2py(NCS)]$	40,000	—	—	*(574)*
	33,000	—	—	
	21,000	—	—	
$[Co(NH_3)_5(NCS)]^{2+}$	32,700	1,490	—	*(134)*
	20,100	179	$^1A_{1g} \rightarrow {}^1T_{1g}$	
$[Co(NH_3)_5(SCN)]^{2+}$	34,700	15,600	—	*(134)*
	19,500	74	$^1A_{1g} \rightarrow {}^1T_{1g}$[b]	
$[Rh(NH_3)_5NCS]^{2+}$	46,500	5,100	Internal NCS bands	*(659, 660)*
	41,700	2,200		
	31,200	460	$^1A_{1g} \rightarrow {}^1T_{1g}$	
$[Rh(NH_3)_5SCN)]^{2+}$	42,900	19,200	Internal NCS band	*(659, 661)*
	35,700	450	—	
	31,000	220	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	26,700	85	$^1A_{1g} \rightarrow {}^1T_{1g}$	
$[Ir(NH_3)_5NCS]^{2+}$	43,500	2,260	$^1A_{1g} \rightarrow {}^1T_{2g}$	*(659, 661)*
	38,500	560	$^1A_{1g} \rightarrow {}^1T_{1g}$	

$[Ir(NH_3)_5SCN]^{2+}$	42,500	820	${}^1A_{1g} \rightarrow {}^1T_{2g}$	(*659, 661*)
	36,400	165	${}^1A_{1g} \rightarrow {}^1T_{1g}$[b]	
$Pd(AsPh_3)_2(NCS)_2$	28,600	—	—	(*143*)
$Pd(AsPh_3)_2(SCN)_2$	25,300	—	—	(*143*)
	21,050	—	—	
$Pd(Ph_2PCH_2CH_2NMe_2)(NCS)(SCN)$	29,600	5,280	—	(*526*)
	24,400	615	—	
$Cu(tripyam)(SCN)_2$	26,300	—	—	(*473*)
	15,400	—	—	
	13,700	—	—	
Cu(tripyam)(SCN)(NCS)	26,300	—	—	(*473*)
	16,400	—	—	
	14,300	—	—	
$Cu(tripyam)(NCS)_2$	26,300	—	—	(*473*)
	23,500	—	—	
	15,400	—	—	

---

[a] The assignments are described using the nomenclature of the original papers and it may be necessary to consult these in some cases. Generally the conventional description of d—d transitions has been used and has been added in some cases where the authors did not make the assignments.

[b] Broad bands observed implying some splitting of the first crystal field transition.

Electronic spectra may not always be of prime importance in determining the mode of coordination of a monodentate chalcogenocyanate, although the chromophore MN_5S is sufficiently different from MN_5N to show some effects (see Table XVI), but they can be useful in the study of bridging systems. Thus, $Nian_2(NCS)_2$ was shown to contain octahedral nickel(II) with Ni—NCS—Ni bridges since S coordination is sufficiently different from the alternative nitrogen atoms to distort the ligand field and produce splitting of the first and second electronic absorption bands (*167*). Similar examples may be found in particular for nickel(II) and cobalt(II) complexes (see Sections IV, H and I).

Many of these spectra have been interpreted so as to distinguish between the extent of σ and π bonding in different systems, but some controversy is associated with the validity of these interpretations and they have not been included generally in this review.

The *N*-cyanato and *N*-selenocyanato groups have been shown to cause very similar splitting of the d orbitals to —NCS. Table XVII shows the spectral parameters for $[Co(NCX)_4]^{2-}$ (X = O, S, and Se) and for $[Co(NCX)_4Hg]$ (X = S and Se), and illustrates the similarity. It can be seen also that the values for Δ are in general accord with those expected for an N-bonded group, and the changes occurring as the terminal noncoordinating atom is changed suggest a small but significant transmitted effect. Other examples may be obtained from the references in Section IV.

The compound $Cu(pic)_2 \cdot KNCS$ was shown to be a double salt, but the electronic spectra suggested that the corresponding cyanate was five-coordinate: by comparing the spectra and making assumptions concerning the difference in behavior between the Cu—NCS and Cu—NCO moieties (if they had existed in this system), it was deduced that the latter compound should be formulated $K[Cu(pic)_2(OCN)]$ (*321*).

Apart from the preceding example, which depends on a rather indirect argument, electronic spectra are only useful to provide supporting evidence for the mode of coordination of cyanate and selenocyanate complexes. The arguments must necessarily be based on the magnitudes of crystal field parameters, and these can be assessed only by comparison with other related values.

C. ^{14}N NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The values for the chemical shifts for the free ions were discussed in Section II, D, 3, and a general review of ^{14}N NMR data in inorganic molecules has appeared (*501*). The application of ^{14}N NMR to the problem of determining the mode of coordination of the thiocyanate ion was

TABLE XVII

ELECTRONIC SPECTRAL DATA AND CRYSTAL FIELD PARAMETERS FOR $[Co(NCX)_4]^{2-}$ (X = O, S, and Se)

Parameter	$[Co(NCO)_4]^{2-}$ [a]	$[Co(NCS)_4]^{2-}$ [b]	$[Co(NCS)_4Hg]$[b]	$[Co(NCSe)_4]^{2-}$ [c]	$[Co(NCSe)_4Hg]$[c]
ν_1 (cm^{-1})	—	—	—	—	—
ν_2 (cm^{-1})	7,150	7,780	8,300	7,840	8,400
ν_3 (cm^{-1})	16,100	16,250	16,700	16,000	16,000
Δ (cm^{-1})	4,150	4,550	4,880	4,710	4,980
B' (cm^{-1})	720	691	691	644	631
β ($B'/967$)	0.745	0.715	0.715	0.666	0.652

[a] Data from Ref. *211*.

[b] Data from Ref. *213*.

[c] Data from Ref. *212*.

first demonstrated by Howarth, Richards, and Venanzi (*390*). Some results are listed in Table XVIII, where it can be seen that there is only a small downfield nitrogen chemical shift relative to the thiocyanate ion if coordination occurs through sulfur, whereas nitrogen coordination produces a significant high-field shift. These authors assumed that N bonding lowers the energy of the nonbonding orbital containing the pair of electrons and shifts the ^{14}N resonance upfield; S bonding however does not affect the nonbonding orbital but lowers the energy of the delocalized antibonding orbital by mixing with metal d orbitals and so causes a small downfield shift relative to the free ion. Recently, a further study on similar compounds (*111*) has confirmed these results, including the observation that the large solvent effect on the ^{14}N shift for $[Cd(NCS)_4]^{2-}$ is due to the presence in solution of both N and S isomers in kinetic equilibrium (*390*).

TABLE XVIII

^{14}N CHEMICAL SHIFTS FOR SOME THIOCYANATE COMPLEXES

Thiocyanate	Solvent	δ (NO_3^-) (ppm)	References
$(NH_4)_2[Hg(SCN)_4]$	H_2O	+146	(*111*)
$Na_2[Pd(SCN)_4]$	H_2O	+148	(*390*)
$Na_2[Hg(SCN)_4]$	H_2O	+157	(*390*)
$K_3[Rh(SCN)_6]$	H_2O	+158	(*390*)
$Na_3[Ir(SCN)_6]$	H_2O	+163	(*390*)
$K_2[Pt(SCN)_4]$	H_2O	+166	(*390*)
NCS^-	H_2O	+166	(*390*)
NCS^-	H_2O	+170	(*111*)
$Na_2[Cd(NCS)_4]$	H_2O	+178	(*390*)
$K_4[Cd(NCS)_6]$	H_2O	+183	(*111*)
$Na_2[Cd(NCS)_4]$	MeOH	+220	(*390*)
$K_2[Zn(NCS)_4]\cdot 2Me_2CO$	H_2O	+220	(*111*)
$K_2[Zn(NCS)_4]$	H_2O	+238	(*111*)
trans-$Pt(PEt_3)_2(NCS)_2$	$CHCl_3$	+239	(*390*)
$K_2[Ru(NCS)_5NO]$	H_2O	+245	(*390*)
cis-$Pt(PPhBu_2)_2(NCS)_2$	$CHCl_3$	+249	(*390*)
$Na_2[Zn(NCS)_4]$	EtOH	+255.5	(*390*)
trans-$Ni(PPhBu_2)_2(NCS)_2$	$CHCl_3$	+291	(*390*)
trans-$Ni(PEt_3)_2(NCS)_2$	$CHCl_3$	+293	(*390*)
cis-$Pt(PBu_3)_2(NCS)_2$	$CHCl_3$	+302	(*390*)
cis-$Pt(AsBu_3)_2(NCS)_2$	$CHCl_3$	+303	(*390*)

Table XIX gives some ^{14}N shift data for cyanate compounds, where a high-field shift is seen for *N*-cyanato complexes and a downfield shift observed for EtOCN (*192*). Similar arguments to those used for thiocyanate complexes presumably may be also applied here.

TABLE XIX

^{14}N CHEMICAL SHIFTS FOR SOME CYANATE COMPLEXES

Cyanate	Solvent	δ (NO_3^-) (ppm)	References
$(Et_4N)[Ag(NCO)_2]$	Me_2CO	+344	(*192*)
$Pt(PPh_3)_2(NCO)_2$	CH_2Cl_2	+340	(*84*)
$(Et_2NH_2)_2[Zn(NCO)_4]$	Me_2CO	+325	(*192*)
$(Me_4N)_2[Hg(NCO)_4]$	Me_2CO	+317	(*192*)
$(Et_4N)_2[Hg(NCO)_4]$	$MeNO_2$	+312	(*192*)
NCO^-	H_2O	+300	(*192*)
EtOCN	—	+222	(*192*)
PhOCN	—	+208	(*84*)

Compound $K[Ph_3Sn(NCSe)_2]$ resonates at +215 ppm, and $NCSe^-$ at +136 ppm (relative to NO_3^-) (*111*) so that the same behavior as was described in the foregoing seems likely for selenocyanate complexes. The absence of further data precludes this tentative generalization from being more firmly based at present.

D. CHEMICAL METHODS

There are no general chemical methods for determining the mode of chalcogenocyanate bonding in complexes in the way that there are for organic compounds (*41*). This is no doubt a reflection on the ready occurrence of substitution reactions and on the lability of these groups in many cases. A pair linkage of isomers may be assigned on the basis of the easy conversion of one into the other (if the stable isomer is known), but such evidence is not sufficient by itself and needs further spectroscopic results for confirmation.

The compound *trans*-$[Rhen_2Cl(NCS)]NCS$ reacts with twice the amount of mercuric nitrate necessary to determine the free thiocyanate ion, whereas only one equivalent of silver nitrate is consumed using the Volhard titration. This was explained by assuming that the mercuric ion was able to form a Rh—NCS—Hg bridge, which is less readily achieved with silver, and, under the conditions of the Volhard titration, the silver is removed as the thiocyanate ions are titrated in (*415*). Orhanovic and Sutin (*587*) also analyzed mixtures containing $[Cr(H_2O)_5NCS]^{2+}$ and $[Cr(H_2O)_5SCN]^{2+}$ by adding mercuric ions and obtaining $[Cr(H_2O)_5NCSHg]^+$ and $[Cr(H_2O)_6]^{3+}$, respectively, which were determined spectrophotometrically. However, they had discovered that some of the bridged complex is also produced from the Cr—SCN compound and allowance was made for this. The same workers also bubbled chlorine through a solution of the mixture of isomers and obtained $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5Cl]^{2+}$. Control experiments had shown that $[Cr(H_2O)_5NCS]^{2+}$ gave the hexahydrate under these conditions, but comparison with the mercury reaction indicated that $[Cr(H_2O)_5SCN]^{2+}$ did not form $[Cr(H_2O)_5Cl]^{2+}$ exclusively, and again corrections have to be made.

The nature of the noncoordinated end of the chalcogenocyanate group may also be used, with caution, to distinguish between N- and Se-bonded selenocyanates. The compound π-cpFe(CO)(PPh_3)SeCN is stable but its N-bonded isomer readily deselenates at 27°C (*410*). Similarly, it is difficult to study Rh(I)—NCSe complexes because of rapid deselenation, and the loss of tellurium is a similar feature of tellurocyanate chemistry (*36*).

Although the foregoing reactions are not ideal for determining the mode of bonding, they do suggest that such methods are worth further study in the future and may yield interesting results.

E. MASS SPECTROSCOPY

The mass spectrum of HNCO showed intense peaks corresponding to HN^+ and COH^+, and thus to a mixture of isomers, but the presence of CH^+, OH^+, and NO^+ indicated rather a triangular structure for the ion in the transition state (*692*). Such rearrangements make this an unreliable technique for these structural assignments, and, indeed, the isomeric compounds $(\pi\text{-}C_5H_5)_2W(NCS)_2$ and $(\pi\text{-}C_5H_5)_2W(NCS)(SCN)$ have similar fragmentation patterns (*344*). Burmeister *et al.* (*145*) have reported characteristic TiO^+, ZrO^+, and HfO^+ peaks in the spectra of $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$ and the zirconium and hafnium analogs, but there is some doubt that all these compounds are as designated.

F. ^{1}H NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The chemical shifts of the α-hydrogen atoms allow the distinction to be made between RNCS and RSCN (*522*). Similar measurements may be used in coordination chemistry, for example, the methyl protons in $Co(DH)_2py(NCS)$ resonate at higher field to those in $Co(DH)_2py(NCS)$ (*574*), but here the correlations are purely empirical, and the direction of the shift cannot be associated with a particular isomer. Among the many observations of such chemical shift measurements are included those on the systems $Rh(PMe_2Ph)_3Cl_2(NCS)$ (*126*), $(\pi\text{-}C_5H_5)Fe(CO)_2$-NCS and $(\pi\text{-}C_5H_5)Mo(CO)_3NCS$ (*690*), and $(\pi\text{-}C_5H_5)_2W(NCS)(SCN)$ (*344*) together with their linkage isomers and other related compounds.

G. DIPOLE MOMENTS

Although dipole moments have been used to distinguish between geometric isomers in, for example, square planar complexes there are no examples of the use of this technique in distinguishing between linkage isomers. Thus, Chatt and Hart (*188*) used dipole moments to show that the two isomers $(PPr_3)_2Pt_2Cl_2(CNS)$ contained phosphines that are trans to each other, but they were unable to draw any further structural conclusions without use of other techniques. On the other hand, dipole moments were used not only to show that the compounds $Znpy_2(NCX)_2$ (X = O and S) are tetrahedral, but also that they contain N-bonded anions (*655*). An indirect application of this method has been developed by Jensen *et al.* (*411*) who showed that

$$\frac{\mu \text{ for } cp_2Ti(NCS)_2}{\mu \text{ for } cp_2TiCl_2} = \frac{\mu \text{ for } cp_2Zr(NCS)_2}{\mu \text{ for } cp_2ZrCl_2}$$

whereas

$$\frac{\mu \text{ for } cp_2Ti(OCN)_2}{\mu \text{ for } cp_2TiCl_2} \neq \frac{\mu \text{ for } cp_2Zr(OCN)_2}{\mu \text{ for } cp_2ZrCl_2}$$

from which it was deduced that the cyanate bonding modes in the two compounds are not the same. The authors were unable to conclude from this evidence whether the titanium or the zirconium compound contained the O-bonded species.

H. THERMODYNAMIC METHODS

The theories for the interaction of the different donor atoms with different types of metal centers are discussed in Section V. These theories predict positive enthalpy and entropy changes for the reaction of a "hard" base with a hard or class a metal, whereas the reaction of a "soft" base with a class b metal shows a negative enthalpy of reaction (*15*). A study of the heats of formation of some polyamine copper(II) complexes with NCS^- shows a small positive enthalpy change for the reaction, and a larger positive entropy change (*71*). The analogous reaction with NCS^- and $[Ptdiars]^{2+}$ exhibits a negative enthalpy change (*255*).

IV. Chalcogenocyanate Complexes of the Transition Elements

A. SCANDIUM, YTTRIUM, LANTHANUM, AND THE LANTHANIDES

1. *Cyanates*

The compound $(n\text{-}Bu_4N)_3[Er(NCO)_6]$ contaminated with silver cyanate has been reported, and infrared data suggest this formulation even though the compound is impure (*160*). The same workers (*144*), without retracting the foregoing, later reported that the same reaction can result in the formation of $(n\text{-}Bu_4N)[Ag(NCO)_2]$. The tricyclopentadienyl and bisindenyl compounds of cerium(IV), $Ce(C_5H_5)_3NCO$ and $Ce(C_9H_7)_2(NCO)_2$, have been characterized (423).

2. *Thiocyanates*

The X-ray structure of $(n\text{-}Bu_4N)_3[Er(NCS)_6]$ shows the complex to have six octahedrally coordinated *N*-thiocyanato groups with an average Er—N distance 2.34(2) Å. The Er-NCS groups are approximately linear with Er—NC and NCS angles 174(2)° and 176(3)°, respectively. The N—C and C—S bonds are 1.10(3) and 1.61(3) Å. The cations do not penetrate significantly into the sphere of influence of the terminal sulfur atoms. Related complexes of other lanthanides (Pr, Nd, Sm, Eu, Ho, Tm, and Yb, and also Y) were also prepared and have infrared mull spectra similar to the preceding. Conductivity measurements in nitromethane and nitrobenzene suggest some dissociation of the complexes, especially for the lighter lanthanides, and this is confirmed by spectral measurements in the visible region (*518*). Burmeister *et al.* (*160*) have reported a very similar series of complexes $(n\text{-}Bu_4N)_3[Ln(NCS)_6]$ Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb) also with high molar conductivities in solution. Surprisingly, these solutions show very high integrated intensities for ν_{CN} $(13\text{–}32 \times 10^4\ M^{-1}\ cm^{-2})$, but perhaps these data reflect the lack of knowledge of their origin (see Section III, A) rather than contradicting the conductivity results; Bailey *et al.* (*60*) have recorded a lower intensity value $(10.5 \times 10^4\ M^{-1}\ cm^{-2})$ for $(Et_4N)_3[Yb(NCS)_6]$.

Alkali metal hexa-*N*-thiocyanatoscandates have been prepared and characterized from infrared mull spectra (*653*). The complexes $(R_4N)_3[Sc(NCS)_6]$ (R = Me, Et, *n*-Bu) have also been prepared and their solubilities determined: they are N-bonded from infrared data, and dissociate on dilution (*270*). The thermal stabilities of the alkali metal salts increase with M in the order $Li < Na < K < Rb < Cs$ (*352*).

All the examples reported so far appear to contain N-bonded thiocyanate groups and to dissociate readily in solution. Thus, $[ScL_3](NCS)_3$ (L = bipy or phen) has been prepared and characterized (*223*). Treatment with warm EtOH gives $[ScL_2(NCS)_2](NCS)$ where the formulation is supported by conductivity measurements (in CH_3CN or CH_3NO_2) and infrared mull spectra; in aqueous solutions the coordinated NCS^- is displaced (*223*, *225*, *464*). Other mixed liquid complexes of these metals with NCS^- are listed in Table XX. A 1:1 adduct is formed between 1,3,5-trinitrobenzene and several lanthanide thiocyanates. No

TABLE XX

Some Thiocyanate Complexes of Scandium, Yttrium, and the Lanthanides

Complex	Composition	References
$Sc(NCS)_3\cdot n$py	$n = 2$–4	(*652*)
$Sc(NCS)_3\cdot L_3$	L = py-NO, 2-, 3-, and 4-MepyNO, Ph_3MO (M = P, As), DMSO, DMF	(*225*)
$Sc(NCS)_3\cdot L_n$	$n = 2$; L = isoamyl alcohol, $C_4H_8O_2$	(*465*)
	$n = 1$; L = $C_4H_8O_2$	(*465*)
$Ln(NCS)_3(OPPh_3)_3$	Ln = Y, Sm-Lu	(*218*)
$Ln(NCS)_3(OPPh_3)_4$	Ln = La-Sm (not Pm)	(*218*)
$Ln(NCS)_3(OAsPh_3)_3$	Ln = Ce, Pr	(*218*)
$Ln(NCS)_32H_2O\cdot 4C_4H_8O_2$	Ln = La, Ce, Pr, Nd	(*769*)
$[Ln(phen)_3](NCS)_3$	Ln = La-Lu (not Pm)	(*369*)
$Ln(NCS)_2(OC_2H_4NHC_2H_4OH)MeOH$	Ln = La, Ce, Pr, Nd	(*330*)
$Ln(NCS)_2$8–ox·6MeOH	Ln = La, Pr, Nd, Sm, Eu, Gd	(*331*)
$Ln(NCS)_3\cdot n$DMA	$n = 5$; Ln = Ce, Pr, Nd	(*770*)
	$n = 4$; Ln = Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	(*770*)
$MSm(NCS)_4\cdot 4EtOH$	M = K, Rb, or Cs	(*740*)
$Na_2Gd(NCS)_5\cdot 5C_4H_8O_2$		(*740*)
$KGd(NCS)_4\cdot 4EtOH$		(*740*)
$Sm(NCS)_3\cdot 4C_4H_8O_2$		(*740*)
$Ln(NCS)_3\cdot n$TMU	$n = 5$; Ln = La—Nd,	(*601*)
	$n = 4$; Ln = Sm—Er, Y	(*601*)
	$n = 3$; Ln = Tm—Lu	(*601*)

structural details are given but the order of increasing complexing facility is La < Ce < Nd < Yb < Gd (*731*). The species $[O_3SO—Ce—NCS—Ce—OSO_3]^{3+}$ has been suggested as an intermediate in the reduction of ceric ions by NCS^- on the basis of kinetic evidence only (*730*). Golub *et al.* have reported some further complexes of La, Pr, Nd (*332*), Sm (*324*), and Eu (*325*) but without structural data; these complexes are not listed specifically. The Mössbauer spectrum of $Eu(NCS)_3$ has been reported (*205*).

The tricyclopentadienyl and bisindenyl compounds of cerium(IV), $Ce(C_5H_5)_3NCS$ and $Ce(C_9H_7)_2(NCS)_2$, have been characterized (*423*).

3. *Selenocyanates*

The compound $(n\text{-}Bu_4N)_3[Y(NCSe)_6]$ has been prepared (*162*) as well as the corresponding lanthanide complexes (Ln = Pr, Nd, Sm, Dy, Ho, Er) (*144*). Infrared spectra indicate that they are N-bonded. The compounds show a slightly greater tendency to dissociate in solution than the corresponding thiocyanate complexes. The magnitudes of the molar absorptivities of the absorption maxima in the visible spectra indicate pronounced deviations from O_h symmetry—a similar effect was noted for the thiocyanate complexes (*160*). The authors suggest this may arise from the nonlinearity of the M—NCSe (or M—NCS) moiety, but the structural data for the latter complexes (*518*) do not support this view. Coordination of solvent molecules in solution could account for the effect. Mixed-ligand selenocyanate complexes of Y, Sc, La, Ce, Pr, and Nd have been reported with various nitrogen and oxygen donors but in no case is the selenocyanate group coordinated other than as a monodentate ligand through nitrogen (*327*, *328*, *733*).

B. THE ACTINIDES

1. Cyanates

The preparation of uranyl cyanate, $UO_2(CNO)_2$, and of some of its corresponding anionic complexes were reported in 1914 (*592*); $(Et_4N)_2$-$[UO_2(NCO)_4H_2O]$ has been characterized from infrared data (*59*).

2. Thiocyanates

An X-ray structure determination has shown $(Et_4N)_4[U(NCS)_8]$ to have uranium at the center, and the nitrogen ligand atoms at the eight vertices, of a regular cube (*216*). The compounds $(Et_4N)_4[M(NCS)_8]$ (M = Th, Pa, U, Np, Pu) are all isostructural (*26*). Splitting of ν_{CN} occurs in $M_4[U(NCS)_8]$ (M = K, Cs) (*26*) and in $Cs_4[U(NCS)_8]$ which suggests some lowering of the symmetry of the complex anion with these Group I cations (*57*). The number of bands observed in infrared studies of $M_4[Th(NCS)_8].2H_2O$ (M = Rb, Cs), the monohydrates of the analogous uranium compounds, and $(NH_4)_4[U(NCS)_8]$ suggests that these compounds exist with dodecahedral coordination in the solid or as Archimedean antiprisms in solution (*349*). Changes in the electronic spectrum of $(Et_4N)_4[U(NCS)_8]$ as a solid and in nitromethane have been attributed to changes in the nature of the cation–anion interaction on dissolution (*311*). Other eight-coordinate complexes include $U(NCS)_4 \cdot 4DMA$ (*50*) and $M(NCS)_4(R_3PO)_4$ (R = Me; M = U, Np, Pu or R = NMe_2; M = Th, U, Np, Pu or R = Ph; M = Th, U, Np) (*25*, *51*). Also $Th(NCS)_4 \cdot 6Me_3PO$ has been reported (*25*) as have some uncharacterized mixed-ligand complexes of thorium (*538*, *539*). Of these, $U(NCS)_4 \cdot 4DMA$ as a typical example shows a single sharp band at 2047 cm^{-1}, in a similar position to that observed in various uncharacterized compounds $M_3[UO_2(C_2O_4)_2CNS]$ ($M = NH_4$, K, Na, CN_3H_6, Et_3NH) (*676*).

Similar infrared results for other uranyl complexes have been interpreted as indicating N-bonded thiocyanate groups for $M_3UO_2(NCS)_5$, $UO_2(NCS)_2L_3$, and $MUO_2(NCS)_3L_2$ ($M = NH_4$, K, Rb, Cs; $L = H_2O$) (*435*, *675*). The preparation of these compounds is perhaps surprising in view of the fact that the former oxalato complexes contain only one coordinated thiocyanate group, regardless of the course of the reaction (*676*), and that the kinetic results of Kustin and Hurwitz (*475*), who used the temperature-jump method, show that only the 1:1 complex between the uranyl and thiocyanate ions is kinetically significant. However, the first three, stepwise stability constants have been determined for the reaction between UO_2^{2+} and thiocyanate ions (*16*). The foregoing infrared results are contrasted with those for the compounds $UO_2(NCS)_2(TBP)_2$ and $UO_2(NCS)_2H_2O$ and with the $[UO_2(NCS)_3]^-$ anion to show that in these systems the bridging thiocyanate group is present (*764*)—this mode has been suggested in other similar uranyl systems without any evidence (*763*).

The formation constants of thiocyanate complexes of Am(III), Cm(III), Bk(III), Cf(III), and Es(III) have been determined (*367*), and a spectrophotometric study made of the Am(III) complexes (*366*); no structural data are avilable.

3. *Selenocyanates*

The compounds $(Et_4N)_4[M(NSCe)_8]$ (M = Pa, U) have been characterized by comparing their spectral and crystallographic properties with the corresponding thiocyanate complexes (*26*). Some thorium(IV) complexes have been prepared containing DMF and N-bonded selenocyanate groups (*326*). Although various uranyl selenocyanate complexes have been reported, no structural data are available (*686*).

C. TITANIUM, ZIRCONIUM, AND HAFNIUM

1. *Cyanates*

A number of metallocene cyanate complexes have been reported for these metals. Samuel (*648*) and Coutts and Wailes (*219*) reported $cp_2M(CNO)_2$ (M = Ti, Zr) independently in 1966. Samuel made no definite assignments of the structure, but Coutts and Wailes suggested the compounds were *N*-cyanato complexes. Later, Burmeister *et al.* (*145*, *146*) reexamined the compounds in more detail and argued that they, and the hafnium analog, were *O*-cyanato complexes. This was subsequently confirmed for the titanium compound by Beck (*85*) using ^{14}N NMR. Later, however, dipole moment measurements suggested that the titanium and zirconium compounds could not both be O-bonded, in spite of their spectral similarities (*411*); the titanium(III) compound, $cp_2Ti(NCO)$, however, does contain the *N*-cyanato group (*145*, *220*).

2. *Thiocyanates*

The compound $K_2[Ti(CNS)_6]$ has been reported (*668*, *669*) and the effect of different bases on its preparation has been studied (*718*). The compound $(n\text{-}Bu_4N)_3[Ti(NCS)_6]$ has been shown to contain *N*-thiocyanato groups by comparing its crystal field parameters with those of other complexes (*486*); $K_2TiO(CNS)_4.2NH_3$ has been reported (*667*). A series of complexes $TiL_2(NCS)_4$ with a variety of phosphine oxide-type ligands has been described, with *N*-thiocyanato groups in every case: the assignment is based on their infrared spectra and includes a discussion of Ti—NCS stretching frequencies (*484*). Equilibrium studies indicate the existence of a 1:1 adduct between NCS^- and Ti(III) (*246*). Orange $(NH_4)[Ti(CNS)_4]$ and violet $(NH_4)[Ti(CNS)_4(H_2O)_2]$ are 1:1 electrolytes and are oxidized to $(NH_4)[Ti(CNS)_4(OH)(H_2O)]$ (*709*); the low magnetic moment of the first of these compounds has been confirmed (*647*).

Golub *et al.* have shown that zirconium(IV) and hafnium(IV) form eight-coordinate complexes in solution with NCS^- alone or in the presence of DMF (*329*, *333*). The compounds $(Et_4N)_2[M(NCS)_6]$ (M = Zr, Hf) both contain *N*-thiocyanato groups, as determined by infrared studies, and are isomorphous (*61*). Benzyl phenyl arsinic acid has been used as an extractant and, unlike most systems, hafnium complexes are extracted better than zirconium complexes in the presence of NCS^- (*302*).

Metallocene–thiocyanate complexes have been reported similar to the cyanate complexes described previously. There is general agreement that these are *N*-thiocyanato complexes, $cp_2M(NCS)_2$ (M = Ti, Zr, Hf) (*145*, *146*, *219*, *320*, *648*). The compound $cpTi(NCS)_3$ has been prepared, and infrared measurements show it to be as written (*458*); $cp_2Ti(NCS)$ is trimeric but the mode of bridging is not known (*220*).

3. *Selenocyanates*

The compound $(n\text{-}Bu_4N)_2Ti(NCSe)_6$ is known (*163*), and $co_2M\text{-}(NSCe)_2)$ (M = Ti, Zr, Hf) are *N*-selenocyanato complexes (*145*, *146*, *459*); $(Et_4N)_2[M(NSCe)_6]$ (M = Zr, Hf) have been characterized (*307*).

D. VANADIUM, NIOBIUM, AND TANTALUM

1. *Cyanates*

Although the only cyanate compound reported for these metals is $cp_2V(NCO)_2$ (the analogous NCS and NCSe compounds are also known) which is in contrast to the *O*-cyanatotitanium analog (*145*, *261*), there are numerous examples of thiocyanate complexes.

2. *Thiocyanates*

X-Ray structures have been determined for $(NH_4)_2VO(NCS)_4 \cdot 5H_2O$ (*374*) and $(Ph_4As)_2[NbO(NCS)_5]$ (*424*). The deviations from linearity of the NCS group in the latter case are not statistically significant, but the Nb—N bond trans to oxygen is appreciably longer than those in the cis plane (*424*). There are only planar NCS groups in the vanadium(IV) compound.

The compound $VO(phen)(CNS)_2$ has been formulated as an *S*-thiocyanato complex with $\nu_{CN} = 2040\ cm^{-1}$ (*627*). This frequency is very low and is much more characteristic of an *N*-thiocyanato complex, as is observed for most other thiocyanate complexes of these metals (see Table XXI in which the recorded changes in the oxidation number of the central metal and the changes in its ligational environment apparently have no effect on the thiocyanate mode of bonding). The compounds $M(NCS)_2(OR)_3bipy$ (M = Nb, Ta; R = Me, Et) are eight-coordinate, probably distorted dodecahedral, with bridging alkoxide and terminal thiocyanate groups (*771*).

Gutmann *et al.* (*355–357*) have investigated the effect of solvents on the ease of formation of thiocyanate complexes. In the series $[VO(NCS)_n]^{(2-n)+}$ ($n = 1$–4) complexes with low values of n are formed more readily in solvents with low donor numbers and vice versa (*355*, *356*). The NCS^- is a stronger donor toward $VO(acac)_2$ than either the neutral molecules investigated or the halide ions (*367*).

The rate constants for the oxidation of $[V(H_2O)_6]^{2+}$ by $Fe(OH_2)^{3+}$, $FeCl^{2+}$, $FeNCS^{2+}$, and $FeN_3{}^{2+}$ are 4×10^5, $(4.6 \pm 0.5) \times 10^5$, $(6.6 \pm 0.7) \times 10^5$, and $(5.2 \pm 0.6) \times 10^5\ M^{-1}\ sec^{1-}$, respectively, at 25°C and ionic strength 1.0 M. No spectrophotometric evidence indicating that VX^{2+} species were formed in the reaction was obtained. When the oxidation is carried out with $[Cr(H_2O)_5SCN]^{2+}$ (see Section IV, E), the reaction proceeds in two stages:

$$CrSCN^{2+} + V^{2+} \longrightarrow Cr^{2+} + VNCS^{2+}$$

$$VNCS^{2+} \longrightarrow V^{3+} + NCS^-$$

TABLE XXI

SOME THIOCYANATE COMPLEXES OF VANADIUM, NIOBIUM, AND TANTALUM

Complex	Composition	References
$VO(NCS)_2 \cdot nL$	$n = 4$ or 5; L = pyridine *N*-oxide $n = 2$; L = 4-pic *N*-oxide	(*112*) (*112*)
$[VO(NCS)_5]^{3-}$		(*666*)
$cp_2V(NCS)_2$		(*145, 261*)
$[V(NCS)_6]^{3-\,a}$		(*112, 145, 666, 774*)
$[VX_a(NCS)_bL_3]^a$	X = Cl or Br; $a = 0$, 1, or 2; $b = 3$ 2, or 1; L = CH_3CN, py, THF	(*110*)
$[V(CNS)_4L_2]^-$	L = py, 3-pic, 4-pic, 3,4-lut, 3,5-lut, $\frac{1}{2}$bipy, $\frac{1}{2}$phen	(*361*)
$[V(CNS)_3L_3]$	L = py, 3-pic, 4-pic, 3,4-lut, 3,5-lut, isoquin	(*361*)
$[V(CNS)_3(MeOH)_2L]$	L = Et_3N, an, quin, 2-pic, R_3P; R = Me, Et, *n*Pr, *n*Bu	(*361*)
$[V(NCS)_3(THF)_3]^-$		(*109*)
$[Nb(NCS)_6]^{-\,a}$		(*114, 131, 455*)
$[Nb(NCS)_5MeCN]^a$		(*115*)
$[Nb(NCS)_5]_2$		(*115*)
$[NbCl_a(NCS)_bMeCN]^a$	$a = 4$–1; $b = 1$–4	(*114*)
$[NbCl_a(NCS)_bEt_2O]$	$a = 4$ or 3; $b = 1$ or 2	(*114*)
$[NbO(NCS)_5]^-$		(*424*)
$[Nb(NCS)_6]^{2-}$		(*455*)
$[Ta(NCS)_6]^{-\,a}$		(*113, 131, 455*)
$[Ta(NCS)_5]_2$		(*115*)
$[Ta(NCS)_5L]^a$	L = CH_3CN, py	(*113*)
$[TaCl_a(NCS)_bMeCN]^a$	$a = 4$–1; $b = 1$–4	(*113*)
$[TaCl_a(NCS)_bEt_2O]$	$a = 4$ or 3; $b = 1$ or 2	(*113*)
$TaOCl_a(NCS)_b \cdot 2CH_3CN$	$a = 0$–2; $b = 3$–1	(*116*)
$[TaO(NCS)_4]^{-\,a}$		(*116*)
$TaSCl_a(NCS)_bC_6H_5NCCl_2$	$a = 0$–2; $b = 3$–1	(*116*)
$[TaS(NCS)_4 \cdot C_6H_5NCCl_2]^-$		(*116*)

[a] Some solvent molecules may also be present in the lattice—see the original literature.

The rates for these reactions are 7.1 ± 0.4 M^{-1} sec^{-1} and 0.99 sec^{-1}, respectively. At the concentrations used the rate of isomerization of $CrSCN^{2+}$ was negligible relative to these values. Sutin *et al.* (*62*) suggest that these results indicate that, in contrast to the V(II)–Fe(III) reactions, the reaction of $CrSCN^{2+}$ with V^{2+} proceeds via an anion-bridged intermediate. It would be entirely consistent with what is now known of vanadium–thiocyanate complexes, and with the foregoing, for this intermediate to have the structure $[(H_2O)_5V\text{—}NCS\text{—}Cr(H_2O)_5]^{4+}$.

The forward and reverse rate constants for the reaction

$$V^{2+} + NCS^- \rightleftharpoons VNCS^+$$

are 15 ± 2 M^{-1} sec^{-1} and 1.04 ± 0.2 sec^{-1} at 24°C and $\mu = 1\ M$ (*471*). The rates for the corresponding vanadium(III) reactions have been found independently as 104 ± 10 M^{-1} sec^{-1} and 0.7 ± 0.1 sec^{-1} at 23°C and $\mu = 1\ M$ (*471*), and 114 ± 10 M^{-1} sec^{-1} and 1.03 ± 0.06 sec^{-1} at 25°C and $\mu = 1\ M$ (*63*). In DMSO the forward and reverse rates for the reaction,

$$[V(DMSO)_6]^{3+} + NCS^- \rightleftharpoons [V(DMSO)_5NCS]^{2+}$$

are 210 ± 10 M^{-1} sec^{-1} and 1.5 sec^{-1} at 25°C and $\mu = 0.15\ M$ (*478*).

3. *Selenocyanates*

Only for vanadium have selenocyanate complexes been reported, and they all appear to be N-bonded. The compounds $[VO(NCSe)_4]^{2-}$ (*163*, *666*) and $[V(NCSe)_6]^{3-}$ (*163*, *647*, *666*, *685*, *739*) have each been reported in the presence of various cations, and their structures confirmed by infrared and electronic spectroscopy. X-Ray data suggested that the V—Se bond distance in the latter anion lies between 5.0 and 5.1 Å, providing further evidence for this mode of bonding (*739*). Also $cp_2V(NCSe)_2$ (*261*) has been reported and, although the authors were reluctant to define the mode of bonding in 1968, the similarity of the infrared peaks in this compound to those in other *N*-selenocyanatovanadium compounds suggests that it is correctly formulated as written. Compounds $VO(NCSe)^+$, $VO(NCSe)_2$, and $VO(NCSe)_4{}^{2-}$ have been observed in acetone and DMF, and a number of mixed-ligand complexes with nitrogen donors (py, bipy, phen) have been reported with these species (*684*, *687*).

E. CHROMIUM, MOLYBDENUM, AND TUNGSTEN

1. *Cyanates*

The crystal structures of π-$cpCr(NO)_2NCO$ (*165*) and π-$cpMo(CO)(PPh_3)_2NCO$ (*508*) have been determined. Each structure contains a linearly bound *N*-cyanato group with M—N, N—C, and C—O distances of 1.982(*8*) and 2.127(*7*), 1.126(*4*) and 1.118(*14*), and 1.179(*5*) and 1.238(*16*) Å, respectively. The C—O distance is particularly sensitive to vibrational motions, and its corrected value in the chromium compound is 1.27 Å. Therefore, too much should not be made of the apparent difference in these distances in the two compounds.

The anion $[Cr(NCO)_6]^{3-}$ has been characterized spectroscopically

(*59*) but the analogous molybdenum species is O-bonded (*56*). The mixed molybdenum(IV) compounds *mer*-$MoO(NCO)_2L_3$ (L = Et_2PhP or Me_2PhP) are as written (*166*), the assignments in each case being on the basis of infrared measurements.

The preparation of the compounds $M(CO)_5NCO$ (M = Cr, Mo, W) has been achieved by a number of interesting reactions. The hexacarbonyls react with the azide ion to give the preceding products (*92*), for which kinetic studies suggest that nucleophilic attacks occurs at a carbon atom, followed by synchronous formation of the M—N bond and expulsion of N_2 (*782*). In other systems, it is proposed that the reaction of CO with a coordinated azide proceeds via a similar intermediate, but in the photochemical formation of π-$cpMo(CO)(PPh_3)_2NCO$ from a molybdenum nitrosyl or azido complex, a nitrene is proposed as intermediate (*508*). Also $Cr(CO)_5NCO$ has been formed by the reaction of NH_2OH or NH_2Cl with $Cr(CO)_6$, presumably via a hydroxamic (or *N*-haloamide) intermediate with subsequent loss of H_2O (or HCl) (*88*); $(\pi\text{-cp})_2W(NCO)_2$ has been reported (*344*).

2. *Thiocyanates*

Details of X-ray structure determinations of thiocyanate complexes of these metals are given in Table XXII. Not included are the incomplete results which indicated sulfur bonding in $K_3Cr(SCN)_6 \cdot 4H_2O$ (*793*) —these findings have been superseded by the recent results on the hexa-*N*-thiocyanatochromate salt of a complex lanthanide cation (*427*).

Infrared and electronic spectra confirm the nature of the hexa-*N*-thiocyanatometallate anions of chromium(III) (*293*, *639*, *647*, *656*, *663*, *665*) and molybdenum(III) (*293*, *489*, *647*, *663*, *664*), and molybdenum(II) (*534*); a variety of salts have been reported containing these anions (see the foregoing and also Refs. *30* and *528*). Infrared spectra and magnetic measurements have been used to characterize $[M(NCS)_6]^{2-}$ (M = Mo, W) and $[W(NCS)_6]^-$ (*386*). A large number of mixed-ligand thiocyanate complexes of chromium(III) have been reported, and many of these are of the type $M[Cr(CNS)_4L_2]$, similar to the original Reinecke's salt where L = NH_3.

In general, treatment of an ethanolic solution containing $[Cr(NCS)_6]^{3-}$ with the appropriate ligand under reflux conditions results in the corresponding reineckate salt; some representative examples with nitrogen donors are given in Refs. *48*, *308–310*, *317*, *633*, *756*, and *757*. Phosphine ligands also undergo the same type of reaction (*399*) and with this ligand, examples of the intermediate anion $[Cr(CNS)_5L]^{2-}$ have also been reported (*723*). In view of the number of compounds that

TABLE XXII

X-RAY DATA FOR SOME CHROMIUM AND MOLYBDENUM THIOCYANATES

Compound	M—N	N—C	C—S	∠NCS	∠MNC	Reference
$M[Cr(NCS)_6]$[a]	2.002	1.144	1.619	176.6	164.3	(*427*)
$NH_4[Cr(NH_3)_2(NCS)_4]$	2.05	1.14	1.80	180	180	(*717*)
$pyH[Cr(NH_3)_2(NCS)_4]$	1.95	1.15	1.76	180	180	(*717*)
$C_5H_{15}NOH[Cr(NH_3)_2(NCS)_4]$[b]	1.94	1.27	1.64	180	155.5	(*717*)
$K_3Mo(NCS)_6 \cdot CH_3CO_2H \cdot H_2O$	2.088(19)[e]	1.159(27)	1.630(24)	177.2[e]	169.3[e]	(*271, 272*)
$(\pi\text{-}C_3H_5)Mo(bipy)(CO)_2NCS$[c]	2.119(7)	1.163(10)	1.644(8)	175.8(5)	176.4(7)	(*340*)
$(\pi\text{-}C_4H_7)Mo(phen)(CO)_2NCS$[d]	2.146(9)	1.168(14)	1.613(12)	161.0(8)	179.2(10)	(*341*)

[a] M = Complex lanthanide cation.

[b] $C_5H_{15}NOH$ = cholinium.

[c] $\pi\text{-}C_3H_5 = \pi$-allyl.

[d] $\pi\text{-}C_4H_7 = \pi$-2-Methylallyl.

[e] These average figures obscure the fact that there are some marked differences between the coordination of the different thiocyanate groups in this compound.

have been prepared, it is perhaps surprising that so little attention has been paid to the structural aspects of these compounds. It is clear from X-ray data and spectral sources that trans isomers are formed in most circumstances, unless chelating ligands are used or when L = Ph_2EtP (*98*).

There are two reports giving full spectral data for reineckate complexes. One by Bennett *et al.* (*98*) examines the infrared data down to 70 cm^{-1} for L = NH_3, py, bipy, diars, and various phosphines, assigns the M—NCS stretching frequencies, and records the electronic transitions, although the higher-energy d-d bands are obscured by phosphine charge transfer bands. In the other, by Contreras and Schmidt (the same paper being published twice in the same journal) (*208*, *209*) more limited infrared data are available but both $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{2g}(F) \leftarrow {}^4A_{2g}$ transitions are observed, permitting the calculation of appropriate ligand field parameters. In the former case (*98*), it is concluded that all the complexes contain *N*-thiocyanato groups, based largely on the Cr—NCS stretching frequencies assigned at 335 to 382 cm^{-1}. In the latter case (*209*), anomalies exist in the spectrochemical series derived and these, taken with some variations in the positions of ν_{CN} and ν_{CS}, lead the authors to conclude that *N*-thiocyanato reineckate salts are formed when L = urea, 1,2-diamine cyclohexantetraacetate, thiosemicarbazide, glycinate, or alaminate and that *S*-thiocyanato complexes are obtained when L = acetamide, thiourea, ethyl xanthate, or salicylate. These two sets of results illustrate the difficulty of drawing conclusions regarding NCS coordination. The obscuring of important d-d bands in the one case or the lack of sufficient infrared data in the other mean that no firm decision can be reached at this stage, although, on chemical grounds, there seems to be no rationale for the particular ligands cited to cause the thiocyanate group to change the mode of coordination established in the starting material, $[Cr(NCS)_6]^{3-}$, nor to establish a difference in behavior from other stable chromium(III) thiocyanate complexes.

The solid state deamination of $[CrL_3](NCS)_3$ (L = en or pn) has been studied (*363*). The reaction is catalyzed by NH_4NCS, and the formation of *trans*-$[CrL—L_2(NCS)_2]NCS$ in contrast to the formation of the corresponding *cis*-chloro complex under similar conditions is tentatively ascribed to a strong trans effect for NCS^- relative to a cis effect for Cl^-. In the former case this supposes a trans intermediate with two monodentate en or pn ligands. A large number of complexes of the type *cis*- and *trans*-$[Cren_2XY]Z_n$ have been prepared (*282*). From infrared and electronic spectral data, all the thiocyanate complexes contain *N*-thiocyanato linkages, regardless of the other ligands. The complete series of anions $[Cr(NCS)_xCN_{6-x}]^{3-}$ (x = 0–6) has been prepared and separated by gel electrophoresis (*108*): the d-d spectra show a regular variation from $x = 0$ to $x = 6$, from which it may be concluded that no drastic changes in coordination occur and that *N*-thiocyanato species are present throughout.

Salts of the hexa-*N*-thiocyanatochromate(III) anion with Cu(I), Ag(I), Cd(II), Hg(II), Tl(I), and Pb(II) contain Cr—NCS—M bridges. Infrared and electronic spectral data support this, and the latter indicate that the —NCS—M ligand forms a less covalent bond with chromium than does monodentate —NCS but that the metal-to-ligand π backbonding is increased (*779*). Similar conclusions were reached for kinetic and spectral measurements in solution (*39*) regarding the nature of the bridge in $[(H_2O)_5CrNCSHg]^{4+}$. The interactions between divalent transition metal ions and Reinecke's anion are stronger for Co(II) and Cu(II) (*583*) than for Mn(II), Ni(II), or Fe(III) (*584*) and suggest similar bridging to that described previously. For the 1:1 adduct between $[Cr(NH_3)_5NCS]^{2+}$ and Ag^+, log K is 5.11 mole^{-1} (*617*). A spectrophotometric study of the interaction of Hg^{2+} and Ag^+ ions with $[Cr(NH_3)_5NCS]^{2+}$ and *cis*-$[Cren_2(NCS)_2]^+$ using the method of continuous variations indicated the formation of 1:1 adducts (*773*).

Chromium(VI) compounds are reduced to chromium(III) species in molten KNCS with the formation of a variety of products (*433*). The reaction between NCS^- and $HCrO_4^-$ in solution indicates the formation of an intermediate $[CrO_3(CNS)]^-$ species (*562*), which is tentatively assumed to be N-bonded (*545*).

In contrast to chromium, little is known about mixed-ligand thiocyanate complexes of molybdenum and tungsten. Infrared mull spectra indicate the structures of $Mo(bipy)(NCS)_4$ (*130*) and *mer*-$MoO(NCS)_2(PR_3)_3$ ($PR_3 = Et_2PhP$ or Me_2PhP) (*166*) and, when coupled with magnetic measurements, are the basis for ascribing the anion in $(pyH)_4[Mo_2O_4(NCS)_6]$ as a μ-dioxo compound with terminal *N*-thiocyanato groups (*534*). Other workers have reported related compounds without confirming the mode of thiocyanate coordination (*343, 644*). Some compounds $MoX(CNS)_5 2L$ (X = Cl or NCS; L = Me_2CP, MeCO·Et, or $C_4H_8O_2$) have been prepared (*306*).

The compounds $WL_2(NCS)_4$ (L = py or $\frac{1}{2}$bipy) have been characterized (*130*), and a series of tungsten(V) (*750*) and tungsten(VI) (*306, 751*) compounds prepared without structural data.

The organometallic complexes of these metals with thiocyanate are important because linkage isomers have been obtained (*690*). Some of the relevant compounds are included in Table XXIII. The compound π-$cpW(CO)_3SCN$, which was characterized by the positions of its CN and CS frequencies and by the integrated intensity of the former, resists all attempts to convert it to the *N*-thiocyanato isomer, unlike

TABLE XXIII

Some Organometallic Thiocyanates of Chromium, Molybdenum and Tungsten

Formal Oxidation State	Chromium thiocyanate	References	Molybdenum thiocyanate	References	Tungsten thiocyanate	References
0	$[Cr(CO)_5NCS]^-$	*(95, 491)*	$[Mo(CO)_5NCS]^-$	*(633)*	$[W(CO)_5NCS]^-$	*(633)*
0 and 1	$(OC)_5Cr—NCS—Cr(CO)_5$	*(96, 491)*				
I	$Cr(CO)_5NCS$	*(96, 491, 787)*				
II	$(\pi\text{-cp})Cr(NO)_2NCS$	*(690)*	$(\pi\text{-cp})\ Mo(CO)_3NCS$	*(690)*		
			$(\pi\text{-cp})\ Mo(CO)_3SCN$	*(690)*	$(\pi\text{-cp})W(CO)_3SCN$	*(690)*
			$[Mo(CO)_2(NCS)_2]_n$[a]	*(206)*	$[W(CO)_2(NCS)_2]_n$[a]	*(206)*
			$Mo(CO)_2(PPh_3)_2(NCS)_2$	*(206)*	$W(CO)_2(PPh_3)_2(NCS)_2$	*(206)*
			$Mo(CO)_2dpm_2(NCS)_2$	*(206)*	$W(CO)_2dpm_2(NCS)_2$	*(206)*
			$\pi\text{-}C_3H_5Mo(CO)_2(CH_3CN)_2NCS$	*(247)*		
			$[\pi\text{-}C_3H_5Mo(CO)_2(CH_3CN)NCS]_2$[b]	*(247)*		
			$[\pi\text{-}C_3H_5Mo(CO)_2(PhCN)NCS]_2$[b]	*(247)*		
			$\pi\text{-}C_3H_5Mo(CO)_2bipyNCS$	*(340)*		
			$\pi\text{-}C_4H_7Mo(CO)_2phenNCS$	*(341)*		
IV	—	—	$(\pi\text{-cp})_2Mo(NCS)_2$	*(344)*	$(\pi\text{-cp})_2W(NCS)_2$	*(344)*
					$(\pi\text{-cp})_2W(NCS)(SCN)$	*(344)*

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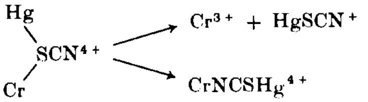
[a] These molecules were not isolated but their solutions show similar spectra to those of their analogs: solvent molecules may be coordinated since there is no indication of bridging NCS from the infrared data.

[b] These dimers almost certainly contain bridging NCS groups by comparison with the preceding compound.

the similarly characterized molybdenum analog that isomerizes in solution in a matter of hours (*690*). Other *S*-thiocyanato complexes of molybdenum, isomers of the compounds listed, may be able to be prepared by modifying the careful preparative techniques of Sloan and Wojcicki (*690*) and by similarly taking advantage of the kinetic factors that permitted the isolation of π-cpMo$(CO)_3$SCN. The tungsten compound on the other hand, appears to be stable, and it suggests that other similar *S*-thiocyanato complexes may be able to be prepared for that element. Thus, treatment of $(\pi\text{-cp})_2MoCl_2$ with aqueous KNCS gave $(\pi\text{-cp})_2Mo(NCS)_2$ but the similar reaction with $(\pi\text{-cp})_2WCl_2$ gave a mixture of $(\pi\text{-cp})_2W(NCS)$ and $(\pi\text{-cp})_2W(NCS)(SCN)$ (*344*). No attempts were made to interconvert these isomers but their existence seems to lend support to the foregoing prediction.

The reduction of $[Co(NH_3)_5NCS]^{2+}$ with $[Cr(H_2O)_6]^{2+}$ to give $[(H_2O)_5CrNCS]^{2+}$ with extensive exchange of free NCS^- was studied in 1958 (*177*). Subsequently it was shown that the similar reduction of *trans*-$[Coen_2X(NCS)]^+$ proceeded via both remote and adjacent attacks at the coordinated NCS resulting in both $CrSCN^+$ and $CrNCS^+$ species in solution (*363*, *364*). The two isomers have been characterized in solution from their electronic spectra, and kinetic studies have shown that the former isomerizes to the latter at a rate that implies either an intimate ion pair as an intermediate or, perhaps, that the chromium "slides" along the filled π orbitals of the thiocyanate. The difference in stabilities of the two isomers is ascribed mainly to the difference in their rates of aquation (*363*, *364*). The isomerization of $[Cr[H_2O)_5SCN]^{2+}$ is catalyzed by Hg^{2+}, which attacks the coordinated —SCN at the sulfur to decompose in both of two ways (*586*):



The severance of the Cr—S bond to form the stable $HgSCN^+$ species requires no further comment, and the isomerism is assumed to proceed by either of the routes just described. The stable $[(H_2O)_5Cr\text{—}NCS\text{—}Hg]^{2+}$ species has been separately characterized in solution (*39*). More recently the attack of Cr^{2+} on $[Co(NH_3)_5NCS]^{2+}$ has been shown to be remote only, whereas the attack on the linkage isomer is both adjacent and remote (*677*). The reduction of $FeNCS^{2+}$ by Cr^{2+} in the presence of NCS^- leads to kinetic and spectroscopic evidence for $[Cr(H_2O)_4(NCS)(SCN)]^+$. The analysis of the results is made more difficult by the uncertainty concerning the ratio of geometric isomers present and the mechanism by which this species is formed (*129*).

There is spectroscopic evidence for the association of NCS^- with a number of chromium(III) complexes (*603*, *790*), and such a stable ion pair has been identified in the substitution of H_2O in $[Cr(NH_3)_5H_2O]^{3+}$ by NCS^-. The further kinetic results have been interpreted on the basis of a rate-limiting loss of coordinated H_2O, followed by the collapse of the solvation shell to fill the vacancy created (*264*, *381*). Ion pairs were also indicated in the reaction of NCS^- with $[Cren_2Cl_2]^+$ in methanol but no further mechanistic conclusions were reached (*382*). The rate of substitution of H_2O in $[Cr(H_2O)_6]^{3+}$ by NCS^- is catalyzed by methanol due to a more favorable dissociative activation mode involving coordinated MeOH (*67*). The same reaction is also catalyzed by the sulfite ion, and, although evidence is offered that the formation of $[Cr(H_2O)_5OSO_2]^+$ is crucial to the subsequent substitution, the mechanism for this stage is not clear (*178*). Exchange between NCS^- and $[Cr(H_2O)_5NCS]^{2+}$ has been studied using $^{35}SCN^-$ (*449*), and the displacement of NCS^- from various complexes has also been reported (*40*, *795*). Much of the preceding work was given direction by Adamson's earlier work in which a photochemical exchange of ligands in an ion pair was shown to take place between NCS^- and H_2O in either $[Cr(H_2O)_6]^{3+}$ or $[Cr(NH_3)_5H_2O]^{3+}$ (*12*).

3. *Selenocyanates*

A number of systems containing the $[Cr(NCSe)_6]^{3-}$ ion are known, and spectroscopic measurements confirm the mode of coordination (*132*, *530*, *615*, *663*, *665*, *738*). Compounds with $[Mo(NCSe)_6]^{3-}$ have been studied similarly (*647*, *663*, *665*). Yellow and red forms of $Cr(py)_3(NCSe)_3$ have been reported (*738*), but Cr—NCSe linkages are present in both cases (*132*, *738*).

Jennings and Wojcicki (*409*) have reported the preparation of π-cpCr(NO)$_2$NCSe and π-cpM(CO)$_3$SeCN (M = Mo, W); the mode of bonding is determined by the position of CN and CSe stretching frequencies, and by integrated intensity measurements. No indication of linkage isomerism was observed in the carbonyl compounds [cf. π-cpMo(CO)$_3$CNS], and the chromium compound readily lost Se to give the cyano complex.

F. MANGANESE, TECHNETIUM, AND RHENIUM

1. *Cyanates*

Tetrahedral anionic complexes $[Mn(NCO)_4]^{2-}$ have been reported and characterized by infrared and electronic spectral data (*292*, *296*, *639*). The octahedral anion $[Re(OCN)_6]^{2-}$ has been reported and its structure assigned on the basis of the positions of the infrared frequencies (*56*). Mixed-ligand complexes of manganese(II) cyanate have been reported with 2,2′-bipyridine and 1,10-phenanthroline (*335*) and with urotropine (*735*)—in all cases N-bonded cyanato complexes are formed. The compounds $MnL_2(NCO)_2$ (L = 3-cyanopyridine or 4-cyanopyridine) contain Mn—N—Mn bridges rather than bridges of the type Mn—NCO—Mn (*557*). The thermal analysis of $MnL_n(NCO)_2$ (L = py and related ligands) have been reported (*496*).

Several organometallic cyanates of these metals have been reported. In addition to substitution methods, these may be prepared by nucleophilic attack on a coordinated CO by a suitable nitrogen-containing nucleophile. Thus, $Mn(CO)_3(PMe_2Ph)_2Br$ gives $Mn(CO)_2(PMe_2Ph)_2(N_2H_4)(NCO)$ when treated with hydrazine (*536*) and the $[Mn_2(CO)_6(N_3)_x(NCO)_{3-x}]^-$ anion is formed by the reaction of N_3^- with $Mn(CO)_5Br$ in THF at temperatures above ambient (*520*). The analogous trisisocyanato complex is obtained when NCO^- is used, and $Mn(CO)_3(PPh_3)_2NCO$ has been prepared by a nucleophilic displacement of Br^- (*520*). Compounds $Re(CO)_5NCO$ (*34*) and $Re(CO)_4(NCO)_2$ (*646*) have been prepared, as have many of the rhenium analogs to the foregoing (*520*). The reaction of hydrazine with a variety of rhenium carbonyl compounds gives a similar variety of N-bonded cyanato complexes—the reaction is believed to proceed via a carbamoyl intermediate (*535*).

2. *Thiocyanates*

Both tetrahedral and octahedral anions are known for manganese, and $[Mn(NCS)_4]^{2-}$ and $[Mn(NCS)_6]^{4-}$ have been assigned from their electronic and infrared spectra (*293, 297, 647, 665, 666*). Reduction of an acidic solution of TcO_4^- with thiocyanate ions led to various thiocyanate–technetate complexes which, when carefully oxidized with TcO_4^-, resulted in the isolation and characterization of $(Me_4N)_2[Tc(NCS)_6]$ (*672*); the .bonding is confirmed by preliminary X-ray results indicating a Tc—S distance of 4.7 Å (*372*). Potentiometric titration of acidic ReO_4^- with $Hg_2(ClO_4)_2$ in the presence of NH_4NCS had indicated reduction to give an uncharged $Re(CNS)_4$ species in solution (*719*), and subsequently anionic thiocyanate complexes of rhenium(III) (*214*), (IV) (*54, 55, 214*), and (V) (*55*) have been reported but with disagreement over the mode of bonding present. Cotton *et al.* (*214*) concluded that the ions $[Re_2(NCS)_8]^{2-}$ and $[Re(NCS)_6]^{2-}$ were formed from the position and broad nature of ν_{CN} and from the position of δ_{NCS}.

Bailey and Kozak (*54*) prepared $[Re(CNS)_6]^{2-}$ in a fused salt and, although they also observed a strong broad CN stretching frequency, they concluded that $[Re(SCN)_6]^{2-}$ had been formed because, having no onium cations to absorb around 700 cm^{-1}, they assigned a band in that region to an S-bonded CS stretching frequency. Subsequently the latter authors reported $[Re(SCN)_6]^{-}$ and offered further evidence in the form of integrated intensities (*55*) to support their assignments for $[Re(SCN)_6]^{2-}$. When these measurements were repeated at a later stage, Bailey *et al.* (*60*) reported the compounds as $[Re(NCS)_6]^{2-}$ and $[Re(NCS)_6]^{-}$. Thus it was finally concluded that these rhenium thiocyanato complexes are all N-bonded, in agreement with the interpretation of their electronic spectra (*663*). The difficulties in reaching this conclusion illustrate the hazards of using infrared data to determine the mode of bonding of NCS^-; the results still await unambiguous confirmation from X-ray analysis.

The mercury(II) compounds of $[Mn(NCS)_4]^{2-}$ contain Mn—NCS—Hg bridges (*293, 654*). Anhydrous $Mn(NCS)_2$ probably contains manganese(II) octahedrally coordinated by two nitrogen and four sulfur atoms, with triply ligating NCS^- (*287*). The Mn—NCS—Mn bridges are present in $Mn(py)_2(NCS)_2$, and Mn is in an octahedral environment, as in $Mn(py)_4(NCS)_2$ (*201*). The tetrahedral molecule $MnL_2(NCS)_2$ (L = HMPT) have been reported and assigned from spectral data (*485*). Preliminary X-ray results show that $Mn(tu)_2(NCS)_2$ is isostructural (*552*) with the trans-octahedral nickel(II) compound (with S-bridging tu and terminal—NCS) (see Section IV, I). As part of an investigation into the magnetic properties of the MS_4N_2 system, $Mn(tu)_2(NCS)_2$ has been examined (*287*), and $Mn(ROH)_2(NCS)_2$ (R = Me, Et) was shown to be very similar but with —NCS— bridges (*287*). The compound $MnL_4(NCS)_1$ (L = *N*-*n*-butylimidazole) has been reported (*631*). Preliminary results suggest that $Mn(DMF)_4(NCS)_2$ contains *N*-thiocyanato groups (*688*). Although the structural data are not entirely adequate, the complexes $MnL(NCS)_2$ (L = *N*,*N'*-di-(3-aminopropyl)piperazine (*319*) and 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)-pyrazine (*337*)) are each probably five-coordinate with *N*-thiocyanato coordination. A complex with urotropine has been reported (*735*). The thermal decomposition of $Mnpy_4(NCS)_2$ has been studied (*94, 425, 496*).

Magnetic measurements indicate that the previously discussed $[Re_2(NCS)_8]^{2-}$ has a dinuclear structure with a metal–metal bond (*214*). The reaction of NCS^- with $Re_2Cl_8{}^{2-}$ in the presence of Ph_3P results in the formation of $[Re_2(NCS)_8(PPh_3)_2]^{2-}$, but here the magnetic data indicate no metal–metal bonding. The infrared spectra and other physical data are consistent with a dimeric anion in which the two rhenium atoms are bridged by two NCS groups (*214*). The compound $(n\text{-}Bu_4N)_3[Re_2(NCS)_8(CO)_2]$ has been prepared and, although it probably contains at least some *N*-thiocyanato groups, its structure remains unknown (*214*).

The oxygen-bridged species $Cs_3H[Re_2O(CNS)_{10}]$ and $Cs_4H_2[Re_3O_2(CNS)_{14}]$ have been reported and formulated as *S*-thiocyanato complexes from ambiguous infrared data (*776*). Exchange of NCS$^-$ has been studied with these two species: in the former compound, one NCS$^-$ exchanges faster than the other nine (*775*), and in the latter, two thiocyanate groups exchange faster than the other twelve (*777*).

Some rhenium(V) compounds have been reported of the form $ReXY(PPh_3)_2(NCS)_2$ (X = Y = O; X = O, Y = OH, OEt, or Cl); $ReO(OEt)py_2(NCS)_2$ was also reported (*304*). Also $M[Re(CN)_5(CNS)]$ (M = K, Ag, Cu) have been prepared, but no structural data are available (*651*).

The anionic manganese carbonyl complexes $[Mn(CO)_4(NCS)_2]^-$ (*729*) and $[Mn_2(CO)_6(CNS)_4]^{2-}$ (*278*) are known, the latter containing both bridging —NCS— and terminal —NCS groups (*278*); $[Re(CO)_3(NCS)_3]^{2-}$ is also known (*278*, *280*). However, the most interesting compounds in this category are those prepared by Wojcicki and Farona (*279*, *280*), which are listed in Table XXIV.

Infrared spectra suggest that the solid compound prepared by the reaction of thiocyanogen chloride and sodium pentacarbonylmanganate(-I) is $[Mn(CO)_5SCN]$. The N-bonded linkage isomer is formed in acetonitrile, and an equilibrium mixture of the two isomers exists in dichloromethane, 1,2-dichloroethane, chloroform, and ethyl acetate. The relative positions of equilibrium, as indicated by the intensities of various infrared bands, change on adding acetonitrile or on altering the temperature. These changes are reversible for all the solutions and, on removal of the solvent, solid $Mn(CO)_5SCN$ may be recovered with little if any decomposition (*279*).

When neutral ligands are reacted with the preceding compound, a further series of N- and S-bonded products are obtained (*280*) (see Table XXIV). The significance of these products will be discussed later, but it is important at this stage to note the geometric isomerism associated with the linkage isomerism for *mer*-$Mn(CO)_3(AsPh_3)_2NCS$ and *fac*-$Mn(CO)_3(AsPh_3)_2SCN$, and for the corresponding $SbPh_3$ complexes. No N-bonded fac product could be detected even when the reaction was carried out in acetonitrile, a solvent already known to promote *N*-thiocyanato bonding in $Mn(CO)_5NCS$.

Further evidence for this solvent effect was obtained by comparing the infrared spectra of *cis*-$Mn(CO)_4(AsPh_3)SCN$ in chloroform and

TABLE XXIV

SOME THIOCYANATE CARBONYL COMPLEXES OF MANGANESE

Compound	References	Compound	References
$Mn(CO)_5NCS$[a]	(*279*)	$Mn(CO)_5SCN$	(*279*)
cis-$[Mn(CO)_4(NCS)_2]$	(*729*)		
		cis-$Mn(CO)_4(PPh_3)SCN$	(*280*)
		cis-$Mn(CO)_4(AsPh_3)SCN$	(*280*)
		cis-$Mn(CO)_4(SbPh_3)SCN$	(*280*)
mer-$Mn(CO)_3(PPh_3)_2NCS$[b]	(*280*)		
mer-$Mn(CO)_3(AsPh_3)_2NCS$[b]	(*280*)	*fac*-$Mn(CO)_3(AsPh_3)_2SCN$	(*280*)
mer-$Mn(CO)_3(SbPh_3)_2NCS$[b]	(*280*)	*fac*-$Mn(CO)_3(SbPh_3)_2SCN$	(*280*)
fac-$Mn(CO)_3py_2NCS$	(*280*)		
fac-$Mn(CO)_3(\gamma\text{-pic})_2NCS$	(*280*)		
fac-$Mn(CO)_3(p\text{-tol})_2NCS$	(*280*)		
fac-$Mn(CO)_3(p\text{-can})_2NCS$	(*280*)		
fac-$Mn(CO)_3(p\text{-fan})_2NCS$	(*280*)		
fac-$Mn(CO)_3bipyNCS$	(*280*)		
fac-$Mn(CO)_3diphosNCS$	(*280*)		

[a] Exists in solution only.

[b] The mer complexes can exist in two forms. The authors (*280*) consider the isomer with CO trans to CNS to be more probable than that with a noncarbonyl ligand trans to CNS, and cis to its auxiliary.

acetonitrile. The spectra were significantly different, and could be varied reversibly by using mixed solvents of different proportions. The S-bonded complex was recovered from the solutions without decomposition on evaporation. The most plausible explanation for these and associated spectral changes involves linkage isomerism to give *cis*-$Mn(CO)_4(AsPh_3)NCS$ in acetonitrile solution. The spectra of the PPh_3 and $SbPh_3$ analogs in these solvents resemble those of *cis*-$Mn(CO)_4$-$(AsPh_3)SCN$, but additional complexities in these cases suggest that the isomerization that goes to virtual completion for the arsine is here arrested at an intermediate stage (*280*).

3. *Selenocyanates*

Tetrahedral $[Mn(NCSe)_4]^{2-}$ and octahedral $[Mn(NCSe)_6]^{4-}$ anions are known (*162*, *295*, *647*, *655*, *656*), and $[Re_2(NCSe)_8]^{2-}$ has been tentatively identified (*377*). There seem to be no reports of similar Tc compounds, nor indeed of any mixed-ligand selenocyanate complexes of either technetium or rhenium. Some mixed-ligand complexes of manganese(II) selenocyanate have been prepared, and in every case so far described the selenocyanate is N-bonded. Analogous to the thiocyanate complexes, $MnL_2(NCSe)_2$ (L = HMPT) is tetrahedral (*485*), $MnL(NCSe)_2$ [L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine] is probably five-coordinate (*337*), and $Mn(DMF)_4(NCSe)_2$ is octahedral (*688*). A complex with urotropine is isostructural with the corresponding thiocyanate (*735*), and a series of complexes $ML(NCSe)_2$ (L = dioxane, 3 THF, 2 phen, or 2 bipy) has been characterized (*700*).

The organometallic anions $[Mn_2(CO)_6Cl_2(NCSe)_2]^{2-}$ and $[Mn_2(CO)_6(NCSe)_4]^{2-}$ are each believed to contain terminal *N*-selenocyanato groups, and the latter also has two bridging selenocyanates (*278*).

G. Iron, Ruthenium, and Osmium

1. *Cyanates*

The tetrahedral anions $[Fe(NCO)_4]^-$ (*296*) and $[Fe(NCO)_4]^{2-}$ (*298*) have been characterized from vibrational and electronic spectra. Mixed-ligand complexes $FeL_4(NCO)_2$ [L = py (*137*, *732*), 4Mepy, isoquin (*137*), 3CN-py (*557*)] are octahedral with *N*-cyanato coordination, and the compounds containing six molecules of pyridine and five of 4-methylpyridine are correctly formulated $[Fepy_4(NCO)_2]\cdot 2py$ and $[Fe(4\text{-}Mepy)_4(NCO)_2]\cdot 4\text{-}Mepy$, respectively (*137*). The system $FeL_2(NCO)_2$ (L = 3-CN-py, 4-CN-py) is also octahedral with cyanate bridges of the form Fe—N—Fe (*557*). In methanol, there is some evidence that $[Fe(H_2O)_6](ClO_4)_2$ is oxidized to an iron(III) species by an excess of cyanate ions (*618*).

The compounds $[Ru(NH_3)_5NCO]^{2+}$ (*490*) and $Ru(NCO)(CO)(NO)(PPh_3)_2$ (*476*) have been prepared. Also π-cpFe$(CO)_2$NCO is formed either by nucleophilic attack of N_3^- on a coordinated CO, followed by elimination of N_2, or by nucleophilic displacement of CO by NCO^- (*33*).

Kinetic studies on the hydrolysis of $[Ru(NH_3)_5NCO]^{2+}$ to give $[Ru(NH_3)_6]^{3+}$ and CO_2 suggest that the reaction proceeds via N protonation of the coordinated NCO^-, followed by addition of H_2O to give a carbamic acid complex, which subsequently loses H_2O and CO_2 to give the product (*290*).

2. *Thiocyanates*

Reports in the early literature of a black and a yellow isomer of $Fepy_4(NCS)_2$ have been disproved by the X-ray analysis of both forms. The black compound is crystallographically equivalent to the yellow form which is a *trans*-*N*-thiocyanato complex with Fe—N, N—C, and C—S distances of 2.088, 1.140, and 1.604 Å, respectively (*696*). A trans-pentagonal bipyramidal structure is found in $[FeL(NCS)_2]ClO_4$, where

L is the macrocyclic pentadentate ligand, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.13.1]octadeca-1(18),2,12,14,16-pentaene. Here the Fe—N distance is 2.01 ± 0.02 Å (*285*).

The octahedral anions $[M(NCS)_6]^{3-}$ have been characterized by spectral methods for iron (*293*, *297*, *647*, *663*, *665*), ruthenium (*647*, *662*, *663*, *665*), and osmium (*647*, *663*, *665*). The anion $[Fe(NCS)_6]^{3-}$ has the characteristic charge-transfer band associated with mixtures of iron(III) and NCS^- in analysis (*297*). The tetrahedral $[Fe(NCS)_4]^{2-}$ is also well-characterized (*293*, *297*, *647*, *663*). The mixed complex $Fe(NCS)_4Hg$ with an extended network of Fe—NCS—Hg bridges has been studied (*293*, *654*).

Drickamer *et al.* (*262*) have made the interesting observation from Mössbauer measurements that iron(III) compounds are reversibly reduced to iron(II) at high pressures. They record that the asymmetric spectrum of a compound they formulate as $K_3Fe(SCN)_6$ shows an increasing proportion of iron(II) with pressure and, on pressure release, a symmetric spectrum that is regenerated on repeating the experiment. The authors ascribe these changes to reversible reduction associated with linkage isomerism. However, since the original formulation of $K_3Fe(NCS)_6$ as the *S*-thiocyanato complex was incorrect, further experiments are necessary before this interesting interpretation can be confirmed.

A number of iron–thiocyanate complexes with different stereochemistries are listed in Table XXV; the thiocyanate group is N-bonded in every case. The anomalous magnetic behavior of *cis*-$Fe(phen)_2(NCS)_2$ (*64*) has been interpreted in terms of a thermal equilibrium between $^5T_2$ and $^1A_1$ ground states: the low-temperature, low-spin form shows significant changes in its infrared spectrum relative to that of the high-spin form, but, since no phase change is observed using X-ray techniques, this is not ascribed to linkage isomerism but rather to changes in the strength of bonding arising from the change in radius of the iron (*456*). The same phenomenon occurs for *cis*-$Fe(bipy)_2(NCS)_2$, and here the structures of the high- and low-spin forms have been confirmed by an X-ray structural determination (*466*). Other illustrations of this type of behavior are known for *N*-thiocyanato–iron(II) compounds. For example, $Fe(phen)py_2(NCS)_2$ behaves similarly, although $Fe(py)_4(NCS)_2$ shows no such variations with temperature (*697*). Mössbauer (*698*) and low-frequency infrared (*716*) measurements have been reported for these compounds.

The oxidation of $[Fe(CN)_5CNS]^{4-}$ with excess $[Fe(CN)_6]^{3-}$ results in a transient purple species which changes, via an isosbestic point, to a blue solution (*702*) characteristic of the species obtained directly from

TABLE XXV

SOME MIXED-LIGAND COMPLEXES WITH IRON THIOCYANATE

Complex	Composition	Structure	References
Iron(III)			
$FeL_3(NCS)_3$	L = R_3PO, R_2SO, or substituted pyridine *N*-oxides	Octahedral	(*704*)
$Fe(Ph_3PO)_2(NCS)_3$		Trigonal bipyramidal	(*215*)
$[Fe(L{-}L)_2(NCS)_2]\overline{NCS}$	L—L = phen, bipy	Octahedral	(*236*)
$Fe_2(L{-}L)_4O(NCS)_4$	L—L = phen, bipy	Oxygen-bridged	(*236*)
Iron(II)			
$Fe(phen)_2(NCS)_2$		Cis octahedral	(*64*, *456*, *658*)
$Fe(bipy)_2(NCS)_2$		Cis octahedral	(*466*)
$Fe(phen)py_2(NCS)_2$		Octahedral	(*697*)
$FeL_4(NCS)_2$	L = py, 4pic, isoquin	Trans octahedral	(*137*, *201*, *732*)
$[Fe(py)_4(NCS)_2]2py$		Octahedral	(*137*)
$[Fe(4pic)_4(NCS)_2]4pic$		Octahedral	(*137*)
$Fe(tu)_2(NCS)_2$		Tetragonal MS_4N_2	(*287*)
$FeL(NCS)_2$	L = pmp[a]	Trigonal bipyramidal	(*231*)
	L = pnp[b]	Trigonal bipyramidal	(*559*)
	L = L′[c]	?	(*337*)

[a] pmp = 2,6-di(diphenylphosphinomethyl pyridine)

[b] pnp = 2,6-di(diphenylphosphinoethyl pyridine)

[c] L′ = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine

$[Fe(CN)_5NH_3]^{2-}$ and NCS^- (*405*). Stasiw and Wilkins (*702*) tentatively suggested that the iron(II)–thiocyanate complex is N-bonded and that rapid oxidation gives an unstable *N*-thiocyanato–iron(III) complex which rearranges to the blue linkage isomer. However, orange $[Fe(CN)_5NCS]^{3-}$ has been characterized, and its solutions range in color from orange in acetone to purple in ethanol or methanol. No evidence bearing on the possibility of linkage isomers was available (*360*).

The thermal decomposition of $Fepy_4(NCS)_2$ has been investigated (*94*, *425*). The stepwise formation constants of $Fe(NCS)^+$ and $Fe(NCS)_2$ in CH_3CN have been measured (*469*).

^{14}N Nuclear magnetic resonance spectroscopy was used to characterize the bonding in $K_2[Ru(NCS)_5NO]$ (*390*). When heated at 70°C for

70 hrs under nitrogen, $[Ru(NH_3)_5SCN]^{2+}$ isomerizes to $[Ru(NH_3)_5NCS]^{2+}$ as indicated by changes in the UV spectra corresponding to the different positions in spectrochemical series of —NCS and —SCN; the infrared spectra were also different (*490*). The polynuclear ions $[Ru_2N(NCS)_8(H_2O)_2]^{3-}$, $[Os_2N(NH_3)_8(NCS)_2]^{2+}$, and $[Ru_2N(NH_3)_6(NCS)_3H_2O]^{2+}$ are believed to contain a linear M—N—M unit with N-bonded thiocyanates (*202*). Also $[Ru(NCS)(CO)(NO)(PPh_3)_2]$ (*476*) and $[Ru(O_2)(NCS)(NO)(PPh_3)_2]$ (*342*) have been characterized by infrared measurements—the latter compound is an efficient catalyst for the homogeneous oxidation of Ph_3P (*342*).

Aerial oxidation of $[\pi\text{-cpFe(CO)}_2]_2$ in the presence of hexafluorophosphoric acid and KNCS leads to the linkage isomers, π-cpFe$(CO)_2$NCS and π-cpFe$(CO)_2$SCN, which may be separated by column chromatography. No appreciable isomerization was detected in solution, but the S-bonded complex is converted to its N-bonded isomer by heating the solid. Sloan and Wojcicki suggest that isomerism may involve either a dimeric or polymeric intermediate with bridging NCS groups (*690*). This suggestion gains some support from more recent work (*413*) which showed that the most convenient conditions for the oxidation of $[\pi\text{-cpFe(CO)}_2]_2$ required iron(III) in acetonitrile or acetone, and that the reaction proceeded via an intermediate $[\pi\text{-cpFe(CO)}_2S]^+$ (S = solvent); addition of KNCS gave the two linkage isomers, which were separated as described previously. The solvent molecule is, therefore, incorporated on rupturing the thiocyanate bridge in a random fashion and prevents further isomerization. Also $[Fe(CO)_5NCS]^-$ has been prepared by a photolytic reaction, and no evidence was found for linkage isomerism (*638*).

The reaction of $Os_3(CO)_{12}$ with Ph_3PAuX (X = Cl, Br, I, or SCN) gives $Os_3(CO)_{19}(AuPPh_3)X$. The basic framework of the molecule is believed to be an Os_3 triangle with $AuPPh_3$ and X each bridging two $Os(CO)_3$ units. When X = SCN, ν_{NC} indicates S-bonding. If the compound is left on an alumina column for 1 hr, decomposition occurs to give $[Os_3(CO)_{10}(AuPPh_3)_2S_2]$ (*200*). The nature of the SCN-bridging is not discussed by the authors, but the foregoing would be consistent with an Os—S—Os structure which hitherto has only been suggested when N is also involved with a third center (see, for example, Ref. *287*).

The rate of formation of $[Fe(H_2O)_5NCS]^{2+}$ by displacement of water from $[Fe(H_2O)_6]^{3+}$ by NCS^- has been reported as $127 \pm 10\ M^{-1}\ sec^{-1}$ (25°C, $\mu = 0.4$) (*97*) or as $122 \pm 6\ M^{-1}\ sec^{-1}$ (25°C, $\mu = 3.0$) (*207*). In solutions of high $[NCS^-]$, the exchange of NCS^- with $[Fe(NCS)_4]^-$, which is assumed to predominate, has been studied by

^{14}N NMR line broadening: the degree of broadening is interpreted as showing Fe—N bonding (*254*). The cation $[Fe(H_2O)_6]^{2+}$ exchanges separately with both $FeNCS^{2+}$ and $Fe(NCS)_2{}^+$ (*232*). The reaction of NCS^- is faster with $[Fe(H_2O)_6]^{3+}$ than with $[Fe(H_2O)_6]_2{}^+$ (*207*), but the former is catalyzed by iron(II) (*207*, *483*). It is not possible to assess the relative contributions of adjacent and remote attack but the kinetic data do suggest that linkage isomerism does not provide a major pathway to $[Fe(H_2O)_5NCS]^{2+}$ (*207*). The kinetics of the reduction of $[Co(NH_3)_5SCN]^{2+}$ (*281*) and of $[Co(NH_3)_5NCS]^{2+}$ (*273*) by Fe^{2+} have been compared, and show rate constants of 0.12 and $< 3 \times 10^{-6}$ $M^{-1}sec^{-1}$, respectively. The possibility of adjacent and remote attacks was not considered specifically, but no evidence is offered for the formation of $[Fe(H_2O)_5SCN]^{2+}$, so that the fast reduction of $[Co(NH_3)_5SCN]^{2+}$ perhaps proceeds via remote attack, and the slower reduction of $[Co(NH_3)_5NCS]^{2+}$ by adjacent attack. In DMSO the second-order rate constant for the formation of $[Fe(DMSO)_5CNS]^{2+}$ is 670 ± 10 M^{-1} sec^{-1} (*477*).

The substitution of pyridine by NCS^- in optically active *cis*-$[Ru(phen)_2py_2]^{2+}$ in dry acetone proceeds by a first-order reaction with retention of configuration; the mode of coordination of NCS^- in the product was not reported (*120–122*). In aqueous solution, H_2O is displaced by NCS^- from $[Ru(H_2O)(bipy)terpy]^{2+}$ and $[Ru(H_2O)bipy_2]^{2+}$ in second-order reaction with k_2 equal to 1.36×10^{-2} and 6.57×10^{-2} $1\ mole^{-1}\ min^{-1}$, respectively. Again, the mode of coordination was not reported (*237*).

3. *Selenocyanates*

The anions $[Fe(NCSe)_4]^{2-}$ (*162, 295, 647, 663, 665*), $[Fe(NCSe)_6]^{4-}$ (*295, 663*), and $[Fe(NCSe)_6]^{3-}$ (*162, 663, 665*) have been characterized by spectral methods. No anionic selenocyanate complexes of ruthenium or osmium appear to have been reported.

Since —NCSe and —NCS are close to each other in the spectrochemical series, it is not surprising that a number of selenocyanate complexes of iron(II) have been prepared, similar to the thiocyanate complexes already described, with a view to studying the magnetic crossover from $^5T_2$ to $^1A_1$. These and some other mixed-ligand selenocyanate complexes are listed in Table XXVI; invariably they contain N-bonded selenocyanate groups. One compound deserves special mention, namely, the product obtained by the thermal decomposition of $[Fe(bipy)_3](NCSe)_2$. This product is formulated as $[Fe^{sp}(bipy)_2(NCSe)_2]_2[Fe^{sf}(bipy)_2$

$(NCSe)_2$](bipy), where Fe^{sp} and Fe^{sf} denote spin-paired and spin-free iron(II), respectively (*457*).

The only selenocyanate-containing complex of ruthenium or osmium is believed to be $[Ru(NH_3)_5SeCN](ClO_4)_2$ which was characterized by comparing the UV data with expected band positions from the spectrochemical series (*490*).

The reaction of KSeCN with π-cpFe$(CO)_2$Cl or of $Se(SeCN)_2$ with π-cpFe$(CO)_2CH_2C_6H_5$ results in each case in π-cpFe$(CO)_2$SeCN, characterized by infrared data (*409*). However, the reaction of $Se(SeCN)_2$ with π-cpFe(CO)$(PPh_3)CH_2C_6H_5$ affords the linkage isomers π-cpFe(CO)(PPh_3)(NCSe) and π-cpFe(CO)(PPh_3)(SeCN) (*410*). Both isomers, as solids or in solution, are stable with respect to interconversion at room temperature, but, at higher temperatures, deselenation rather than isomerization occurs; the deselenation is faster for the N-bonded isomer and is enhanced by the presence of Ph_3P. The interaction of [π-cpFe$(CO)_2$SeCN] with PPh_3, $P(C_6H_{11})_3$, or $P(OPh)_3$ yielded the compounds [π-cpFe$(CO)_2(PR_3)$] NCSe (R = Ph or C_6H_{11}) and [π-cpFe(CO)$(P(OPh)_3)$SeCN], respectively. The compound [π-cpFe$(CO)_2(PPh_3)$] NCSe lost CO on heating to give [π-cpFe(CO)(PPh_3)SeCN], but the $P(C_6H_{11})_3$ compound gave a number of products on similar treatment (*410*).

TABLE XXVI

SOME MIXED-LIGAND COMPLEXES WITH IRON SELENOCYANATE

Complex	Composition	Structure	References
Iron(III)			
$(n\text{-}Bu_4N)_3[Fe(CN)_5NCSe]$		Octahedral	(*360*)
Iron(II)			
$(Et_4N)_3[Fe(NCSe)_5H_2O]$		Octahedral	(*616*)
$Fe(phen)_2(NCSe)_2$		Cis octahedral	(*64, 456, 683*)
$[Fe(bipy)py_2NCSe](NCSe)$		Octahedral	(*683*)
$Fe(bipy)_2(NCSe)_2$		Octahedral	(*683*)
$Fe(DMF)_4(NCSe)_2$		Octahedral	(*683*)
$FeL_4(NCSe)_2$	L = py, 4pic, isoquin	Octahedral	(*137, 732*)
$[Fe(py)_4(NCSe)_2]2py$		Octahedral	(*137*)
$[Fe(4pic)_4(NCSe)_2]4pic$		Octahedral	(*137*)
$FeL(NCSe)_2$	L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine		(*137*)

H. COBALT, RHODIUM, AND IRIDIUM

1. Cyanates

The tetrahedral complex anion $[Co(NCO)_4]^{2-}$ has been characterized by infrared and electronic spectra (*292*, *296*, *432*, *639*) in the presence of a variety of cations. The infrared spectrum of the potassium salt is considerably more complex than that of the tetraethylammonium salt, indicating some loss of symmetry in the former compound. It is suggested that there is a strong interaction between K^+ and O of the cyanate group which leads to the distortion (*296*, *743*).

A number of mixed-ligand cyanates of cobalt(III) and (II) are given in Table XXVII, which lists only a representative sample of the large number of such complexes available. In many cases the results were discussed in terms of variations in σ or π bonding or of steric effects. These discussions will not be rehearsed in this section but, where relevant to this review, will be referred to later. With the exception of

TABLE XXVII

SOME MIXED-LIGAND CYANATE COMPLEXES OF COBALT

Complex	Ligand	References
Cobalt(III)		
Octahedral		
$[Co(DH)_2L(NCO)]$	L = H_2O, OH^-, NCO^-	(*2*)
	L = Cl^-, Br^-, I^-, NO_2^-	(*10*)
	L = Me	(*253*)
$[Co(NH_3)_5NCO]^{2+}$		(*65, 149*)
$[Co(CN)_5NCO]^{3-}$		(*204*)
Cobalt(II)		
Octahedral		
$Copy_4(NCO)_2$		(*240, 290, 450, 451, 558*)
$Co(2pic)_4(NCO)_2$		(*451*)
$CoL_4(NCO)_2$	L = 3-CN-py, 4-CN-py	(*557*)
$Co(urt)(H_2O)_2(NCO)_2$		(*735*)
$CoL_2(NCO)_2$	L = bipy, phen	(*335*)
Trigonal bipyramidal		
$CoEt_4dien(NCO)_2$		(*159*)
Tetrahedral		
$Co(py)_2(NCO)_2$		(*450, 451, 558*)
$Co(2pic)_2(NCO)_2$		(*451*)
$CoL_2(NCO)_2$	L = quin, isoquin, 2,6-DMP, py, 2-, 3-, or 4R-py	(*488*)
$Co(HMPA)_2(NCO)_2$		(*655*)

$CoL_2(NCO)_2$ (L = 3- or 4-cyanopyridine) which contain Co—N—Co bridges (*557*), the cyanate groups are N-bonded and monodentate. Measurements have been made of various thermodynamic parameters associated with the formation and the thermal decomposition of $Copy_4(NCO)_2$ (*241, 451, 496, 500*).

Compounds $[M(CO)(PPh_3)_2NCO]$ (M = Rh or Ir) have been prepared by a number of routes (*87, 150, 155, 762*) and show no evidence of isomerization in solution (*155*). In addition to $[Rh(PPh_3)_3NCO]$, however, the linkage isomer has been obtained—this is at present the only example where both cyanate isomers have been isolated (*37*). The compound $[Rh(CO)_2(NCO)]_2$ probably contains single-atom bridges of the type found in $CoL_2(NCO)_2$ (L = 3- or 4-cyanopyridine) (*557*) (see preceding text) and not the Rh—NCO—Rh bridges indicated (*164*). Oxidative addition reactions have been reported with $Ir(CO)(PPh_3)_2$-(NCO) to give the 1:1 adduct with tetracyanoethylene (*47*) and the products $[IrCO(PPh_3)_2(NCO)Y_2]$ (Y = Cl, Br, NO_3) (*181*). Also *trans*-$[Ir(pip)_4H(NCO)]^+$ has been reported (*107*).

Both $[Co(NH_3)_5NCO]^{2+}$ (*65, 66*) and $[Rh(NH_3)_5NCO]^{2+}$ (*290*) are hydrolyzed under acid conditions to the corresponding hexamine, and the rates of these reactions have been studied. Initial protonation of the nitrogen followed by reaction with H_2O to give a carbamic acid intermediate seems to provide a reasonable mechanism in each case. Such an intermediate has been observed in the reaction of $[Co(NH_3)_5H_2O]^{3+}$ with NCO^- (*650*). Hydrolysis of $K[Co(DH)_2L(NCO)]$ gives $Co(DH)_2L$-(NH_3) for L = H_2O, Cl, and Br and for L = I or NO_2 at pH 5 to 7, but at pH <5 $[Co(DH)_2L(H_2O)]$ is formed in the last two cases (*10*). Similarly, $K[Co(DH)_2(NCO)_2]$ hydrolyzes to $[Co(DH)_2(NH_3)_2][Co$-$(DH)_2(NCO)_2]\cdot 3H_2O$ at pH 2 and to $[Co(DH)_2(NCO)NH_3]$ at pH 5 (2).

The apparent association and dissociation rate constants for the reaction of NCO^- with aquocobalamin have been determined over a range of pH, which is limited at the lower end due to hydrolysis of NCO^- (*626*).

A number of reactions on the coordinated cyanate group in $[M(CO)(PPh_3)_2NCO]$ (M = Rh, Ir) have been discussed (*91, 783*).

2. *Thiocyanates*

a. Cobalt. The X-ray structures of a number of cobalt thiocyanates have been determined. Some examples are listed in Table XXVIII and illustrate the interatomic distances associated with N—, S—, and bridging modes of coordination.

Tetrahedral $[Co(NCS)_4]^{2-}$ with a variety of cations is known (*184,*

TABLE XXVIII

INTERATOMIC DISTANCES AND BOND ANGLES OF SOME COBALT THIOCYANATES

Compound[a]	M—N or M—S (Å)	N—C (Å)	C—S (Å)	∠NCS	∠MNC or ∠MSC	References
I. $(C_{20}H_{17}N_4)_2[Co(NCS)_4]$[b]	1.945(3)	1.166(5)	1.601(4)	178.3(4)°	—	*(184)*
II. $Co(N_3S)(NCS)_2$,[c]						
apex	1.986(12)	1.141(18)	1.641(14)	176.7(1.3)°	172.9(1.1)°	*(235)*
plane	1.971(11)	1.147(18)	1.636(15)	176.9(1.2)°	161.1(1.1)°	
III. $Co(N_2O)(NCS)_2$,[d]						
apex	2.01(1)	1.14(2)	1.61(2)	179.6(1.5)°	166.9(1.3)°	*(316)*
plane	1.99(1)	1.21(2)	1.57(2)	177.2(1.8)°	156.9(1.4)°	
IV. $Co(NCS)_4Hg$,						
Co	1.926(16)	1.207(21)	1.638(14)	178.0(2)°	179(1)°	*(406, 407)*
Hg	2.559(4)	—	—	—	97.3(5)°	
V. $Co(NCS)_6Hg_2 \cdot C_6H_6$,						
Co—N(1)	2.17	1.20	1.60	179°	160°	*(351)*
Co—N(2)	2.08	1.11	1.76	176°	171°	
Co—N(3)	2.09	1.16	1.64	177°	167°	
Hg—S(1)	2.455	—	—	—	96°	
Hg—S(2)	2.424	—	—	—	98°	
Hg—S(3)	2.855	—	—	—	105°	
VI. *trans*-$[Co(en)_2(NCS)(SO_3)] \cdot H_2O$	1.974(18)	1.174(29)	1.629(18)	177.5(1.2)°	170.7(1.0)°	*(49)*
VII. $[Co(NH_3)_5(NCS)]Cl_2$	1.90(2)	1.43(11)[e]	1.32(13)[e]	—	—	*(693)*
VIII. $[Co(NH_3)_5(SCN)Cl_2$	2.272(7)	1.14(4)	1.64(3)	175.0(3.0)°	104.9(1.1)°	*(693)*
IX. $(NH_4)[Co(DH)_2(SCN)_2] \cdot H_2O$	2.316	1.25	1.68	174°	105°	*(649)*

[a] The coordination around the central metal is as follows: I, tetrahedral CoN_4; II and III, distorted trigonal bipyramidal CoN_5 and $CoON_4$; IV, tetrahedral CoN_4 linked by thiocyanate to tetrahedral HgS_4; V, octahedral CoN_6 linked by thiocyanate to distorted tetrahedral HgS_4; VI, trans-octahedral CoN_5S; VII, octahedral CoN_6; VIII, octahedral CoN_5S; IX, trans-octahedral CoN_4S_2.

[b] $C_{20}H_{17}N_4$: nitron.

[c] N_3S: *N,N*-bis-(2-diethylaminoethyl)-2-methylthioethylamine.

[d] N_2O: [2-{[2-(diethylamino)ethyl]amino}ethyl]diphenylphosphine oxide.

[e] These values are less accurate because of difficulty in placing C precisely between N and S in this disordered structure.

293, *294*, *432*, *599*, *647*, *663*). Cobalt(II) forms Co—NCS—M bridges in the presence of Hg(II) (*293*, *407*, *654*), Cd(II) (*734*), Pt(IV) (*728*), or with the reineckate anion (*583*). The compound $Co(NCS)_4Hg$ contains the tetrahedral cobalt ion, but further ligands can be added to give $L_2Co(NCS)_4Hg$ (L = THF, dioxane, py, an, PPh_3) in which similar NCS bridging occurs and the cobalt is in an octahedral environment (*511*).

The relative donor properties of various solvents toward Co(II) have been compared with that of NCS^- (*354*, *515*).

The combination of cobalt, a popular metal for crystal field theory, and thiocyanate, an accessible and stable ligand, has led to a very large number of mixed-ligand cobalt thiocyanate complexes. Of the Co(II) complexes studied there has been only one reported to contain the *S*-thiocyanato group. A careful comparison was made of the electronic spectra and magnetic moments of $Co(PPh_3)_2X_2$ (X = Cl, Br, I, and NCS) and of some Ph_3PO analogs, and from the position of NCS in the spectrochemical series for these compounds it was concluded that $Co(PPh_3)_2(SCN)_2$ was tetrahedral with *S*-thiocyanato groups (*213*). Infrared measurements, on the other hand, indicated that the compound should be formulated $Co(PPh_3)_2(NCS)_2$ (*599*). Both infrared and electronic spectral data indicate *N*-thiocyanato bonding in $[Co(PEt_3)_2(NCS)_2]$ and $[Co(P(C_6H_{11})_3)_2(NCS)_2]$ with the former compound exhibiting an equilibrium between high-spin, tetrahedral and low-spin, pentacoordinate structures; the latter compound is tetrahedral (*563*). It is perhaps possible that high spin–low spin equilibria, or some such phenomenon, could account for the contradictory results obtained for $Co(PPh_3)_2(CNS)_2$. No doubts have arisen about other cobalt(II) thiocyanates, which are N-bonded. Some examples are given in Table XXIX, of which many of the pentacoordinate species are close to the magnetic crossover point.

Cobalt(III) thiocyanates, isolated as solids, are listed in Table XXX where the coordination behavior is seen to be more varied. The compound $K_3[Co(CN)_5(SCN)]$ was characterized by Burmeister (*139*), and its linkage isomer subsequently prepared by Stotz *et al.* (*708*). Later it was shown that the preferred mode of bonding was influenced by the nature of the cation in the ionic lattice. The two most stable forms are $[n\text{-}Bu_4N]_3[Co(CN)_5NCS]$ and $K_3[Co(CN)_5SCN]$ (*358*, *359*). A consequence of this work has led to the novel linkage isomers $[(NH_3)_5CO—NCS—Co(CN)_5]$ and $[(NH_3)_5Co—SCN—Co(CN)_5]$ (*135*). One of the most extensively studied systems is that containing bis(dimethylglyoximato)cobalt(III) moiety with NCS and another ligand in the trans positions. The mode of coordination of the thiocyanate ion is dependent on the ligand trans to it, and both *N*- and *S*-thiocyanatobis-(dimethylglyoximato)cobalt(III) complexes have been isolated with different ligands (see Table XXX). Linkage isomers have been isolated, for example with L = py (*574*) or 4*t*-bu-py (*269*). A careful study of changes in the positions and intensities of infrared frequencies, combined with NMR measurements of the methyl protons established that an equilibrium existed between the two isomers in solution,

$$Co(DH)_2L(SCN) \rightleftharpoons Co(DH)_2L(NCS)$$

in which the equilibrium position is affected both by the nature of the ligand and that of the solvent (*571*). This view was challenged by Hassel and Burmeister (*370*) who ascribed the solvent effect to kinetic factors. However, using as an additional probe the NMR signals of the *t*-butyl group in the *t*-bu-py complex, Epps and Marzilli (*269*) confirmed that the equilibrium existed. Both *N*- and *S*-thiocyanato groups have also been observed in solutions containing the anion $[MeCo(DH)_2NCS]^-$, and there is evidence for thiocyanate bridging (*253*).

A number of these trans compounds have been prepared by Ablov and his co-workers (*4–6*, *9*, *11*) who have recently described *cis*-$[Co(DH)_2H_2O(NCS)]$ (*3*), whereas the previous discussion shows that S-bonding predominates in the trans series unless modified by solvent effects. Although no evidence was observed for the N-bonded isomer in the study of *trans*-$[Co(DH)_2(H_2O)(SCN)]$ (*9*, *572*), this isomer has been claimed (*193*) from the position of ν_{CS}, a frequency which is difficult to observe in these compounds due to ligand vibrations. The difficulties in determining the coordination of NCS in bis(dimethylglyoximato)-cobalt(III) compounds are illustrated by the report of hydrolysis studies of twenty-six new salts of the bisthiocyanate anion in which the results were discussed on the basis of N-bonding (*284*) in spite of the available X-ray evidence to the contrary (*649*).

The $[Cobipy_2(CNS)_2]^+$ species has been formulated as both N- (*590*) and S-bonded (*513*, *570*) compounds; the former designation may have arisen due to the presence of $[Co(bipy)_2(SCN)_2]_2[Co(NCS)_4]$ in the reaction product (*570*).

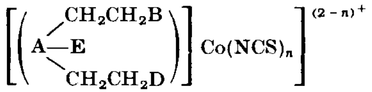
Whereas the previous discussion has been concerned with cobalt(II) and (III) compounds, the coordination of NCS toward cobalt in a formally lower oxidation state is illustrated by the isolation of $[Co(NO)_2L(NCS)]$ [L = Ph_3P, Ph_3As, $(C_6H_{11})_3P$] with terminal *N*-thiocyanato groups and of $[Co(NO)_2(NCS)]_2$ with —SCN— bridges (*89*).

The oxidation of coordinated NCS^- in $[Co(NH_3)_5NCS]^{2+}$ generally leads to both the NH_3- and CN-substituted products: for a given oxidant the proportion of these products is dependent on the concentrations of both oxidant and acid (*168*, *580*, *670*).

TABLE XXIX

SOME COBALT(II) THIOCYANATE AND SELENOCYANATE COMPLEXES[a]

Complex	Composition	References
Octahedral[b]		
$Co(py)_4(NCS)_2$*		(*201, 291,* 436,* 450,* 451,* 610, 671*)
$Co(4pic)_4(NCS)_2$		(*339*)
$Co(py)_4(NCS)_2 \cdot 2I_2$		(*300, 602*)
$Co(phen)_2(NCS)_2$*		(*658, 683**)
$Co(tripyam)_2(NCS)_2$	tripyam = tri-2-pyridylamine	(*473*)
$Co(Dben)_2(NCS)_2$*	Dben = *N,N′*-dibenzylethylene diamine	(*593**)
$CoL_4(NCS)_2$	L = *N*-*n*-butyl imidazole	(*631*)
$CoL_4(NCS)_2$	L = thiazole	(*393*)
$Co(H_2O)_3(NCS)_2L_2$*	L = hexamethylenetetramine	(*735**)
$CoL_2(NCS)_2$	L = 2,5-dithiahexane or 1,2-di(isopropylthio)ethane	(*286*)
$Co(DMF)_4(NCS)_2$*		(*688**)
$Cotu_2(NCS)_2$	S-bridging by tu	(*256, 287, 552*)
Octahedral with —NCS— bridges		
$CoL_2(NCS)_2$*	L = py, 4pic	(*339, 558*, 582, 611*)
$CoL_2(NCS)_2$	L = 2,6-dimethylpyridine *N*-oxide, 2,4,6-trimethylpyridine *N*-oxide	(*624*)
$CoL_2(NCS)_2$	L = selenourea	(*256*)
$Co(ROH)_2(NCS)_2$	R = Me or Et	(*288*)
Tetrahedral		
$CoL_2(NCS)_2$*	L = py, 2Me-py, 3Me-py, 4Me-py, quin, isoquin, 2,6-dimethylpyrazine	(*201, 339, 429, 450,* 451,* 488**)

$Co(HMPA)_2(NCS)_2$	HMPA = hexamethylphosphoramide						(*655*)
$Co(HMPT)_2(NCS)_2$*	HMPT = hexamethylphosphoric triamide						(*485**)
$Co(NIPA)_2(NCS)_2$	NIPA = nonamethylimidodiphosphoramide						(*243*)
$CoL_2(NCS)_2$	L = thioacetamide						(*553*)
Pentacoordinate							
	A	B	D	E	*n*		
	N	NH_2	NH_2	$CH_2 \cdot CH_2NH_2$	1		(*196*)
	N	NH_2	NH_2	H	2*		(*159,* 257*)
	N	OMe	PPh_2	$CH_2CH_2PPh_2$	1		(*541, 642*)
	N	OMe	NEt_2	$CH_2CH_2PPh_2$	1		(*542*)
	N	SMe	NEt_2	$CH_2CH_2NEt_2$	2		(*235*)
	N	SMe	NEt_2	$CH_2CH_2PPh_2$	1		(*542*)
	N	OMe	PPh_2	$CH_2CH_2PPh_2$	2		(*541*)
	N	CH_3	PPh_2	$CH_2CH_2PPh_2$	1		(*541*)
	N	CH_2OMe	PPh_2	$CH_2CH_2PPh_2$	2		(*541*)
	N	NEt_2	PPh_2	H	2		(*540*)
	N	NEt_2	PPh_2	CH_2CH_2Me	2		(*540*)
$CoL(NCS)_2$	L = 1,1,1-tris-(diphenylphosphinomethyl)ethane						(*238*)
	L = 2,6-di(diphenylphosphinomethyl)pyridine						(*231*)
	L = 2,6-di(diphenylphosphinoethyl)pyridine						(*559*)
	L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine*						(*337**)

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[a] An asterisk indicates that the corresponding selenocyanate complexes are also discussed.

[b] Octahedral $Co(bipy)_2(NCSe)_2$ is also known (*683*).

TABLE XXX

SOME COBALT(III) THIOCYANATE COMPLEXES

Co(III)—NCS compounds	References	Co(III)—SCN compounds	References
$K_3[Co(CN)_5(NCS)]$	*(708)*	$K_3[Co(CN)_5(SCN)]$[a]	*(139)*
$(n\mathrm{Bu}_4N)_3[Co(CN)_5(NCS)]$[a]	*(358)*	$n(\mathrm{Bu}_4N)_3[Co(CN)_5(SCN)]$	*(358, 359)*
		Cobalamin—SCN	*(380)*
trans-$[Co(DH)_2L(NCS)]$; L = py	*(574)*	*trans*-$[Co(DH)_2L(SCN)]$; L = py	*(574)*
4*t*-bu-py	*(269)*	4*t*-bu-py	*(269)*
Me[b]	*(253)*	SCN, Cl, Br, I, NH_3, H_2O, PPh_3, pip, 3Me-py,[b] 4Me-py,[b] 3Cl-py,[b] 3B4-py,[b] 4NH_2-py,[b] 4CN-py,[b] an,[b] pMe-an,[b] *m*NO_2-an,[b] *p*Cl-an,[b] NO_2[b]	*(572)*
cis-$[Co(DH)_2(H_2O)(NCS)]$	(3)		
		trans-$[Co(MH)_2(SCN)]^-$	*(715)*
$[Co(bipy)_2(NCS)_2]^+$ (see text)	*(590)*	$[Co(bipy)_2(SCN)_2]^+$	*(513, 570)*
		$[Co(phen)_2(SCN)_2]^+$	*(513)*

$[\text{CoTAAB(NCS)}_2]^{+}$[c]	(*227*)		
$[\text{Co(Me}_2\text{AsCH{=}CHAsMe}_2)_2\text{(NCS)}_2]^+$	(*100*)		
$[\text{Co(C}_{16}\text{H}_{32}\text{N}_4)\text{(NCS)}_2]^{+}$[d]	(*643*)		
cis-$[\text{Co(cyclam)(NCS)}_2]^{+}$[e]	(*608*)		
$[\text{CoL(NCS)}_2]^+$; L = tet a or tet b[f]	(*784*)		
cis- and *trans*-$[\text{Co(NH}_2\text{(CH}_2)_3\text{NH}_2)_2\text{(NCS)}_2]^+$	(*426*)		
cis- and *trans*-$[\text{Co(en)}_2\text{(NCS)}_2]^+$	(*185, 498*)		
cis- and *trans*-$[\text{Co(en)}_2\text{X(NCS)}]^+$; X = NO_2	(*498*)		
= Cl	(*185, 703*)		
cis-$[\text{CoNH}_3\text{en}_2\text{(NCS)}]^{2+}$[a]	(*133*)	*trans*-$[\text{CoNH}_3\text{en}_2\text{(SCN)}]^{2+}$	(*133*)
$[\text{Co(NH}_3)_5\text{(NCS)}]^{2+}$[a]	(*134*)	$[\text{Co(NH}_3)_5\text{(SCN)}]^{2+}$	(*134*)
trans-$[\text{Co(NH}_3)_4\text{(NCS)}_2]^+$	(*185*)		
$\{[\text{Co(NH}_3)_4\text{(NCS)}]_2\text{NH}_2\}^{3+}$	(*289*)		
$\{[\text{Co(en)}_2\text{(NCS)}]_2\text{O}_2\}^{2+}$	(*680*)		

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[a] Stable isomer.

[b] Linkage isomer formed in solution but not isolated as solid.

[c] TAAB = Tetrabenzo[b,f,j,n][1,5,9,13] tetraazacyclohexadecine.

[d] $C_{16}H_{32}N_4$ = hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

[e] cyclam = 1,4,8,11-tetraazacyclotetradecane.

[f] tet a and tet b = *trans*- and *cis*-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

The association of NCS^- and ClO_4^- with *trans*-$[Coen_2(NCS)_2]^+$ has been studied (*480*) and the equilibrium constants measured for the reactions of H^+ (*701*), Ag^+ (*617*), and Hg^{2+} (*276*) with various cobalt(III) amine–thiocyanate complexes. Thermodynamic data have also been obtained by various methods on a number of cobalt(II) complexes in different environments (*94*, *291*, *387*, *425*, *451*, *500*, *607*, *645*).

Although the kinetics of hydrolysis, anation, and other substitution reactions involving cobalt(III) thiocyanates have been extensively studied, in most cases only the overall rates have been measured and only rarely has account been taken of the possibility of attack by nitrogen or sulfur of NCS^-, although the reality of this possibility is illustrated by the isolation of both $[Co(NH_3)_5(NCS)]^{2+}$ and $[Co(NH_3)_5(SCN)]^{2+}$ species from the reaction of NaNCS with $[Co(NH_3)_5Cl](ClO_4)_2$ (*134*). After speculation concerning the mode of isomerization of $[Co(NH_3)_5SCN]^{2+}$ the same workers observed that *trans*-$[Co(NH)_3en_2SCN]^{2+}$ gave *cis*-$[Co(NH_3)en_2NCS]^{2+}$ and concluded that the isomerization involves rupture of the Co—SCN bond (*133*). However, in this review, kinetic data will not generally be included when there is doubt regarding the mode of coordination.

b. Rhodium and Iridium. Octahedral $[M(SCN)_6]^{3-}$ (M = Rh or Ir) have been characterized by infrared (*665*), electronic (*663*), and ^{14}N NMR (*390*) spectroscopy. The *trans*-$[Men_2Cl(NCS)]^+$ cations have been characterized for rhodium (*415*) and iridium (*80*), as have *cis*-$[Rh(cyclam)(NCS)_2]^+$ and *trans*-$[Rh(cyclam)(X)(NCS)]^+$ (X = NCS, Cl, Br, I; cyclam = 1,4,8,11-tetraazacyclotetradecane) (*124*). The kinetics of the formation of $[RhCl_5(CNS)]^{3-}$ have been studied but the product was not isolated (*634*). The linkage isomers have been isolated for $[Rh(PMe_2Ph)_3Cl_2(CNS)]$ (*126*), $[Rh(NH_3)_5(CNS)]^{2+}$ (*659*, *660*), and $[Ir(NH_3)_5(CNS)]^{2+}$ (*659*, *661*), whereas *trans*-$[Ir(pip)_4(H)NCS]^+$ isomerizes in solution (*107*). Luminescence from $[Rh(NH_3)_5(NCS)]^{2+}$ has been measured (*724*).

Compounds $[M(CO)(PPh_3)_2NCS]$ (M = Rh, Ir) have been characterized (*150*, *155*, *762*) and show no evidence of isomerization in solution (*155*). The compounds $RhL_2(CO)(NCS)$ [L = $P(C_6H_{11})_3$, PEt_3, PMe_2Ph, $P(p\text{-}ClC_6H_{11})_3$, EPh_3, $E(p\text{-}ClC_6H_{11})_3$, (E = As or Sb)] are N-bonded in the solid and solution. The arsine complexes and $Rh[P(OPh)_3]_3(NCS)$ dissociate in solution, and the bridged compound $Rh_2[P(OPh)_3]_4(CNS)_2$ was isolated. The anionic species $[Rh(CO)_2(NCS)_2]^-$ was also characterized as the tetra-*n*-butyl ammonium salt (*408*). Compound $Rh(PPh_3)_3NCS$ is superficially similar to the previously mentioned species in that it remains N-bonded in the solid, but in solution in the absence of oxygen, one Ph_3P molecule is labile, and compounds $Rh(PPh_3)_2L(SCN)$

$[\mathrm{L} = (\mathrm{CH_3})_2\mathrm{CO}, \mathrm{CH_3CN}, \mathrm{Et_2O}, \mathrm{C_6H_6}]$ have been characterized. The $\mathrm{Rh(PPh_3)_2(C_6H_6)(SCN)}$ reverts to the N-bonded starting material on treatment with excess $\mathrm{PPh_3}$, and the $\mathrm{C_6H_6}$ can be displaced to give $\mathrm{Rh(PPh_3)_2pip(NCS)}$; the N-bonded species have been detected in pyridine or aniline solutions but have not been isolated (*35*).

Oxidative addition reactions of $\mathrm{Ir(CO)(PPh_3)_2NCS}$ give the 1:1 adduct with tetracyanoethylene (*47*, *760*) and the products $[\mathrm{IrCO(PPh_3)_2(NCS)Y_2}]$ ($\mathrm{Y} = \mathrm{Cl}, \mathrm{Br}, \mathrm{NO_3}$) (*181*). By reacting $\mathrm{M(CO)(PPh_3)_2X}$ ($\mathrm{M} = \mathrm{Rh}, \mathrm{Ir}$; $\mathrm{X} = \mathrm{Cl}, \mathrm{NCS}, \mathrm{NCO}$) with $\mathrm{(SCN)_2}$ the corresponding *S*-thiocyanato complexes have been obtained in every case (*161*).

3. *Selenocyanates*

The only selenocyanate of this group of metals to have its structure determined by X-ray crystallography is $\mathrm{NH_4[Co(DH)_2(SeCN)_2]}$; the information available suggests that this is a trans-octahedral complex with a Co—Se distance of 2.4 Å (*8*). The anionic complexes $[\mathrm{Co(NCSe)_4}]^{2-}$ (*212*, *295*, *647*, *663*, *746*, *747*), $[\mathrm{Co(NCSe)_6}]^{4-}$ (*295*, *616*, *647*, *663*), and $[\mathrm{Rh(SeCN)_6}]^{3-}$ (*162*, *662*, *663*, *665*) have been reported and characterized by infrared and electronic spectroscopy. The bridged species $\mathrm{Co(NCSe)_4Hg}$ has a comparable structure to its thiocyanate analog, with cobalt(II) tetrahedrally surrounded by four nitrogen atoms and mercury(II), similarly, by four selenium atoms (*436*, *600*, *714*, *747*). The compound $\mathrm{Co(NCSe)_4Hg}$ is blue, but a pink form has been reported (*714*), suggesting the presence of octahedrally coordinated cobalt(II); also $\mathrm{Co[(NCSe)_3Hg]_2}$ has been reported (*714*). Other cobalt(II) selenocyanates are listed in Table XXIX.

Fewer cobalt(II) selenocyanates than thiocyanates are known, and the bonding is not so varied. The species $[\mathrm{Co(CN)_5(NCS3)}]^{3-}$ shows no signs of forming the Se-bonded isomer (*142*, *359*), nor do $[\mathrm{Co(NH_3)_5(NCSe)}]^{2+}$ and $[\mathrm{Co(NH_3)_4(CN)(NCSe)}]^+$ (*142*). Ablov and Samus (*7*) have reported $[\mathrm{Co(DH)_2L(SeCN)}]$ ($\mathrm{L} = \mathrm{SeCN}, \mathrm{NO_2}$, py,an) in which the mode of coordination is presumed by analogy with *trans*-$[\mathrm{Co(DH)_2(SeCN)_2}]^-$ (*4*) (see earlier). A number of salts of this anion have been prepared and its aquation studied (*683*, *759*). Similar compounds with different oximes have been examined (*755*, *758*). The *cis*-$[\mathrm{Co(DH)_2H_2O(NCSe)}]$ shows a similar reversal in the mode of selenocyanate coordination to that observed in the corresponding thiocyanate complexes (*3*).

The compound *trans*-$[\mathrm{Ir(pip)_4H(NCSe)}]$ has been characterized (*107*). Also $[\mathrm{M(CO)(PPh_3)_2(NCSe)}]$ ($\mathrm{M} = \mathrm{Rh}, \mathrm{Ir}$) have been prepared by a number of different methods (*148*); the compounds show no tendency to isomerize in solution (*155*). The compound $\mathrm{Rh(CO)(PPh_3)_2NCSe}$

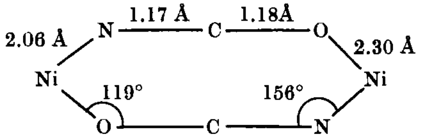
deselenates easily in the presence of excess Ph_3P, and this type of reaction may also account for the difficulty found in attempting to prepare $Rh(PPh_3)_3NCSe$. The compound $Rh(PPh_3)_2(CH_3CN)(SeCN)$ has been isolated and characterized (*36*).

I. Nickel, Palladium, and Platinum

It is convenient to treat each metal, nickel, palladium, and platinum, in turn, because of the large number of compounds involved.

1. Nickel

a. Cyanates. The X-ray structure (*265*) of $[Ni_2tren_2(NCO)_2](BPh_4)_2$ reveals that it has bridged cyanate groups of the type:



This is the first example of this type of bridging confirmed for the cyanate group.

The tetrahedral complex anion $[Ni(NCO)_4]^{2-}$ has been characterized by infrared spectroscopy (*275, 296, 639*) and by electronic spectral and magnetic (*275, 292, 647*) measurements. With the exception of $[NiEt_4dien(NCO)]BPh_4$, which has square planar coordination around the nickel (*159*), other mixed-ligand nickel(II) cyanates, for example, the compounds $NiL(H_2O)(NCO)_2$ (L = hexamethylenetetramine) (*735*), $NiL_2(NCO)_2$ (L = bipy, phen) (*335*), and $NiL_4(NCO)_2$ (L = py, 3pic, 4pic, isoquin) (*560*) are all octahedral. The compound $Ni(py)_6(NCO)_2$ is correctly formulated $[Ni(py)_4(NCO)_2]2py$ (*569*). Attempts to decompose thermally the foregoing tetrakis complexes to give the bis-ligand compounds were unsuccessful (*560*). However, with 3- and 4-cyanopyridines, Nelson and Nelson were able to prepare $NiL_2(NCO)_2$ in which the nickel was coordinated octahedrally, with Ni—N(CO)—Ni bridges (*557*). Other workers tentatively suggested Ni—NCO—Ni bridges in the similar $NiL_2(NCO)_2$ (L = 4CN-py, 4MeO, 4-MeO_2, C-py, $\frac{1}{2}$phen (*158*), but, in spite of the preceding structure, their arguments are not as convincing as those of Nelson and Nelson (*557*). Proton NMR measurements have been made on $Nipy_4(NCO)_2$ (*291*), and its thermal decomposition has been studied (*241, 496, 500*).

b. Thiocyanates. The structures of a number of nickel(II) thiocyanate complexes have been determined by X-ray methods, and are included in Table XXXI as are some other complexes whose structures have been elucidated by spectroscopic techniques. Results of X-ray structure determinations are not listed specifically in this case.

The hexacoordinate anion $[Ni(NCS)_6]^{4-}$ has been characterized (*293*, *294*, *639*, *647*, *663*) as well as $[Ni(NCS)_4]^{2-}$ (*293*, *294*, *639*, *647*, *663*). The latter exists either as a discrete, distorted tetrahedral anion, which is the case in the presence of large cations, or as part of a structure containing bridging thiocyanate groups with tetragonal hexacoordination around the nickel. Small cations seem to favor the tetragonal species, and both forms have been observed with the tetraphenylarsonium ion (*294*); such a polymeric structure is found for $[NiL_2][Ni(NCS)_4]$ (L = 2,2′,2″-terpyridyl (*368*). Tetragonal coordination is also observed in $NiHg(SCN)_4$ (*294*), and presumably in NiCd-$(SCN)_4$ (*734*). Bridging and terminal *N*-thiocyanato groups are present in $MNi(NCS)_3 \cdot nH_2O$ (M = alkali metal) (*441*, *447*). Compounds $Ni[Hg(SCN)_3]_2 \cdot H_2O$ and $Ni[Hg(SCN)_4] \cdot H_2O$ also contain bridging and terminal thiocyanate groups, and there is slight evidence for two types of bridging thiocyanate, as observed in $Co[Hg(SCN)_3]_2 \cdot C_6H_6$ (*351*); the compounds are thermochromic (*322*). Thiocyanate bridges are present in nickel(II) reineckate (*584*) and in $[Ni(NO)NCS]_x$, although $Ni(NO)L_2$-(NCS) [L = $(PhO)_3P$, Ph_3P, $(C_6H_{11})_3P$] are monomeric (*89*). Other examples occur below.

Many mixed-ligand nickel thiocyanates are known and some are listed in Table XXXI. All the compounds appear to be *N*-thiocyanates in spite of the different ligational environments and stereochemistries observed. However, in a discussion of the electronic spectra of [Ni-$(diars)_2(NCS)]ClO_4$, Preer and Gray (*614*) state that N- and S-bonded isomers of this compound are in equilibrium in CH_3CN, CH_2Cl_2, and DMSO at room temperature. Further, it has been reported that some anionic complexes of the form $[NiL(CNS)_2LH(H_2O)_2]^-$ contain Ni—SCN linkages for L = glycinate or alaninate, and Ni—NCS bonding in the dianion when L = EDTA. Monomeric $Ni(DMSO)_2(SCN)_2$ was also reported, together with $NiL_2(NCS)_2$ (L = urea, α- or β-naphthylamine) which have thiocyanate bridges (*173*). However, the analytical data are not always good enough to be certain about the number of molecules of water present which could modify the interpretation of the visible spectra, and the infrared data and the assignments are unconvincing.

Of particular interest in Table XXXI is the variation in the steric hindrance of the ligands and also in their π-bonding propensities. Reference will be made to these results in the later discussion, but here changes in the stereochemistry of the nickel provide the main feature of interest.

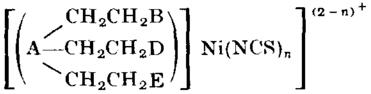
TABLE XXXI

SOME NICKEL THIOCYANATES

Complex	Composition	References
Octahedral		
trans-$Ni(NH_3)_4(NCS)_2$		*(791)*
trans-$Ni(en)_2(NCS)_2$		*(127, 277, 495)*
trans-$NiL_2(NCS)_2$	L = 2Me-pn, bn, *N,N'*-dimeen, *N,N'*-dieten	*(277)*
	= *N,N'*-dibenen	*(593)*
trans-$Ni(pn)(NCS)_2$		*(228, 277)*
$NiL(NCS)_2$	L = trien, tet a, tet b	*(228)*
trans-$Ni(dtet)(NCS)_2$	dtet = 3.3-dimethyl-1,5,8,11-tetra-aza-cyclotrideca-1-ene	*(229)*
cis-$NiL(NCS)_2$	L = tren	*(628, 629)*
trans-$Ni(py)_4(NCS)_2$		*(38, 201, 560, 561, 671)*
trans-$Ni(py)_4(NCS)_2 \cdot 2I_2$		*(300, 602)*
trans-$Ni(py)_4(NCS)_2 \cdot 2py$		*(569)*
$NiL_4(NCS)_2$	L = 3pic, 4pic, isoquin	*(560, 561)*
	= quin	*(460, 699)*
	= 2Me-quin	*(532)*
$NiL_2(NCS)_2$	L = tri-2-pyridylamine	*(473)*
$NiL(NCS)_2$	L = tri-(6-methyl-2-pyridylmethyl)amine	*(234)*
$Ni(phen)_2(NCS)_2$		*(658)*
$NiL(NCS)_2$	L = R-dionebis(3-aminopropylimine); R = 2,3-butane-, 2,3-pentane-, 1,2-cyclohexane	*(721)*
$Ni(DMF)_4(NCS)_2$		*(688)*
$Ni(NIPA)_2(NCS)_2$		*(243)*
$NiL_4(NCS)_2$	L = *o*-toluidine, *o*-anisidine, *o*-phenetidine, 3,4-xylidine	*(167)*
$NiL_2(NCS)_2$	L = *o*-phenylenediamine, 4Me-L	*(516)*
$NiL_4(NCS)_2$	L = thiazole	*(393)*
	L = *N*-*n*-butyl-imidazole	

$Niquin_2(H_2O)_2(NCS)_2$		*(460)*
$NiL_2(H_2O)_2(NCS)_2$	L = hexamethylenetretramine	*(735)*
$NiL_2(NCS)_2$	L = 2,5-dithiahexane, 1,2-di(isopropylthio)ethane	*(286)*
$NiL_2(NCS)_2 \cdot 2I_2$		
$Ni(tu)_2(NCS)_2$		*(256, 287, 552, 554)*
$Ni(SeC(NH_2)_2)_2(NCS)_2$		*(256)*
$NiL_2(NCS)_2$	L = diphenyl-(*o*-diphenylarsinophenyl)phosphine	*(263)*
$Ni(SN)_2(NCS)_2$	SN = 1,2-bis-(*o*-aminophenylthio)ethane	*(170)*
$Ni(NS)_2(NCS)_2$	NS = thiosemicarbazide	*(313)*
$Ni(PS)_2(NCS)_2$	PS = 2-diethylphosphinoethyl-1-thioethane	*(681)*

Five-coordinate



A	B	D	E	*n*	
N	OMe	PPh_2	PPh_2	1	*(104, 541, 642)*
N	NEt_2	NEt_2	$AsPh_2$	2	*(251, 252)*
N	NEt_2	OMe	PPh_2	1	*(542)*
N	NEt_2	SMe	PPh_2	1	*(542)*
N	Me	PPh_2	PPh_2	1	*(541)*
N	CH_2OMe	PPh_2	PPh_2	1	*(541)*

$NiL_3(NCS)_2$	L = 9-alkyl-9-phosphafluorene; alkyl = Me, Et	*(27)*
	= PMe_3	*(529)*
$[NiL_2NCS]^+$	L = diars	*(614)*
	= diphenyl(-*o*-diphenylarsinophenyl)phosphine	*(263)*
	= 1,2-ethylmercaptocyclohexylphenylphosphine	*(781)*
$NiL(NCS)_2$	L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine	*(337)*
$[NiL(NCS)]^+$	L = 2,6-di(diphenylphosphinomethyl)pyridine	*(231, 559)*

Square planar

$[NiEt_4dienNCS]BPh_4$		*(159)*
$[Ninas NCS]BPh_4$	nas = *N,N*-bis-[2-(diethylamino)ethyl]-2-(diphenylarsino)ethylamine	*(250)*

(continued)

TABLE XXXI—*continued*

Complex	Composition	References
Ni(quin)$_2$(NCS)$_2$		*(460, 699)*
NiL$_2$(NCS)$_2$	L = 1-benzyl-2-phenylbenzimidazole	*(119)*
Ni(PR$_3$)$_2$(NCS)$_2$	R = *n*-Pr, *i*-Pr, *s*-but, cyclohexyl	*(318)*
	= *i*-Pr	*(599)*
	= Ph	*(599, 765)*
	= Me	*(412)*
NiL$_2$(NCS)$_2$	L = 9-phenyl-9-phosphafluorene	*(27)*
NiL(NCS)$_2$	L = 1,2-bis-(diphenylphosphino)ethane	*(392)*
	= 1,4-bis-(diphenylphosphino)butane	*(641)*
	= 2,6-bis-(2-diphenylphosphinoethyl)pyridine	*(559)*
	= 2,2′-biphenylenebisdiethylphosphine	*(28)*
NiL$_2$(NCS)$_2$	L = 2-diethylphosphinoethyl-1-thioethane	*(681)*
[NiQas(NCS)]NCS	Qas = *o*-Me$_2$As(C$_6$H$_4$)$_3$As	*(375)*
NiL(NCS)$_2$	L = diphenyl-(*o*-diphenylaminophenyl)phosphine	*(263)*
	L = 1,2-bis-(isopropylseleno)ethane	*(346)*
Complexes with bridging —NCS—		
NiL(NCS)$_2$	L = dien, dpt	*(228)*
[NiL$_2$(NCS)]ClO$_4$	L = en, $\frac{1}{2}$trien	*(228)*
NiL$_2$(NCS)$_2$	L = various anilines	*(167)*
	L = quin	*(460)*
NiL(NCS)$_2$^{a}	L = methyl-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine	*(234)*
NiL(NCS)$_2$^{a}	L = tri-2-pyridylamine	*(473)*
NiL$_2$(NCS)$_2$	L = hexamethylphosphoric triamide	*(485)*
Ni(ROH)$_2$(NCS)$_2$	R = Me, Et	*(288)*
NiL$_2$(NCS)$_2$	L = 2-thioimidazolidine	*(555)*
	= thioacetamide	*(172, 553)*

[a] One terminal —NCS.

Anhydrous Ni(NCS)$_2$ contains the triply ligating NCS group with an octahedral NiN$_2$S$_4$ environment (*288*). Such an environment is also found in a number of other complexes (see Table XXXI), but it is of interest that it is achieved by bridging tu in Nitu$_2$(NSC)$_2$ (*554*) and bridging NCS in NiL$_2$(NCS)$_2$ for L = 2-thioimidazolidine (*555*) and thioacetamide (*172*). The magnetic properties of these and related compounds have been studied (*268*, *287*, *288*). In NiL$_2$(NCS)$_2$ (L = thiourea, thioimidazolidinone, 2-thiopyrrolidone, thioacetamide) it is suggested that ferromagnetic spin coupling occurs within the structural chains caused by the bridging sulfur atoms, with a superimposed antiferromagnetic interaction between the chains; the latter does not occur in NiL$_2$(NCS)$_2$ (L = *N*,*N'*-dimethylthiourea) since the chains are further apart owing to the substituents (*268*).

Some thermodynamic parameters have been measured for Nipy$_4$(NCS)$_2$ (*94*, *291*, *425*, *496*, *500*) and other complexes (*83*, *416*, *417*, *645*).

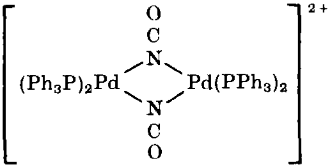
c. Selenocyanates. The compound Ni(DMF)$_4$(NCSe)$_2$ was prepared and characterized as a trans-octahedral complex containing *N*-selenocyanato groups (*668*). This has been confirmed by X-ray analysis which gives the following distances: Ni—N 2.05(2), N—C 1.21(8), and C—Se 1.71(3) Å; the NiNC and NCSe bond angles are 174.5° and 177°, respectively (*736*).

The anionic octahedral complex [Ni(NCSe)$_6$]$^{4-}$ has been reported (*162*, *295*, *647*, *663*), as has [Ni(NCSe)$_4$]$^{2-}$. Unlike its thiocyanate analog, the latter ion only exists in the polymeric octahedral from with —NCSe— bridging (*295*, *647*). Bridging also occurs in Ni(NCSe)$_4$Hg (*714*).

Relatively few mixed-ligand complexes have been reported, and in these the selenocyanate group is N-bonded. The compound NL$_2$(NCSe)$_2$ [L = en, pn, bn, *N*,*N'*-dimeen, *N*,*N'*-dieten (*277*), Dben (*593*)] contains octahedral and [NiEt$_4$dienNCSe]BPh$_4$ (*159*) square planar nickel. Octahedrally coordinated nickel is also found in Ni(urt)$_2$(H$_2$O)$_4$(NCSe)$_2$ (*735*), NiL$_2$(NCSe)$_2$ (L = bipy, phen) (*683*), and NiL$_4$(NCSe)$_2$ (L = py, 3pic, 4pic, isoquin) (*560*); Nipy$_6$(NCSe)$_2$ is, correctly formulated Nipy$_4$(NCSe)$_2\cdot$2py (*569*). Five coordination is believed to occur in NiL(NCSe)$_2$ [L = 2,3,5,6,-tetrakis-(6-methyl-2-pyridyl)pyrazine] (*337*).

2. *Palladium*

a. Cyanates. Palladium(II) forms a square planar tetra-*N*-cyanato anion with the tetramethylammonium (*299*, *573*, *575*) cation. A number of mixed-ligand compounds, PdL$_2$(NCO)$_2$ (L = NH$_3$, py, 2pic, 4pic, $\frac{1}{2}$bipy, $\frac{1}{2}$phen, Ph$_3$P), have been prepared by substitution reactions and shown to be N-bonded (*573, 575*); the Pd—N stretching frequencies have been studied in these compounds (*566, 578*). Also $Pd(PPh_3)_2(NCO)_2$ has been obtained by the reaction of CO with the corresponding azide (*85*), and the complexes, $PdL_2(NCO)$, [L = $C_5H_{11}N$, PBu_3, $P(C_6H_{11})_3$], have been prepared similarly (*87*). The compound $[PdEt_4dien(NCO)]BPh_4$ has also been reported (*147*). Treatment of $Pd(PPh_3)_2(NCO)_2$ with ROH (R = Me, Et) and CO gives $Pd(PPh_3)_2(NCO)(CO_2R)$ (*90*), via $[(Ph_3P)_2Pd(NH_2CO_2Et)(NCO)]BF_4$ (*783*). Further, addition of Et_3O^+-BF_4^- to $Pd(PPh_3)_2(NCO)_2$ yields the *N*-cyanato bridged cation (*90*):



b. Thiocyanates. Complete X-ray structure analyses have been carried out for the compounds $K_2Pd(SCN)_4$ (*524, 525*), $Pd[Ph_2PCH_2CH_2CH_2NMe_2](SCN)(NCS)$ (*198, 199*,) $Pd[Ph_2PCH_2CH_2PPh_2](SCN)(NCS)$ (*102*), and *trans*-$Pd(Ph_2PC{\equiv}CBu^t)_2(SCN)_2$ (*101*). These structures contain features of interest which have been delineated previously (Section III) and will be referred to again in the discussion. The mode of thiocyanate bonding in $K_2Pd(SCN)_4$ had been established previously by infrared (*293, 639*), ultraviolet (*663*), and ^{14}N NMR (*390*) spectroscopy.

A large number of mixed-ligand complexes of palladium(II) thiocyanate have been prepared. The mode of bonding of the thiocyanate group to the metal is markedly dependent on the nature of the other ligands present. Some examples are given in Table XXXII where the compounds are grouped either as *N*- or *S*-thiocyanates for each class of different ligand.

In addition to the compounds reported in Table XXXII, using bidentate ligands in $PdL(CNS)_2$, it has been possible to obtain complexes containing both *N*- and *S*-thiocyanato groups with L = 4,4′-diMe-bipy (*103*), $Ph_2As(\text{-}o\text{-}C_6H_4PPh_2)$ (*526, 565*), $Ph_2PCH_2CH_2NMe_2$ (*526*), $Ph_2P(CH_2)_3NMe_2$ (*198, 199, 526*), and $Ph_2PCH_2CH_2PPh_2$ (*102, 526*). The last result, confirmed by X-ray crystallography (*102*), contradicts the conclusions from the infrared spectrum of this compound, and thus casts some doubt on the correctness of the assignment, on infrared grounds, of $Pd(diars)(SCN)_2$ (*392*). Either similar mixed bonding or a mixture of linkage isomers occurs with L = 2,9-diMe-phen (*606*) and in solution for L = $Ph_2AsCH_2CH_2AsPh_2$, although the latter forms the *S*-thiocyanato complex only in the solid state (*526*). Similarly it

TABLE XXXI—*continued*

Complex	Composition	References
$Ni(quin)_2(NCS)_2$		*(460, 699)*
$NiL_2(NCS)_2$	L = 1-benzyl-2-phenylbenzimidazole	*(119)*
$Ni(PR_3)_2(NCS)_2$	R = *n*-Pr, *i*-Pr, *s*-but, cyclohexyl	*(318)*
	= *i*-Pr	*(599)*
	= Ph	*(599, 765)*
	= Me	*(412)*
$NiL_2(NCS)_2$	L = 9-phenyl-9-phosphafluorene	*(27)*
$NiL(NCS)_2$	L = 1,2-bis-(diphenylphosphino)ethane	*(392)*
	= 1,4-bis-(diphenylphosphino)butane	*(641)*
	= 2,6-bis-(2-diphenylphosphinoethyl)pyridine	*(559)*
	= 2,2′-biphenylenebisdiethylphosphine	*(28)*
$NiL_2(NCS)_2$	L = 2-diethylphosphinoethyl-1-thioethane	*(681)*
[NiQas(NCS)]NCS	Qas = *o*-$Me_2As(C_6H_4)_3As$	*(375)*
$NiL(NCS)_2$	L = diphenyl-(*o*-diphenylaminophenyl)phosphine	*(263)*
	L = 1,2-bis-(isopropylseleno)ethane	*(346)*
Complexes with bridging —NCS—		
$NiL(NCS)_2$	L = dien, dpt	*(228)*
$[NiL_2(NCS)]ClO_4$	L = en, ½trien	*(228)*
$NiL_2(NCS)_2$	L = various anilines	*(167)*
	L = quin	*(460)*
$NiL(NCS)_2{}^a$	L = methyl-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine	*(234)*
$NiL(NCS)_2{}^a$	L = tri-2-pyridylamine	*(473)*
$NiL_2(NCS)_2$	L = hexamethylphosphoric triamide	*(485)*
$Ni(ROH)_2(NCS)_2$	R = Me, Et	*(288)*
$NiL_2(NCS)_2$	L = 2-thioimidazolidine	*(555)*
	= thioacetamide	*(172, 553)*

^{a} One terminal —NCS.

TABLE XXXII—*continued*

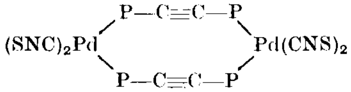
Compound	References	Compound	References
$\mathrm{Pd(CN\text{-}\mathit{i}\text{-}Pr)_2(SCN)_2}$	(*599*)	$\mathrm{Pt(Ph_3As)_2(NCS)_2}$	(*143*)
$\mathrm{Pd(tu)_2(SCN)_2}$	(*143*)	$\mathrm{Pt(\mathit{o}\text{-}allyl\text{-}C_6H_4AsPh_2)_2(NCS)_2}$	(*99*)
$\mathrm{Pdetu_2(SCN)_2}$	(*143*)		
$\mathrm{Pd(Ph_3Sb)_2(SCN)_2}$	(*143, 640*)		
$\mathrm{Pt(Ph_3Sb)_2(SCN)_2}$	(*143*)		
Palladium (L_2 = chelate)		Platinum (L_2 = chelate)	
$\mathrm{Pd(bipy)(NCS)_2}^c$	(*79, 103, 143, 640*)	$\mathrm{Pt(en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(phen)(SCN)_2}$	(*103, 143, 640*)	$\mathrm{Pt(N\text{-}Me\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(5\text{-}Me\text{-}phen)(SCN)_2}$	(*103*)	$\mathrm{Pt(N\text{-}Et\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(5,6\text{-}diMe\text{-}phen)(SCN)_2}$	(*103*)	$\mathrm{Pt(1\text{-}Et\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(4,7\text{-}diMe\text{-}phen)(SCN)_2}$	(*103*)	$\mathrm{Pt(N\text{-}\mathit{i}\text{-}Pr\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(5\text{-}Me\text{-}6\text{-}NO_2\text{-}phen)(SCN)_2}$	(*103*)	$\mathrm{Pt(\mathit{N,N}\text{-}diMe\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(5\text{-}NO_2\text{-}phen)(NCS)_2}$	(*103, 640*)	$\mathrm{Pt(\mathit{N,N'}\text{-}diMe\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(5\text{-}Cl\text{-}phen)(SCN)_2}$	(*103*)	$\mathrm{Pt(\mathit{N,N}\text{-}diEt\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd(4,7\text{-}di\text{-}Ph\text{-}phen)(SCN)_2}^c$	(*103*)	$\mathrm{Pt(\mathit{N,N'}\text{-}diEt\text{-}en)(SCN)_2}$	(*548, 549*)
		$\mathrm{Pt(\mathit{N,N}\text{-}diMe\text{-}\mathit{N'}\text{-}Me\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd[Ph_2P(\text{-}\mathit{o}\text{-}C_6H_4SMe)](SCN)_2}$	(*526*)	$\mathrm{Pt(\mathit{N,N,N',N'}\text{-}tetraMe\text{-}en)(SCN)_2}$	(*548, 549*)
$\mathrm{Pd[Ph_2P(\text{-}\mathit{o}\text{-}C_6F_4SMe)](SCN)_2}$	(*526*)		
$\mathrm{Pd[Ph_2P(\text{-}\mathit{o}\text{-}C_6H_4SeMe)](SCN)_2}$	(*526*)		
$\mathrm{Pd[Ph_2As(\text{-}\mathit{o}\text{-}C_6H_4P(S)Ph_2)](SCN)_2}$	(*526, 565*)		
$\mathrm{Pd[Ph_2AsCH_2CH_2CH_2AsPh_2](SCN)_2}$	(*526*)		

[a] *i*-Nicotin = methyl ester of isonicotinic acid.

[b] S-Bonded isomer as a solid but partially isomerizes on melting.

[c] Stable linkage isomer.

has not been possible to distinguish between these two possibilities in the following dimeric compound (*179*):



(two phenyl groups are omitted from each P for clarity)

A monomeric compound is obtained with L = $Ph_2PCH{=}CHPPh_2$, in which only *S*-thiocyanato groups are present (*194*). Using other bidentate ligands with two different atoms, the compounds $Pd[o\text{-}X{-}C_6H_4{-}YCH_2]_2(CNS)_2$ (X = Ph_2As, Y = O; X = Ph_2As, Y = S; X = NH_2, Y = S) have been reported (*170*). It is not always clear which are the donor atoms of the bidentate ligand and, in view of some of the results already given, the authors' tentative assignment of the complexes as *N*-thiocyanates on the basis of ν_{CN} only, seems worthy of reexamination. The bonding of the thiocyanate group has not been specified in the complex $PdL(CNS)_2$ (L = 8-dimethylarsinoquinoline) (*73*).

Basolo and his co-workers first prepared the ion $[PdEt_4dien(CNS)]^+$ (*77*). Compound $[PdEt_4dienSCN]NCS$ is prepared by the reaction of Et_4dien with $K_2Pd(SCN)_4$, and the solid product isomerizes completely to the *N*-thiocyanate in 3 days. If, however, the original salt is treated with NH_4PF_6, then $[PdEt_4dienSCN]PF_6$ is formed which undergoes no detectable solid state isomerization. The *S*-thiocyanato cation isomerizes in solution, and kinetic studies indicate that the mechanism involves an intermolecular process (*78*). Solid $[PdEt_4dienNCS]BPh_4$, prepared by an analogous method, reisomerizes to the S-bonded form at room temperature (*153*, *156*). The kinetics of the displacement of both N- and S-bonded thiocyanate groups from this system by the bromide ion have been studied (*78*, *157*), and kinetic and thermodynamic parameters obtained for the equilibrium (*379*, *414*):

$$[PdLBr]^+ + NCS^- \rightleftharpoons PdLCNS]^+ + Br^- \quad (L = \text{dien, Et}_4\text{dien})$$

Dimeric compounds of the type $Pd_2L_2X_2(CNS)_2$ [L = As(iso-Pr)$_3$, $AsBu_3$, PBu_3; X = Cl, NCS] have been isolated and shown to contain NCS bridges (*186*), although the assignments of the mode of bonding of the terminal thiocyanate groups in these compounds and in the corresponding $PdL_2(CNS)_2$ were based, in 1956, on insufficient data by current standards. Such bridging is believed to occur in the low-temperature form of 2-methylallyl palladium thiocyanate (see Fig. 2) whereas the coalescence of the NMR spectrum at higher temperatures is believed to

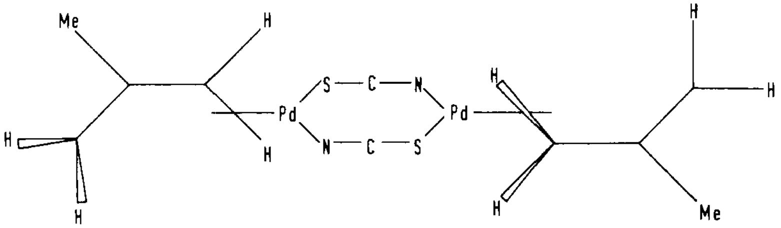


FIG. 2. Dimeric form of 2-methyl allyl palladium thiocyanate. [From Tibbetts and Brown (*725*).]

be due to the formation of a tetramer which is tentatively assigned the structure in Fig. 3 (*725*).

Some five-coordinate palladium(II) thiocyanate complexes have been reported. Both $[Pd(2,9\text{-diMe-phen})_2SCN]ClO_4$ (*606*) and $[Pd(o\text{-}Me_2As\text{-}C_6H_4)_3As(NCS)]NCS$ (*375*) have been characterized, but the mode of coordination is unspecified in $[PdL_2CNS]NCS$ [L = 1,8-naphthylenebis-(dimethylarsine)] (*636*); in the latter system, six coordination seems to occur in solution (*636*).

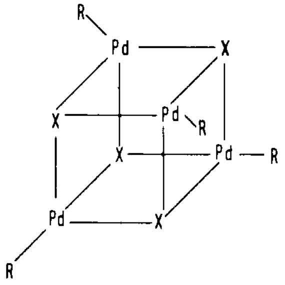


FIG. 3. Tetrametric form of 2-methyl allyl palladium thiocyanate (X = NCS with nature of bridge unspecified). [From Tibbetts and Brown (*725*).]

The effect of different solvents on the type of thiocyanate coordination has been studied by dissolving the two linkage isomers $Pd(AsPh_3)_2(CNS)_2$ in various solvents. It was found that Pd—SCN bonding was promoted by solvents with high dielectric constants and a mixture of Pd—NCS, Pd—SCN, and Pd—SCN—Pd bonding by solvents having low dielectric constants (*154*, *155*). These and related results will be discussed in Section V.

c. *Selenocyanates*. The square planar anions $[Pd(SeCN)_4]^{2-}$ have been characterized (*162*, *662*, *663*, *665*) and some mixed-ligand complexes reported. The compound $Pd(n\text{-}Bu_3P)_2(SeCN)_2$ on standing shows changes in its infrared spectrum which have been tentatively ascribed to isomerization, but some decomposition also occurs, and the N-bonded isomer was not isolated (*152*). The other reported compounds of the type $PdL_2(SeCN)_2$ are as written [L = NH_3, py, 4pic, $4NH_2$-py, 4Ac-py, *N*,*N*-diph-tu, *N*,*N*′-diph-tu, PPh_3, $AsPh_3$, P(*o*-Me)$_3$] (*152*). Selenium-bonded compounds have been reported only for the bidentate ligands bipy (*142*, *152*), en, phen, 5-NO_2-phen, 1,2-$(NH_2)_2C_6H_4$, tripy (*152*) (where tripy = 2,2′,2″-tripyridine acting, in the solid compound, as a bidentate ligand), Ph_2As(-*o*-$C_6H_4PPh_2$), Ph_2As(-*o*-$C_6H_4PS\cdot Ph_2$) (*526*, *565*), and $Ph_2AsCH_2CH_2AsPh_2$ (*526*).

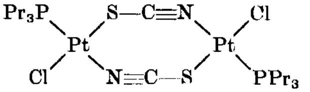
The system [$PdEt_4$dienCNSe]X is very similar to the corresponding thiocyanate compounds. The compound [$PdEt_4$dienSeCN]BPh_4 is the kinetic product of the reaction of Et_4dien with $K_2Pd(SeCN)_4$, but when dissolved in a variety of solvents it isomerizes and solid [$PdEt_4$dienNCSe]BPh_4 may be isolated. This latter compound reisomerizes in the solid state to give again the Se-bonded compound. With dien, only the Se-bonded compound [Pd(dien)SeCN]BPh_4 is observed (*151*, *153*, *156*) The kinetics of displacement of —NCSe and —SeCN from [$PdEt_4$dienCNSe]BPh_4 by the bromide ion have been studied, and by comparing the rates with the corresponding thiocyanate displacements it was originally concluded that displacement of —SeCN involved the opening of one or more of the chelate rings, whereas, for —SCN, a dissociative of S_N1 or solvent-assisted ligand exchange mechanism occurred (*157*). Later, the same authors extended their measurements and rejected the chelate ring opening mechanism in favor of a direct substitution of [$PdEt_4$dienSeCN]$^+$ by Br^-: it was proposed that the steric interaction caused by the outgoing group was responsible for the reagent-dependent path (*414*).

3. *Platinum*

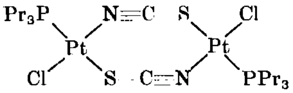
a. Cyanates. The tetraphenylarsonium and tetraethylammonium salts of square planar $[Pt(NCO)_4]^{2-}$ have been prepared and characterized (*575*). A number of mixed ligand complexes $PtL_2(NCO)$ (L = $\frac{1}{2}$bipy, Ph_3P, Ph_3As, Ph_3Sb) have also been reported (*575*) and their far-infrared spectra studied (*578*). Two groups of absorptions due to hydrido resonances were observed in the NMR spectrum of *trans*-$PtH(PEt_3)_2NCO$ which were ascribed to the *N*- and *O*-cyanato isomers (*613*). This view has been challenged and the effects ascribed to phosphine exchange (*13*, *14*), but Pidcock (*604*) has demonstrated that such exchange cannot account for the observed broadening and has supported the idea of linkage isomers. The related compounds, *trans*-$PtHL_2(NCO)$ (L = PPh_3, $PEtPh_3$, PBu_3), were also reported (*13*, *14*).

Similarly to the analogous palladium compounds, $Pt(PPh_3)_2X_2$ ($X = N_3$, NCO) reacts with ROH (R = Me, Et, Pr, *i*-Pr) and CO to give $Pt(PPh_3)_2(NCO)\ CO_2R)$ (*90*, *749*). The bridged species $[(Ph_3P)_2PtX_2Pt(PPh_3)_2](BF_4)$ ($X = N_3$, NCO) reacts with CO to give $[Pt(PPh_3)_2(CO)(NCO)]BF_4$ which further reacts with CO and ROH (Me, Et) to give $[Pt(PPh_3)_2(CO)(CO_2R)]BF_4$ (*90*). The reactions appear to proceed via protonation of the cyanate group to species such as $[(Ph_3P)_2Pt(NH_2CO_2Et)(NCO)]BF_4$, which has been characterized (*783*). The compound $Pt(PPh_3)_2C_2H_4$ reacts with $RCON_3$ (R = OBu^t, OEt) to give $Pt(PPh_3)_2(NCO)N_3$ (*749*).

b. Thiocyanates. The X-ray structures of the α- and β- forms of $Pt_2Cl_2(PPr_3)_2(CNS)_2$, originally prepared by Chatt *et al.* (*187*, *188*), have further refined (*348*) as follows:



α



β

and the appropriate bond distances are listed in Table XXXIII (*348*).

Platinum(IV) forms an octahedral complex anion shown to be $[Pt(SCN)_6]^{2-}$ by infrared (*639*, *665*) and electronic (*663*, *713*) spectroscopy. Square planar $[Pt(SCN)_4]^{2-}$ has been similarly characterized (*293*, *599*, *639*, *663*, *665*, *745*) and additionally by ^{14}N NMR spectroscopy (*390*).

Few mixed-ligand complexes of platinum(IV) thiocyanates appear to have been reported. The *cis*- and *trans*-$Pt(NH_3)_2(NO_2)_2(SCN)_2$ (*46*) and *trans*-$[Pt(NH_3)_4(SCN)_2]^{2+}$ and -$[Pt(NH_3)_4Cl(SCN)]^{2+}$ have been characterized (*521*) as have the bridged compounds, $Pt(SCN)_6M$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) (*58*, *728*). The easy reduction of $K_2Pt(SCN)_6$

TABLE XXXIII

SELECTED BOND DISTANCES AND BOND ANGLES IN THE α AND β FORMS OF $Pt_2Cl_2(PPr_3)_2(CNS)_2$[a]

Bonds	α	β
Pt—S	2.327(5) Å	2.408(4) Å
Pt—N	2.078(13) Å	1.965(13) Å
S—C	1.643(14) Å	1.641(15) Å
C—N	1.124(19) Å	1.168(16) Å
∠Pt—S—C	103.6(6)°	102.9(5)°
∠Pt—N—C	164.9(14)°	167.3(11)°
∠S—C—N	179.3(16)°	178.6(13)°

[a] Data from Ref. *348*.

in aqueous solutions of nitrogen ligands results in platinum(II) complexes (*350*). Tetrameric $[Pt(NCS)Me_3]_4$ has been reported and is believed to break down on addition of pyridine to give an N-bonded product according to the scheme in Fig. 4 (*385*).

Mixed-ligand platinum(II) thiocyanates are quite numerous and many have been included in Table XXXII with some similar palladium(II) compounds. Linkage isomerism has been observed in solution for

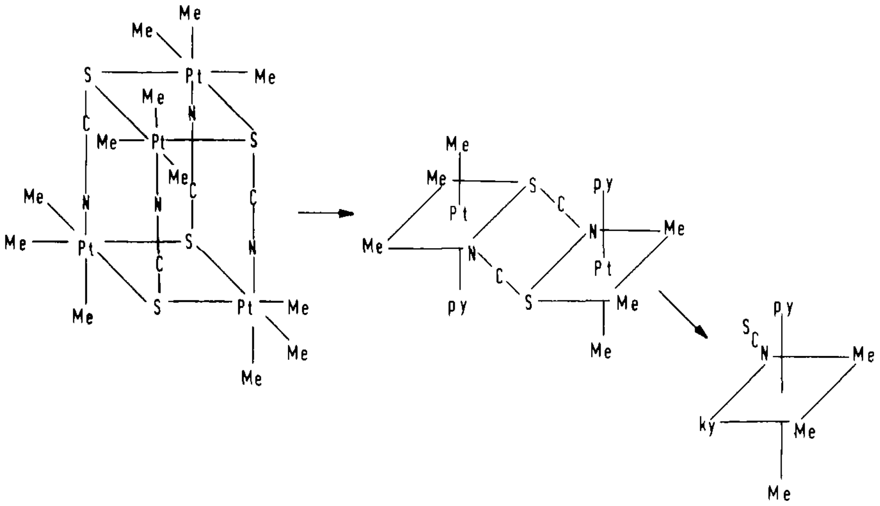


FIG. 4. Reaction scheme for the addition of pyridine to $[Pt(NCS)Me_3]_4$. [From Headley *et al.* (*375*).]

the complexes $PtHL_2(NCS)$ where the —NCS to —SCN ratio increased in the order $Et_3P \sim Bu_3P < Et_3As < Ph_2EtP < Ph_3P$; the S-bonded complex appears to be favored by polar solvents (*13*, *14*). Dimeric $Pt_2(DPPA)_2(CNS)_4$ [DPPA = bis(diphenylphosphino) acetylene], like the palladium(II) analog (see Section IV, I, 2, b) has an infrared spectrum which indicates both N- and S-bonded thiocyanates, but the authors were unable to distinguish whether these arose from a compound containing both types of coordination or from an unresolved mixture of linkage isomers (*179*). The thiocyanate bonding was not characterized in $PtL(CNS)_2$ (L = 8-dimethylarsinoquinoline) (*73*). However, in $PtAP(SCN)_2$ (AP = *o*-allylphenyldiphenylphosphine), the double bond is coordinated to the metal and S coordination occurs [cf. $Pd(AP)_2(NCS)_2$ and the corresponding *N*-thiocyanato complexes in Table XXXII with the related arsine] (*99*). A Pt—SCN bond is reported in $[PtL_3SCN]NCS$ (L = 9-R-9-phosphafluorene; R = Me, Et) (*27*).

Dimeric compounds of the type $Pt(PPr_3)_2X_2$ $CNS)_2$ (X = Cl, NCS) have been shown to contain —NCS— bridges (*186*)—the X-ray structure of the isomers when X = Cl have been mentioned previously in this section.

The five-coordinate compounds $[PtL_2(CNS)]NCS$ [L = 1,8-naphthylenebis(dimethylarsino) (*636*), 8-dimethylarsinoquinoline (*73*)] have been reported but the mode of bonding was not specified; in the latter, six coordination appears to occur in solution (*73*).

c. Selenocyanates. Both $[Pt(SeCN)_6]^{2-}$ (*639*, *663*, *665*) and $[Pt(SeCN)_4]^{2-}$ (*162*, *662*, *663*, *665*, *713*) have been characterized. The mixed-ligand complex $Ptbipy(SeCN)_2$ has been reported (*142*), and the compounds *trans*-$PtHL_2SeCN$ (L = Ph_3P, Bu_3P) (*14*).

J. COPPER, SILVER, AND GOLD

Because of the different relative stabilities of the oxidation states of these elements, it is convenient to treat each element individually as was done with nickel, palladium, and platinum.

1. Copper

a. Cyanates. The preparation of some anionic cyanate complexes of copper(I) has been reported (*694*), but no structural data are available.

Copper(II) forms the anionic species $[Cu(NCO)_4]^{2-}$ (*292*, *296*, *693*). Electronic spectra suggest that the ion has a distorted tetrahedral structure (*639*), and the infrared spectra indicate that the distortion involves the CuN_4 tetrahedron rather than kinking of the Cu—NCO group (*296*). It has been suggested that, in the presence of suitable cations, this distortion can extend to give pseudo-octahedral geometry around the copper (*195*). In $K[Cu(NCO)_3]$ both bridging (Cu—N—Cu) and isocyanate groups occur (*743*). The addition of LiNCO to a solution of copper(II) in acetone has been followed spectrophotometrically and indicates the formation of a 1:1.5 complex (*620*, *752*).

Several mixed-ligand complexes, $CuL_2(NCO)_2$ (L = ½bipy, ½phen, isoquin, quin, $6NO_2$-quin, 4R-py; R = H, Me, NH_2, MeCO, CN, MeO_2C, CH·NOH), have been reported (*158*). In most cases these are essentially *trans*-square planar complexes (except when L = bipy or phen), but when L = isonicotinamide or 4-pyridine aldoxime there is evidence for a bridged octahedral structure; in all these cases the cyanate group acts as a monodentate nitrogen donor (*158*). A similar series of compounds, $CuL_2(NCO)_2$ [L = quin, isoquin, 2Me-isoquin, 3Me-isoquin, 4Me-isoquin (*461*), 2-pic, 3-pic, 4-pic, 2,4-lut, 2,6-lut, 2,4,6-coll (*461*, *462*)], with various 2-substituted pyridines and related ligands show increasing tetragonal distortion but maintain the same overall stereochemistry (*461*, *462*). The compounds $CuL(NCO)_2$ [L = quin, 2Me-isoquin, 3Me-isoquin, 4Me-isoquin (*461*), 2-pic, 2,4-lut (*461*, *462*)] have also been prepared, and seem to have a deformed tetragonal pyramidal structure with extensive Cu—N—Cu bridging (*461*) which is believed to give rise to a ferromagnetic interaction and would account for the observed magnetic properties of the compounds (*462*). With substituted anilines as ligands, the complexes $CuL_2(NCO)_2$ (L = an, *p*Cl-an, *p*I-an, *o*-tol, *m*-tol, *p*-tol) are formed, with the neutral ligands occupying the trans positions to an octahedrally coordinated copper which has the nitrogens from four bridging cyanate groups forming the plane (*463*, *619*). The compound $[CuEt_4dienNCO]BPh_4$ contains four-coordinated copper (*159*). Bispicolinatocopper(II) is square planar and forms a 1:1 adduct with KNCO in which electronic spectral changes are attributed to cyanate coordination: since no thiocyanate coordination occurs in the corresponding KSCN adduct (*705*) (see Table XXXIV) as would have been expected if N coordination occurs, the cyanate adduct is formulated $K[Cu(pic)_2(OCN)]$ (*321*).

b. *Thiocyanates*. The structures of several of these complexes have been determined crystallographically, and some of the resulting data are summarized in Table XXXIV. The variations are particularly interesting for this metal. The mode of coordination of thiocyanate changes apparently with the different coordination geometries around copper(II) (structures I, IV, VI, and IX of Table XXXIV), or with the nature of the ligand (structures II–IV), or both (structures I–IX). Structures VII and VIII are the two most commonly obtained crystalline species of the eight which have been observed for this compound (*53*); structures X and XI are two structural modifications (*422*), whereas crystals of $Cu(en)(CNS)_2$ contain copper(II) in two different environments (*314*). The compound $Cu_2(NH_3)_3(NCS)_3$ has a polymeric structure with sheets of copper(I) tetrahedra cross-linked by pairs of copper(II) octahedra. Each copper(II) has an approximately square-planar array of four nitrogen atoms ($3NH_3$ and —NCS) with two sulfur atoms completing a distorted octahedron in the trans positions. One of these sulfur atoms is also coordinated directly to copper(I), whereas the other allows the existence of a conventional Cu(II)—SCN—Cu(I) bridge. The tetrahedron surrounding copper(I) consists of two N- and two S-bonded thiocyanate groups (*312*).

With large cations, $[Cu(NCS)_4]^{2-}$ exists as a discrete but distorted tetrahedral entity; with smaller cations, it adopts a six-coordinate tetragonal environment (*293*, *294*, *647*, *663*).

TABLE

STRUCTURAL DATA OF SOME

Complex	C—N (Å)	C—S (Å)	∠NCS	Cu—NCS (Å)
I. $Cu(NH_3)_4(SCN)_2$	1.17	1.64	—	—
II. $Cuen_2(SCN)_2$	1.16(3)	1.62(2)	176.9°	—
III. $[Cu(N\text{-meen})_2NCS]NCS$	1.132(18)	1.620(13)	178.5(13)°	2.238(14)
	1.193(20)[c]	1.598(15)[c]	178.3(14)°	—
IV. $Cu(N,N'\text{-dimeen})_2(NCS)_2$	1.164(10)	1.636(8)	176.8(7)°	2.517(7)
V. [Cu(aebg)NCS]NCS[a]	1.16	1.62	178.2°	1.99
VI. [Cu(trien) SCN]NCS	1.164(10)	1.646(8)	178.0(6)°	—
VII. [α-CuL(NCS)]NCS[b]	1.56(18)	1.613(13)	179.2(13)°	2.119(12)
VIII. [γ-CuL(NCS)]NCS[b]	1.111(17)	1.616(13)	179.0(13)°	2.162(14)
IX. [Cu(tren)(NCS)]NCS	1.142(7)	1.612(7)	177.4(5)°	1.959(5)
	1.168(7)[c]	1.624(5)[c]	178.6(5)°[c]	—
X. α-$Cu(NH_3)_2(NCS)_2$	1.20(4)	1.62(3)	178 (11.4)°	1.96(3)
	1.21(4)	1.64(3)	162 (7.9)°	1.91(3)
XI. β-$Cu(NH_3)_2(NCS)_2$	1.20(9)	1.63(9)	159 (7.0)°	1.96(7)
	1.37(9)	1.67(7)	160 (11.8)°	1.83(7)
XII. $Cu(en)(NCS)_2$	1.25(4)	1.68(3)	172.3(1.9)°	2.01(2)
	1.24(4)	1.71(3)	165.0(4.0)°	1.99(2)
	1.29(3)	1.69(2)	161.2(4.0)°	2.01(3)
	1.32(5)	1.65(4)	154.7(4.9)°	2.05(2)
XIII. $Cu(py)_2(NCS)_2$	—	—	—	2.10
XIV. $CuHg(SCN)_4$	1.11	1.66	—	—
XV. $Cu(en)_2Hg(SCN)_4$	1.33	1.57	163°	2.58
XVI. $Cu_2(NH_3)_3(NCS)_3$	1.181(35)	1.638(28)	179.3(2.5)°	1.987(23)[e]
	1.128(35)	1.710(27)	175.1(2.5)°	1.996(24)[d]
	1.127(38)	1.671(29)	176.5(2.7)°	2.006(8)[d]
XVII. $[Cu(PPh_2Me)_2(NCS)]_2$	1.14(2)	1.64(2)	177.2°	2.02(2)
XVIII. $Cu(pic)_2 \cdot KSCN$	1.153[c]	1.628[c]	—	—

[a] aebg = 1-(2-aminoethyl)biguanide.

[b] L = 1,7-bis-(2-pyridyl)-2,6-diazaheptane.

[c] Free thiocyanate ion.

[d] See comments column.

[e] See comments column.

Copper Thiocyanate Complexes

Cu—SCN (Å)	∠ Cu—NCS	∠ Cu—SCN	Comments	References
>3.0	—	90°	Trans-octahedral CuN_4S_2	(*609*)
3.27(1)	—	79.9°	CuN_4S_2. Amino-N at corners of rectangle; *trans*-S completing distorted octahedron.	(*128*)
3.348(4)	178.2(12)°	114.2(5)°	Amino-N at corners of square with bridging NCS completing octahedral CuN_4NS.	(*589*)
—	—	—		
—	128.6(6)°	—	Amino-N at corners of square with *N*-thiocyanates completing distorted octahedral CuN_4N_2	(*467*)
—	158.1°	—	Three amino-N and *N*-thiocyanato group square with two long Cu—NCS distances (3.37 and 2.95 Å) formally completing distorted octahedron.	(*31*)
2.607(2)	—	89.5°	Trien forms an approximately square-based plane around Cu with —SCN at apex completing five coordination.	(*517*)
—	156.6(11)°	—	Approximately trigonal bipyramidal CuN_5.	(*52, 53*)
—	159.8(11)°	—	Approximately trigonal bipyramidal CuN_5.	(*52, 53*)
—	163.3°	—	Approximately trigonal bipyramidal CuN_5, with —NCS in axial position.	(*400, 401*)
—	—	—		
3.11(4) 2.93(4)	174 (5.5)°	85 (0.2)°	Four nitrogens ($2NH_3$ and 2-NCS) form a plane around Cu with S from one NCS bridging two coppers; the other NCS is monodentate. The structures differ in the degree of linearity of NCS.	(*422*)
—	169 (9.5)°	—		
3.05(6) 2.99(6)	168 (7.2)°	84.5(0.3)°		
—	165 (11.8)°	—		
3.01(2) 3.10(2)	175.0(6.0)°	85.9(3.0)° 92.0(3.0)°	As in VII and VIII, Cu has 4N in plane, and two bridging S both of which arise from one molecule which alternates throughout the unit cell with a molecule containing only terminal —NCS.	(*314*)
2.99(2) 3.10(2)	169.0(3.6)°	86.0(1.5)° 97.4(1.5)°		
—	165.4(4.7)°	—		
—	149.8(3.2)°	—		
3.0	—	—	NCS bridging.	(*610*)
—	172–180°	—	NCS bridging resulting in octahedral CuN_4S_2.	(*609*)
—	—	—	NCS bridging resulting in trans-octahedral CuN_4N_2.	(*673*)
3.286(9)[e]	172.3(2.2)°[e]	85.2°[e]	A compound containing Cu(I) and Cu(II) (designated *d* and *e*, respectively) with three different bridging NCS (see text).	(*312*)
2.946(7)[e] 2.470(7)[d]	161.0(2.3)°[d]	88.7(0.9)°[e] 98.3(0.9)°[d]		
2.376(8)[d]	168.2(2.4)°[d]	96.3°[d]		
2.46(1)	158.0(2)°	99.1(6)°	Bridging NCS with each copper in a distorted tetrahedral configuration CuP_2NS.	(*315*)
—	—	—	1:1 adduct.	(*705*)

The X-ray structure of $Cu(en)_2(SCN)_2$ shows long Cu—S bonds of 3.27 Å (*127*) (see Table XXXIV), the infrared results indicate ionic or weakly S-bonded thiocyanates (*69, 277*), and electronic spectral measurements suggest a square structure for the solid that is solvated in solution (*69*). Similarly, infrared studies suggested Cu(*N,N'*-dimeen)$(SCN)_3$ (*277*), whereas X-ray studies showed the compound to be an *N*-thiocyanate (*467*). Thus, it is sometimes difficult to decide from spectral evidence whether or not the thiocyanate group is even bonded to copper(II), let alone the nature of that bond. Similarly, in $Cu(py)_2(NCS)_2$ the existence of the thiocyanate bridge (*610*) is not readily detected by spectroscopic measurements (*201*). In $Cu(NH_3)_2(NCS)_2$ (*422*) and $Cu(en)(NCS)_2$ (*314*) both bridging and N-bonded terminal thiocyanates occur. These conclusions and the effects of changing the sterochemistry make copper(II) thiocyanate complexes particularly difficult to review accurately. For example, in Table XXXV which collates known copper(II) thiocyanate complexes, although some of the compounds reported in Table XXXIV are formulated as $CuL_4(SCN)_2$, the Cu—SCN bond may be very weak and the compounds may be essentially square planar. A similar situation arises in the bridging compounds of the type $CuL_2(NCS)$, where a strong Cu—NCS bond may predominate and the bridge may be so weak as to be scarcely detectable or where more than one type of thiocyanate coordination may occur.

Notwithstanding the foregoing, a number of interesting changes can be detected in the thiocyanate coordination with different amines, especially with the polyamines. Thus, $Cupn_2(SCN)_2$ is a six-coordinate CuN_4S_2 solid which forms a 1:1 electrolyte in solution, and the presence of a weakly coordinating group, such as the solvent molecule or ClO_4^-, causes isomerization (*72*). Further, when L = tren in $[CuL(CNS)]^+$, an *N*-thiocyanato complex ion occurs, but for L = trien, S-bonding is present which is reversed by methyl substitution in L = $trienMe_6$ (*72*). The compound $Cuen_2(NCS)(ClO_4)$ contains a square planar $Cu(en)_2$ moiety with the nitrogen atom from NCS^- in the tetragonal positions (Cu—N = 2.73 Å), but not formally coordinated (*169*). It has been suggested that the presence of the perchlorate ion favors M—NCS for some stereochemistries in polyamine–copper(II) complexes (*226*). The heats of formation of some of these thiocyanate complexes have been measured (*71*).

The complexity of thiocyanate behavior toward copper(II) has also been exploited by McWhinnie with complexes of tri-2-pyridylamine (*472, 473, 509*). The results are shown in Fig. 5.

The differences in the powder photographs between the copper(II) and cobalt(II) salts of the reineckate anion have been attributed to the

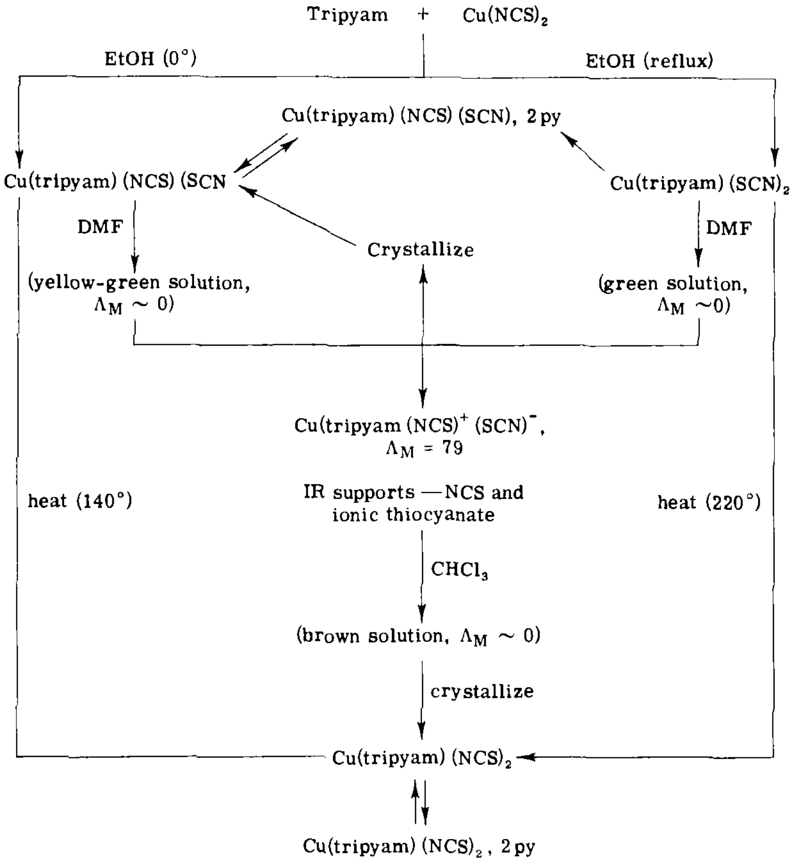
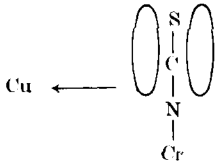


FIG. 5. The Cu(tripyam)(CNS)$_2$ system. [From Kulasingam (*473*).]

formation of a conventional Cr—NCS—Co bridge in the latter case, and in the former to the more compact arrangement involving donation of π electrons from NCS to copper(II) (*583*). Thus,



Bridging thiocyanate has been confirmed by X-ray studies in the case of $Cu(NH_3)_2Ag(SCN)_3$ which contains a trigonal-bipyramidal CuN_5 with axial NH_3 (*371*).

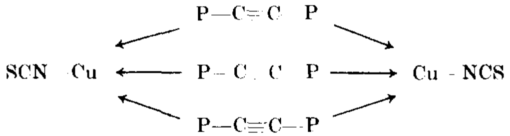
The X-ray structure of $[Cu(PPh_2Me)_2NCS]_2$, which can be prepared

TABLE XXXV

SOME COPPER(II) THIOCYANATE COMPLEXES

Complex	Composition	References
Coordination number = 6		
Monodentate thiocyanate		
$Cu(NH_3)_4(SCN)_2$		(*609*)
$Cu(en)_2(SCN)_2$		(*69, 127, 277*)
$Cu(pn)_2(SCN)_2$		(*72, 277*)
$CuL_2(SCN)_2$	L = *N,N*-dimeen, *N,N'*-dieten	(*277*)
$Cu(MeBen)(SCN)_2$		(*593*)
$Cu(py)_4(NCS)_2$		(*201*)
$Cu(phen)_2(NCS)_2$		(*658*)
$Cu(bipy)_2(NCS)_2$		(*726*)
Bridging thiocyanate		
$Cu(py)_2(NCS)_2$		(*201, 502, 610, 726*)
$CuL_2(NCS)_2$	L = 2-pic, 4-pic	(*726*)
$CuL_2(NCS)_2$	L = 2,4-lut, 2,6-lut, 3,4-lut, 3,5-lut	(*537*)
$CuL_2(NCS)_2$	L = an, benzidine, *o,o'*-diaminobiphenyl	(*502*)
$CuL(NCS)_2$	L = benzidine, *m,m'*-diaminobiphenyl-2,7-diaminofluorene	(*502*)
$CuL(NCS)_2$	L = piperazine, pyrazine	(*726*)
$CuL(NCS)_2$	L = bipy, phen, 5-NO_2-phen	(*266*)
$CuL(NCS)_2$	L = en, pn, 2Me-pn, *N,N*-dimeen, *N,N'*-dimeen, *N,N'*-dieten	(*277*)
$Cu(en)(NCS)_2$		(*314*)
$Cu(NH_3)_2(NCS)_2$		(*422*)
$CuHg(SCN)_4$		(*609*)
$[Cu(dpt)(NCS)(ClO_4)]$	dpt = 3,3'-diaminodipropylamine	(*72*)
Coordination number = 5		
$[Cu(tren)NCS]NCS$		(*69, 196, 630*)
$[Cu(trien)SCN]X$	X = NCS, ClO_4	(*69, 72*)
$[Cu(tpt)NCS]NCS$	tpt = 3,3',3''-triaminotripropylamine	(*69*)
$[Cu(pn)_2NCS]ClO_4$		(*72*)
$[Cu(trienMe_2)NCS]X$	X = NCS, ClO_4	(*72*)
$[Cu(dpt)(NCS)_2]$	dpt = 3,3'-diaminodipropylamine	(*72*)
$[CuLNCS]NCS$	L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine	(*337*)
Coordination number = 4		
$[CuEt_4dienNCS]BPh_4$		(*159*)

by the reaction of CS_2 with the corresponding azide (*794*), has been described (*315*) (see Table XXXIV), and contains two bridging NCS groups. When Cu(CNS) is dissolved in molten $(n\text{-}C_2H_9)_4N \cdot NCS$, it is postulated that the species $[Cu_2(CNS)_6]^{4-}$ is formed with two bridging thiocyanates and two terminal *S*-thiocyanates on each copper (*468*). Thus, in compounds in which copper(I) has an apparent coordination number of two or three, bridging thiocyanates seem very likely due to the ability of the metal to achieve readily four coordination. Terminal *N*-thiocyanates have been reported for $[Cu(NCS)]_2(DPPA)_3$ (*180*):



(two phenyl groups are omitted from each P for clarity)

In view of both the preceding and that bridging has been suggested in Cu(py)(SCN) (*502*), the compounds designated CuL(SCN) (L = py, 2-pic, 4-pic, 3,5-lut, quin), $(CuSCN)_4L_3$ (L = piperidine, pyrazine), $(CuSCN)_2L$ (L = piperazine), and $(CuSCN)_6bipy_5$ (*726*) need reexamining—they probably contain bridging groups in most cases as is found in $Cu_3[Cr(NCS)_6]$ (*779*).

Black copper(II) thiocyanate turns red-brown on heating, and it is postulated that the product is derived from copper(I) thiocyanate distorted by the inclusion of thiocyanogen in the lattice (*395*). A zigzag chain structure analogous to AgSCN (*492*) has been suggested for CuNCS on the basis of their similar infrared spectra (*502*).

The kinetics of the thermal decomposition of $Cupy_4(NCS)_2$ have been studied (*425*), as have the thermodynamics of the reaction of NCS with various polyamine complexes of copper(III) leading to the formation of bonds (*70*).

c. Selenocyanates. The reducing power of the selenocyanate ion has precluded all attempts to prepare anionic selenocyanate complexes of copper(II) (*295*), although some mixed-ligand complexes are known. Preliminary X-ray investigation suggests that $Cu(en)_2(SeCN)_2$ is probably isostructural with $Cu(en)_2(SCN)_2$ (*497*) so that all the problems associated with determining whether or not SCN was coordinated, described in the previous section, apply here also, and in particular to the compounds $CuL_2(SeCN)_2$ (L = en, pn, *N*,*N*′-dimeen, *N*,*N*′-dieten) which contain either ionic or Se-bonded selenocyanate (*217*). The compound $Cu(NH_3)_4(CNSe)_2$ and its monohydrate have been reported without structural data (*688*). Five-coordinate [CuLNCSe]NCSe [L = 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine] (*658*) and square planar

$[Cu(Et_4dien)NCSe]BPh_4$ (*159*) have been characterized. Bridging selenocyanate occurs in $[CuMeben_2(NCSe)]NO_3$ (*593*) and in the copper(II) salt of $[Hg(SeCN)_4]^{2-}$ (*714*).

2. *Silver*

a. Cyanates. The compound AgNCO contains infinite chains of —Ag—N—Ag—N—Ag zigzagging through the lattice with the angles N—Ag—N and Ag—N—Ag at 180° and 97.7°, respectively (*125*). The compound $Bu_4N[Ag(NCO)_2]$ contains discrete approximately linear $[Ag(NCO)_2]^-$ (*1*), and comparative distances for the two structures are given in Table XXXVI. The $[Ag(NCO)_2]^-$ ion had been previously characterized by infrared (*45*, *577*) and ^{14}N NMR spectroscopy (*192*). The AgNCO forms a high-temperature modification at 120°C before decomposing at 335°C to give CO, N_2, CO_2, $(CN)_2$ and NC·NCO [the last is conveniently prepared by this method (*338*)].

b. Thiocyanates. X-Ray measurements show the structure of AgNCS to consist of endless zigzag chains of —Ag—NCS—Ag—NCS—Ag—

TABLE XXXVI

COMPARATIVE STRUCTURAL DATA FOR AgNCO AND AgNCS AND THEIR ANIONIC COMPLEXES

	AgNCO (*125*)	$[Ag(NCO)_2]^-$ (*1*)	
Distances			
Ag—N	2.115(8) Å	2.068(12) Å	2.015(13) Å
N—C	1.195(11) Å	1.111(18) Å	1.076(19) Å
C—O	1.180(11) Å	1.129(18) Å	1.200(17) Å
Angles			
N—Ag—N	—	177.2(5)°	
Ag—N—C	128.2°	170.0(13)°	172.1(12)°
N—C—O	178.2°	178.2(16)°	179.8(17)°
Ag—N—Ag	97.7°	—	—
	AgNCS (*493*)	$(AgSCN)(SCN)^-$ (*494*)	
Distances			
Ag—N	2.223(28) Å	—	—
N—C	1.186(68) Å	1.241(197) Å[a]	1.095(107) Å
C—S	1.636(29) Å	1.599(110) Å[a]	1.707(86) Å
Ag—S	2.428(11) Å	2.474(20) Å[a] 2.630(27) Å	2.654(19) Å 2.742(29) Å
Angles			
N—Ag—S	164.50°	—	—
Ag—N—C	180°	—	—
N—C—S	180°	180°[a]	180°
Ag—S—C	103.79°	110°[a]	—

[a] In molecular AgSCN.

with the sulfur atoms coordinating also to silver in neighboring chains (*492*). However, $NH_4[Ag(SCN)_2]$ has discrete molecules of AgSCN in a lattice containing NH_4^+ and SCN^- ions: each silver is surrounded by a distorted tetrahedron of sulfur (*493*). Zigzag —Ag—SCN—Ag—SCN—Ag— chains with cross-linking by sulfur also occur in n-$Pr_3PAgSCN$ (*591*, *744*), $AgL_2(SCN)$ (L = thiosemicarbazide) (*171*), and $Agtu_2SCN$ (*748*). Under these circumstances the formulation of the compounds as *S*-thiocyanates is a formalism, as is reflected by the "normal" Ag—N and "long" Ag—S distances of 2.24(3) and 2.99(1) Å (shorter of two) relative to those in AgSCN (see Table XXXVI).

Compounds AgL(CNS) [= PMe_3, $P(n\text{-}Bu)_3$, PEt_2Ph], $AgL_2(CNS)$ (L = PPh_3, $AsPh_3$, $SbPh_3$), and $Ag(PPh_2Et)_3(CNS)$ have been reported. The 1:1 complexes are assumed to have double-chain structures, the 1:2 complexes probably have dimeric structures similar to that found for $Ag(PPh_3)_2(CNS)$ (*391*), and the 1:3 compound appears to be monomeric and contain an *N*-thiocyanate group (*221*).

Conductance studies in molten $(n\text{-}C_5H_{11})_4N{\cdot}NCS$ indicate the formation of $[Ag(SCN)_2]^-$ (*430*), but in propylene carbonate there is evidence for $[Ag(CNS)_3]^{2-}$ in addition to the former anion and AgSCN (*213*). The compound $Cu(NH_3)_2Ag(SCN)_3$ has $Ag(SCN)_3$ units but the nitrogen atoms are also coordinated to the copper(II) (*371*). The $[Ag(SCN)_2]^-$ anion has been reported with a number of different cations (*514*).

The infrared and Raman spectra of AgSCN and $[Ag(SCN_2]^-$ have been studied and suggest that the latter should indeed be formulated $(AgSCN)(NCS)^-$ in agreement with X-ray data—there were no spectroscopically detectable units having strong bonds between SCN groups and silver ions (*452*).

The complexes AgL(CNS) (L = 2-pic, 4-pic) have also been reported (*594*).

3. *Gold*

a. Cyanates. The compounds $Ph_4As[Au(NCO)_2]$ and $Ph_3PAuNCO$ have each been prepared by the action of CO on the corresponding azide (*87*); also $Ph_3AsAuNCO$ and $diphos(AuNCO)_2$ have been reported (*150*). Oxidation of these compounds with Br_2 gives $LAuBr_2NCO$ (L = Ph_3P, Ph_3As) and $diphosAu_2Br_4(NCO)_2$ (*150*). The compound $(Me_2AuNCO)_2$ has Au—N—Au bridges that are cleaved with L = Ph_3P or Ph_3As to give *cis*-$Me_2AuNCO.L$ (*706*).

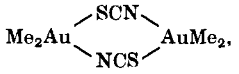
b. *Thiocyanates*. A preliminary report (*507*) has appeared of the X-ray structure of the gold cluster compound $Au_{11}(PPh_3)_7(SCN)_3$.

Although only the heavy atoms (Au, P, and S) have been located, the compound has a central gold atom surrounded by ten remaining gold atoms, each of which has one ligand attached to it; three of these ligands are, thus, *S*-thiocyanato groups. Some isomorphous compounds with other phosphines have been reported (*175*).

The square planar anion $[Au(SCN)_4]^-$ has been characterized by infrared (*428*, *639*, *663*) and electronic (*663*) spectral measurements. In addition to the normal routes to it, the anion is formed by an apparently two-stage reaction, in which the amine is also displaced, between $[Au(Et_4dien—H)X]^+$ (X = Cl, Br) and NCS^- (*780*). The $AuBr_4^-$ anion is reduced by NCS^- to an unspecified gold(I) compound (*428*). The anion $[Au(CNS)_2]^-$ has been identified in solution and the effect of temperature on its stability has been studied (*245*), but the parent compound has not been characterized structurally.

Mixed-ligand gold(I) thiocyanates have been reported. The compounds AuL(SCN) [L = PPh_3, $P(p\text{-}MeC_6H_4)_3$, $\frac{1}{2}$diphos, $PEtPh_2$, $P(p\text{-}ClC_6H_4)_3$], $AuL_2(SCN)$ (L = PPh_3, $PEtPh_2$), $Au[P(p\text{-}MeC_6H_4)_3]_3$-SCN and $Audiphos_2SCN$ have been prepared and their infrared spectra studied (*174*). This work has been confirmed for AuL(SCN) (L = PPh_3, diphos) and extended with the compound $AuAsPh_3(SCN)$ (*150*). The compounds $(CNS)Au \leftarrow PPh_2 \cdot C⋮C \cdot PPh_2 \rightarrow Au(CNS)$ and $(AuCNS)_2$-$(DPPA)_3$ have been described, and the authors suggest S-bonding in the former and N-bonding in the latter, which is believed to have a structure similar to the analogous copper(I) compound (see Section IV, J, 1, b), without being able to obtain confirmatory evidence in either case (*180*).

Oxidation of the appropriate gold(I) compounds with Br_2 or $(SCN)_2$ yields $Au_2diphosBr_4(SCN)_2$ and $Au(PPh_3)Cl(SCN)_2$ (*150*). The thiocyanate-bridge compounds,

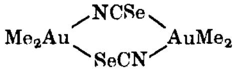


$$Me_2Au\begin{array}{c}\nearrow SCN \searrow \\ \searrow NCS \nearrow\end{array}AuMe_2,$$

have been reported (*674*), and the bridge may be cleaved by various ligands to give *cis*-$Me_2AuL(SCN)$ (L = py, PPh_3, $AsPh_3$) (*707*).

The report (*556*) of the linkage isomers for $[Au(CN)_2(CNS)_2]^-$ has been shown to be erroneous, and $(Me_4N)[$*trans*-$Au(CN)_2(SCN)_2]$ has been characterized (*527*).

c. Selenocyanates. It has been possible to characterize $[Au(SeCN)_4]^-$ by infrared (*665*) and electronic (*663*) spectroscopy. The gold(I) compounds, AuL(SeCN) (L = PPh_3, $\frac{1}{2}$diphos), have been reported, but



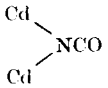
$$Me_2Au\begin{array}{c}\nearrow NCSe \searrow \\ \searrow SeCN \nearrow\end{array}AuMe_2$$

oxidation with Br_2 gives $AuLBr_3$ (*150*). The bridged gold(III) compound is stable and, although the bridge is cleaved quantitatively by Ph_3P in solution, no pure product was isolated (*706*).

K. ZINC, CADMIUM, AND MERCURY

1. *Cyanates*

Tetrahedral $[Zn(NCO)_4]^{2-}$ and $[Cd(NCO)_4]^{2-}$ have been reported as their Me_4N^+ salts by preparation in nonaqueous media (*292*, *296*); force constants have been determined for the former and compared with the corresponding thio- and selenocyanate complexes (*301*). Even in the presence of excess of KNCO (*158*), $K[Cd(NCO)_3]$ precipitates from water and has been shown to contain



bridges (*743*). A similar type of bridging occurs in the dimeric mixed-ligand complexes, $ZnL_2(NCO)_2$ (L = 3-CNpy, 4-CNpy) (*557*) but $Zn(py)_2(NCO)_2$ and $Zn(HMPA)_2(NCO)_2$ are monomeric tetrahedral molecules with monodentate N-bonded cyanate groups (*665*). Octahedral $ZnL_4(NCO)_2$ occurs with L = 3-CNpy, 4-CNpy (*557*), $\frac{1}{2}$bipy, $\frac{1}{2}$phen (*335*). $Cd(bipy)(NCO)_2$ gas been reported (*335*). The ^1H NMR and infrared spectra indicate a donor-acceptor interaction between Me_4NNCO and $CdMe_2$ in solution (*635*). The compound $K_2[Hg(OCN_4]$ has been claimed on the basis of infrared measurements (*742*), but this formulation is not supported by ^{14}N NMR data (*192*), which do not, however, definitely eliminate an equilibrium mixture of N and O forms.

2. *Thiocyanates*

X-Ray structures of [Zn(tren)NCS]NCS (*32*, *402*) and $Zn(N_2H_4)_2(NCS)_2$ (*283*) have been determined: the former contains the trigonal bipyramidal cation in an ionic lattice, and the latter is a trans-octahedral molecule. Preliminary results show $Zn(an)_2(NCS)_2$ to be tetrahedral (*678*). Only *N*-thiocyanato bonds are formed with zinc, whereas X-ray crystallography shows Cd—NCS—Cd bridges in $Cd(etu)_2(NCS)_2$ (*182*, *183*) and in bis(thiocyanato)-*N*,*N*-diethylnicotinamide cadmium(II) (*105*), whereas $K_2[Cd(SCN)_4]\cdot 2H_2O$ contains cadmium octahedrally coordinated by 4S and 2N (*796*). Similarly, $Hg(SCN)_2$ contains mercury with a trans-octahedral HgS_2N_4 coordination but here the Hg—N bonds are very long at 2.81 Å (*81*). Similar Hg—N bond lengths (2.80 Å) are found in

ClHgSCN and BrHgSCN, in which octahedral mercury is achieved with bridging halides and thiocyanate to give $Hg(SX)(X_2N_2)$ coordination (*797*). The compound $K_2[Hg(SCN)_4]$ contains a tetrahedral anion (*796*), and $Hg(phen)_2(SCN)_2$ has a cis-octahedral structure (*82*). The compound $Hg(AsPPh_3)(SCN)_2$ has an apparent coordination number of three, but two nitrogen atoms complete an elongated trigonal bipyramid (*510*).

The tetrahedral anions $[Zn(NCS)_4]^{2-}$ (*293*, *599*, *663*) and $[Hg(SCN)_4]^{2-}$ (*293*, *663*) have been characterized as their tetraalkyl ammonium salts and their bonding determined by infrared spectroscopy; force constant calculations have been carried out in the former (*301*). A Raman study of these ions and the corresponding cadmium complex in water confirms the preceding structural conclusions and indicates that $[Cd(NCS)_2(SCN)_2]^{2-}$ exists in solution (*720*). Similarly ^{14}N NMR measurements agree that $[Zn(NCS)_4]^{2-}$ exists, whereas the facts that the chemical shift for the cadmium complex was independent of concentration but showed a large solvent dependence indicated a lack of lability in addition to the existence of N and S isomers in kinetic equilibrium (*390*).

Although the infrared spectra show some evidence of distortion in the crystal lattice as the cation is changed, the mode of thiocyanate coordination remains the same in $[Zn(NCS)_4]^{2-}$ with Na^+, K^+, Cs^+, or NH_4^+ as cations (*446*) and with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} (some thiocyanate bridges are possible with Mg^{2+}) (*443*). The cadmium complex anion shows a greater dependence on the nature of the cation, since the stability of the Cd—NCS—Cd bridge decreases from the situation in $K_2[Cd(SCN)_4]\cdot 2H_2O$ to the corresponding cesium salt, which is anhydrous, and, if bridges occur, they are very weak (*741*). Bridging thiocyanates are detectable in $M[Cd(SCN)_4]$ (M = Mg, Ca, Sr, Ba), but the bridges are broken when the salts are dissolved in water (*443*). A number of compounds containing the $Hg(SCN)_4$ fragment are known and have been discussed under the appropriate transition metal throughout this review—details are not repeated here. Both $ZnHg(SCN)_4$ and $CdHg(SCN)_4$ have been reported and they also appear to have structures dominated by Hg—S bonds, although some distortion of the coordination polyhedron of mercury is observed (*741*). Preliminary X-ray studies on $CdHg(SCN)_4$ show that it belongs to the $I\bar{4}$ space group with $a = 11.48$ and $c = 4.33$ Å (*396*) [cf. $CoHg(SCN)_4$: $I\bar{4}$; $a = 11.11, c = 4.38$ Å (*259*)]. Also $ZnPb(CNS)_4$ has been reported (*259*).

In view of the readiness with which these metals increase their coordination number and with which thiocyanate bridging occurs, it is not surprising that $M_4[Zn(NCS)_6]$ (M = Na, K, Cs, NH_4) have been reported (*445*) as well as $M_4[Cd(SCN)_6]nH_2O$ (M = Na, K, Cs, NH_4, $\frac{1}{2}$Ba), although when M = Cs or largely Cs in mixed cation compounds, some *N*-thiocyanato bonding is also indicated (*448*). Further, both bridging and *N*-thiocyanato groups occur in $M[Zn(NCS)_3]n \cdot H_2O$ (M = Na, K, Cs, NH_4) (*441*, *442*), whereas in $M[Cd(SCN)_3] \cdot xH_2O$ (M = Na, K, Cs, NH_4, $\frac{1}{2}$Ba), *S*-thiocyanato bonding only is found for the cesium salt and in water, but the remainder as solids show bridging groups in addition (*444*).

Conductance studies have been interpreted to show the existence of $[Cd(CNS)_5]^{3-}$ in melts (*430*), whereas potentiometric and solubility measurements are explained by assuming the formation of $[Hg(CNS)_n]^{(2-n)}$ (n = 1–4) (*197*). The pH at which HgO is precipitated from $M[Hg(SCN)_3]$ varies from 7.71 (Na) to 9.98 (K) and 10.29 (NH_4): hydrogen bonding between NH_4 and NCS groups is assumed to weaken the Hg—S bond (*230*).

The compound $Hg_2(SCN)_2$ forms monoclinic crystals of space group *C*2/*c* (*258*). The Raman spectra of $Hg(SCN)_2$ as a solid and in diglyme have been measured and compared with that of MeHgSCN (*210*); $[MeHg(SCN)_2]^-$ has also been characterized (*632*).

The electric moments of $Znpy_2(NCS)_2$ (and of the corresponding HMPA complex) show it to be a tetrahedral *N*-thiocyanato complex (*655*). This result conflicts with conclusions drawn from infrared studies which assign the compound as $Znpy_2(SCN)_2$ with the possibility of some bridging (*42*). Compounds $ZnL_2(CNS)_2$ (L = 2-pic, 3-pic) are reported to contain bridging —NCS— groups, and $ZnL_2(NCS)_2$ (L = 4-pic, quin, isoquin) as formulated (*42*). These results must be treated with caution since they include the only reported *S*-thiocyanatozinc(II) complex, since they show a thiocyanate sensitivity to a similar group of ligands, the like of which has not been observed elsewhere, and since the infrared spectral data tabulated appear very similar throughout the series of compounds. Other workers confirm the formulation $ZnL_2(NCS)_2$ (L = py, 2-pic, 3-pic, 4-pic, 2Et-py, 3Et-py, 4Et-py, 2,4-dime-py) and find no evidence for any NCS bridging (*18*). Other mixed-ligand thiocyanate complexes are listed in Table XXXVII.

The ^1H NMR and infrared spectra indicate a donor–acceptor interaction between Me_4NNCS and $CdMe_2$ in solution (*635*). Thermogravimetric studies have been made on $ZnL_2(CNS)_2$ and $CdL_4(CNS)_2$ (L = piperidine) (*645*), and the thermal decomposition of $Zn(py)_4(NCS)_2$ has been studied (*94*, *425*). The stepwise stability constants of Zn^{2+}, Cd^{2+}, and Hg^{2+} with NCS^- have been determined (*17*).

TABLE XXXVII: SOME MIXED-LIGAND THIOCYANATE COMPLEXES OF ZINC, CADMIUM, AND MERCURY

Compound	Characteristics	References
Zinc		
$\mathrm{Zn(MeCS\cdot NH_2)_2(NCS)_2}$	Tetrahedral	(*553*)
$\mathrm{Zn(tu)_2(NCS)_2}$	Octahedral with bridging S (from tu)	(*552*)
$\mathrm{Zn(NIPA)_{3/2}(NCS)_2}$	NIPA = nonamethylimidodiphosphoramide; bridging NCS	(*243*)
$\mathrm{ZnL_2(NCS)_2}$	L = morpholine; octahedral with bridging NCS	(*19*)
Cadmium		
$\mathrm{Cd(MeCS\cdot NH_2)_2(NCS)_2}$	Tetrahedral	(*553*)
$\mathrm{CdL_4(NCS)_2}$	L = *N*-*n*-butyl imidazole; trans-octahedral	(*631*)
$\mathrm{K_4[Cd(SeCN)_4(SCN)_2]\cdot 0.5Me_2CO}$	Possibly a double salt; NCSe bridging	(*734*)
$\mathrm{K_2[Cd(SeCN)_2(SCN)_2]}$	Octahedral; NCSe bridging	(*734*)
$\mathrm{Cd[XC(NH_2)_2]_2(NCS)_2}$	X = S, Se; trans-octahedral; X-bridging	(*256, 552*)
$\mathrm{CdL(NCS)_2}$	L = py-NO, 2-pic-NO, 3-pic-NO, 4-pic-NO, 2,6-lut-NO; bridging NCS	(*20*)
$\mathrm{CdL_2(NCS)_2}$	L = 4-CN-py-NO; bridging NCS	(*20*)
$\mathrm{Cd(NIPA)(NCS)_2}$	NIPA = nonamethylimidodiphosphoramide; bridging NCS	(*243*)
$\mathrm{CdL_2(NCS)_2}$	L = morpholine; octahedral with bridging NCS	(*19*)
	L = py, 2-pic, 3-pic, 4-pic, 3Et-py, 4Et-py, an, 2Me-an, 3Me-an, 4Me-an, 3Cl-an; dimeric octahedral with bridging NCS	(*18*)
$\mathrm{CdL(NCS)_2}$	L = 2Et-py, 2,4-dimepy, 2,6-dimepy; polymeric with bridging NCS	(*18*)
Mercury		
Tetrahedral structures:		
$\mathrm{HgL(SCN)_2}$	L = phen, bipy	(*404*)
$\mathrm{Hg(Ph_3P)_2(SCN)_2}$		(*239, 405*)
$\mathrm{Hg(Ph_3As)_2(SCN)_2}$		(*239*)
$\mathrm{HgTmen(SCN)_2}$	Tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine	(*403*)
$\mathrm{HgL_2(SCN)_2}$	L = 3-CN-py, DMSO	(*403*)
$\mathrm{Hg(2\text{-}Etpy)_2(SCN)_2}$		(*18*)
With bridging and terminal —SCN:		
$\mathrm{[Hg(PPh_3)(SCN)_2]_2}$		(*239, 404*)
$\mathrm{[Hg(AsPh_3)(SCN)_2]_2}$		(*239*)
$\mathrm{HgL(SCN)_2}$	L = py, 2Me-py, 2,6-dime-py, 3Et-py	(*18*)
Unassigned:		
$\mathrm{Hg(phen)_2(CNS)_2}$		(*404*)

3. *Selenocyanates*

The tetrahedral anions $[Zn(NCSe)_4]^{2-}$ (*162*, *295*), $[Cd(SeCN)_4]^{2-}$ (*24*), and $[Hg(SeCN)^4]^{2-}$ (*22*) have been characterized as well as the octahedral $[Cd(SeCN)_6]^{4-}$ (*24*). The compound $K[Ce(SeCN)_3]$ has been formulated as a double salt (*24*) containing the $[Cd_2(SeCN)_6]^{2-}$ anion with two bridging selenocyanate groups (*162*). Selenocyanate bridges are common and occur in $Cd(SeCN)_2$ (*24*) and $Hg(SeCN)_2$ (*22*) and in the just mentioned possible double salt (*24*). The compounds $KSeCN.Hg(SeCN)_2$ (*734*), $M[Hg(SeCN)_3]$, and $M[Hg(SeCN)_4]$ (M = Cu, Pb) all contain bridging selenocyanate groups (*22*) which are also found in $M[Hg(SeCN)_4]$ [M = Zn, Co (*436*, *714*), Cd (*714*)]. The nature of the bridge is not always clear but if M—NCSe—M bridging occurs as expected, then cadmium and some of the other lighter elements are coordinated to nitrogen in some of these compounds. Preliminary X-ray data on $CdHg(SeCN)_4$ show electron density maxima at distances corresponding to both long and short Hg—Se distances (*737*).

A few mixed-ligand selenocyanate complexes have been reported for these metals. Tetrahedral $ZnL_2(SeCN)_2$ (L = py, 3-pic, quin, isoquin) and $Zn(4\text{-pic})_2(SeCN)_2$ with selenocyanate bridges have been reported (*42*) but are subject to the same reservations as the corresponding thiocyanates. The compounds $ZnL_2(NCSe)_2$ (L = bipy, phen, antipyrene) (*23*) and $Zn(Me_2SO)_4(NCSe)_2$ (*23*, *689*) are trans-octahedral, whereas $Zn(quin)_2(NCSe)_2$ is tetrahedral (*23*). The hexamethylenetetramine (L) complex, $ZnL_2(NCSe)_4$ $4H_2O$, has been reported (*735*).

The compound $Cd(py)_4(NCSe)_2$ appears to contain *N*-selenocyanato groups, but bridging occurs in $Cdpy_2(SeCN)_2$ (*24*), $Cd(Me_2SO)_2(SeCN)_2$ (*689*), and $K_2[Cd(SeCN)_2X_2]$ (X = Cl, Br, SCN) (734).

V. Factors Affecting the Mode of Chalcogenocyanate Coordination

The previous section has shown that chalcogenocyanate ions can coordinate using different donor atoms toward different metals and that a particular mode of coordination may be modified by a number of different circumstances. A variety of reasons have been offered to account for this behavior, and these explanations will now be examined. The thiocyanate group has been most widely studied and has furnished illustrations for many of the effects supposed to be important in determining the modes of coordination of these ions. Therefore, it will be discussed first followed by the selenocyanate group, which is similar in behavior in many respects; the cyanate group and how it differs from the first two groups will follow. Finally, the coordination behavior of all three groups will be compared.

It is appropriate first to make a few general comments on the nature of the interactions to be discussed and to emphasize that, unlike the problem of dual reactivity of ambidentate organic anions toward organic centers, recently reviewed by Shevelev (*679*), where kinetic factors predominate in importance over thermodynamic factors, in this case the reverse is true and thermodynamic factors are more important. Section IV listed the structures reported for the different complexes and indicated which of two linkage isomers, where they had been reported, was the thermodynamically more stable. Specific evidence that a given compound is thermodynamically stable and is not being prevented from isomerizing by a high activation energy is at best sparse and often lacking completely. However, in those cases where there is evidence for kinetic control [e.g., in the formation not only of $[Co(NH_3)_5NCS]^{2+}$ but also of $[Co(NH_3)_5SCN]^{2+}$ and their subsequent separation using an ion-exchange column (*134*)],* both linkage isomers have been detected and the relative thermodynamic instability of the latter demonstrated. Thus, available evidence indicates that any thermodynamically unstable isomers that are formed by kinetic control will isomerize either so rapidly as to be undetectable or at an appreciable rate at room temperature as is the case with those chromium(III)–SCN complexes that have been reported. This situation is entirely in accord with known features of coordination chemistry where kinetic control of products is generally less important than in organic chemistry where relatively fewer mechanistic pathways exist.

There is one property of the chalcogenocyanate complexes which may temporarily outweigh strictly kinetic or thermodynamic factors, namely, solubility. Precipitation of the less soluble of a pair of linkage isomers may give a false impression as to which is the stable compound. However, such is the wealth of compounds prepared, the majority of the structures may be regarded as the thermodynamically stable forms. This assumption is often supported by evidence concerning the relative stabilities of linkage isomers.

A. THIOCYANATES

1. *Homogeneous Anionic Thiocyanate Complexes*

The mode of thiocyanate coordination in known homogeneous anionic complexes is listed in Table XXXVIII. Although further

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* The significance of this example is that, whereas cobalt(III) forms several *S*-thiocyanato complexes in the presence of ligands capable of participating in back-bonding, this is an example where a conventional σ-bonding ligand, such as NH_3, coexists with the $Co—SCN^{2+}$ moiety.

compounds will no doubt be prepared, the pattern appears to be well-established. Class b metals form *S*-thiocyanato complexes, whereas *N*-thiocyanato complexes are formed by class a metals. The distinction in the behavior of different types of metal toward the thiocyanate group was observed originally by Lindqvist and Strandberg (*493*), and this behavior parallels the division of metals into class a and b acceptors.

Not all ambidentate ligands containing nitrogen and sulfur as donor atoms behave like the thiocyanate group, so that the particular distribution of electrons in the ligand is in part responsible for its varied coordination behavior (*576*). Lewis *et al.* (*489*) made the assumption that (*a*) the lone pairs on the sulfur atom in NCS^- are more easily polarized than those on the nitrogen atom; (*b*) the permanent lone-pair dipole on the nitrogen atom is larger than that on the sulfur atom; and (*c*) the mode of coordination of the thiocyanate group will be decided by the relative bond energies of a covalent M—S bond and of a more ionic M—N bond. They then computed the ratio $R = IP(ne/r)$, where IP is the ionization potential in volts, ne is the formal charge on the ion, and r is the radius in angströms, and obtained a number between 5 and 20. They assumed that higher values of R indicated covalent bonding and hence *S*-thiocyanato complexes, and they obtained numbers for which the values for class b metals were generally larger than those for class a metals. A similar line of argument was developed by Williams and Hale (*785*) and extended to provide the most detailed description so far available of the factors governing classes a and b metal behavior, although without any particular reference to the thiocyanate group. This work also emphasized that the principle of hard and soft acids and bases developed by Pearson (*596, 597*) contained language that tended to obscure the individual effects giving rise to the overall behavior. Nevertheless, in spite of the carefully argued strictures by Williams and Hale (*785*), a commonplace description of thiocyanate coordination is that soft acceptors form *S*-thiocyanato complexes whereas the nitrogen end coordinates to hard acceptors. More examples of this will occur shortly.

A number of mixed metal complexes containing bridging thiocyanate groups have been described in the previous section. In general, the sulfur atom coordinates to the class b or softer metal and the nitrogen end of the bridge bonds to the class a or harder metal.

2. *Mixed-Ligand Thiocyanate Complexes*

Much of the work on mixed-ligand complexes containing the thiocyanate group stems from the discovery by Turco and Pecile in 1961

TABL

HOMOGENEOUS ANION

Sc(NCS)$_6^{3-}$	Ti(NCS)$_6^{3-}$	VO(NCS)$_5^{3-}$ VO(NCS)$_4^{2-}$ V(NCS)$_6^{3-}$	Cr(NCS)$_6^{3-}$	Mn(NCS)$_4^{2-}$ Mn(NCS)$_6^{4-}$
Y(NCS)$_6^{3-}$	Zr(NCS)$_6^{2-}$	NbO(NCS)$_5^{2-}$ Nb(NCS)$_6^{-}$ Nb(NCS)$_6^{2-}$	Mo(NCS)$_6^{3-}$ Mo(NCS)$_6^{2-}$ Mo$_2$O$_4$(NCS)$_6^{4-}$	Tc(NCS)$_6^{2-}$
	Hf(NCS)$_6^{2-}$	Ta(NCS)$_6^{-}$	W(NCS)$_6^{-}$ W(NCS)$_6^{2-}$	Re(NCS)$_6^{-}$ Re(NCS)$_6^{2-}$ Re$_2$(NCS)$_8^{2-}$

	Pr(NCS)$_6^{3-}$	Nd(NCS)$_6^{3-}$		Sm(NCS)$_6^{3-}$	Eu(NCS)$_6$
Th(NCS)$_8^{4-}$	Pa(NCS)$_8^{4-}$	U(NCS)$_8^{4-}$	Np(NCS)$_8^{4-}$	Pu(NCS)$_8^{4-}$	

(*745*) that the mode of coordination toward palladium(II) or platinum(II) depends on the nature of the other ligands present. This observation was used by Basolo *et al.* (*79*, *143*) in the rational synthesis of Pd(bipy)(NCS)$_2$ and Pd(Ph$_3$As)$_2$(NCS)$_2$ and their linkage isomers. There are now many examples where a cooperative ligand effect acts to modify the mode of thiocyanate coordination. Table XXXIX summarizes the data contained in Section IV and indicates which of the thiocyanate atoms donates to the metals in their various oxidation states. Only terminal thiocyanates have been recorded, so that the complexes of copper(I), silver(I), and gold(I) have been largely ignored since the direct evidence is ambiguous and circumstantial evidence suggests that bridging thiocyanato groups are present in most of the complexes. The entries in Table XXXIX for these cases and for some others are based on very few actual compounds so that this table, unlike Table XXXVIII, may change considerably as further experimental data accumulate. In many cases where a metal bonds to either the nitrogen or the sulfur atom, depending on the ligational environment, linkage isomers have been prepared when factors favoring N coordination are about equally offset by those favoring S coordination. It is also anticipated that the number of these isomers will increase considerably.

3. *Nature of Cooperative Effects in Mixed-Ligand Thiocyanate Complexes*

Various explanations have been put forward to account for the effects of neutral ligands on the nature of the metal–thiocyanate bond: π-bonding, symbiosis, and antisymbiosis of hard and soft acids and bases as well as steric effects have all been discussed. In addition, directional

XXXVIII

THIOCYANATE COMPLEXES

$Fe(NCS)_6^{3-}$ $Fe(NCS)_4^{2-}$	$Co(NCS)_4^{2-}$	$Ni(NCS)_6^{4-}$ $Ni(NCS)_4^{2-}$	$Cu(NCS)_4^{2-}$	$Zn(NCS)_4^{2-}$ $Zn(NCS)_6^{4-}$
$Ru(NCS)_6^{3-}$	$Rh(SCN)_6^{3-}$	$Pd(SCN)_4^{2-}$	$(AgSCN)(SCN)^-$	$Cd(NCS)_2(SCN)_2^{2-}$ $Cd(NCS)_6^{4-}$
$Os(NCS)_6^{3-}$	$Ir(SCN)_6^{3-}$	$Pt(SCN)_6^{2-}$ $Pt(SCN)_4^{2-}$	$Au(SCN)_4^-$	$Hg(SCN)_4^{2-}$

$Gd(NCS)_6^{3-}$	$Tb(NCS)_6^{3-}$	$Dy(NCS)_6^{3-}$	$Ho(NCS)_6^{3-}$	$Er(NCS)_6^{3-}$	$Tm(NCS)_6^{3-}$	$Yb(NCS)_6^{3-}$

effects have been ascribed to the nature of the counterion in charged complexes and to the nature of the solvent in solution work. To some extent these effects overlap, but here an attempt will be made to discuss each effect separately.

a. Steric Effects. From the many structural details given in previous tables, it is apparent that the M—SCN bond angle is usually bent, and thus the *S*-thiocyanato group makes greater steric demands than the *N*-thiocyanato group which is usually linear. In some cases values as low as 160° have been recorded for M—NCS angles, but M—SCN angles in the region of 100° are relatively common. It is, of course, impossible to separate steric from electronic factors completely. Nevertheless, the formation of $Pd(SbPh_3)_2(SCN)_2$ in contrast to $Pd(PPh_3)_2(NCS)_2$ has been attributed to the larger antimony atom reducing the steric effects of the phenyl groups, whereas with the smaller phosphorus atom the phenyl groups are brought in and increase the overcrowding around the metal; this overcrowding is reduced by the thiocyanate group adopting a linear Pd—NCS bond (*78*). A clearer indication of such an effect is given by cations $[Pd(dien)(SCN)]^+$ and $[PdEt_4dien(NCS)]^+$ in which the introduction of four ethyl groups around the vacant coordination position causes the only example of the linear Pd—NCS grouping in a saturated amine complex of palladium(II) (*77*). Both kinetic and thermodynamic evidence support the steric effect in Et_4dien complexes (*379*). The formation of complexes containing both *N*- and *S*-thiocyanato groups in the same molecule in the presence of bidentate ligands containing two different donor atoms, such as $Pd[Ph_2P(CH_2)_3NMe_2](NCS)(SCN)$ (*198*, *199*), has been ascribed to electronic effects, although the

TABLE XXXIX

COORDINATION OF THE THIOCYANATE GROUP IN MIXED-LIGAND COMPLEXES[a]

Sc(III)–N	Ti(IV)–N Ti(III)–N	V(IV)–N V(III)–N V(II)–N	Cr(III)–N/S Cr(II)–N/S Cr(O)–N	Mn(II)–N Mn(I)–N/S	Fe(III)–N Fe(II)–N/S Fe(O)–N	Co(III)–N/S Co(II)–N	Ni(II)–N	Cu(II)–N/S Cu(I)–N	Zn(II)–N
Y(III)–N	Zr(IV)–N	Nb(V)–N Nb(IV)–N	Mo(VI)–N Mo(IV)–N Mo(III)–N Mo(II)–N/S Mo(O)–N	Tc(IV)–N	Ru(IV)–N Ru(III)–N/S Ru(II)–N Ru(I)–N	Rh(III)–N/S Rh(I)–N/S	Pd(II)–N/S	Ag(I)–S	Cd(II)–N/S
La(III)–N	Hf(IV)–N	Ta(V)–N	W(IV)–N/S W(II)–N/S W(O)–N	Re(V)–N Re(IV)–N Re(I)–N	Os(III)–N	Ir(III)–N/S Ir(I)–N	Pt(IV)–S Pt(II)–N/S	Au(III)–S	Hg(II)–S

[a] M–N implies *N*-thiocyanato coordination. M–S implies *S*-thiocyanato coordination. M–N/S implies ambidentate behavior of NCS^- to the metal in that oxidation state.

bending of the *S*-thiocyanato group trans to the amine, away from the adjacent PhP grouping, was thought to be a steric effect. The importance of these steric effects becomes apparent in the closely similar $Pd(Ph_2PCH_2CH_2PPh_2)(NCS)(SCN)$ where different types of thiocyanate coordination are observed trans to two equivalent phosphorus atoms and the nonlinear Pd—SCN is bent away from one of the neighboring Ph_2P groups (*102*). Carty *et al.* (*101*) refer to unpublished results by Meek *et al.* (*590a*) whose X-ray studies show that in $Pd(Ph_2PCH_2PPh_2)(SCN)_2$ the P—Pd—P angle is 73.24(*6*)°, whereas it is 85.1(*1*)° in $Pd(Ph_2PCH_2\cdot CH_2PPh_2)(NCS)(SCN)$ (*102*), and 89.31(*4*)° in $Pd(Ph_2CH_2CH_2CH_2PPh_2)(NCS_2)$. As the diphenylphosphine groups are allowed to occupy more space by the decreasing constraints of the increasing methylene chain, so the need for N-bonding becomes greater.

Interesting behavior is observed with $Pd(AsBu_3n)_2(SCN)_2$. As a solid it is S-bonded, on melting it partially isomerizes to give a mixed species, and on cooling it reverts to the S-bonded form (*640*). It is possible that steric effects increase on melting and that they account for the isomerization. Alternatively, lattice effects or packing considerations may tilt the balance in the solid toward S bonding, and, on removal of these constraints, the compound is free to adopt its preferred mixed structure.

Steric effects are possibly important in the formation of *cis*-$Co(DH)_2(H_2O)NCS$, whereas the corresponding trans-compound is S-bonded, but they cannot be separated from the electronic effects of destroying the H bonding which maintains the planar $Co(DH)_2$ moiety (*3*). Steric effects are, however, apparent in the series of compounds $MnL_2(CO)_3(CNS)$ (*280*). The compounds *mer*- $MnL_2(CO)_3(NCS)$ ($L = Ph_3P, Ph_3As, Ph_3Sb$) have been characterized as have *fac*-$MnL_2(CO)_3(SCN)$ ($L = Ph_3Sb$). It was not possible to isolate *fac*-bistriphenylphosphine, but *fac*-Mn diphos$(CO)_3(NCS)$ was isolated together with a number of other *N*-thiocyanato complexes. Although it is not known whether CO or L is trans to the thiocyanate in these complexes, models do show that the *fac*-arsine and stibine complexes are considerably sterically strained. Since this strain is on one side of the molecule only, it is reduced by the formation of a bent Mn—SCN bond, whereas a linear Mn—NCS would exacerbate an already crowded situation. Further, the absence of the *fac*-bis(triphenylphosphine) complex is also consistent with these conclusions since the smaller phosphorus atom brings the phenyl group even closer to the metal and prevents the two neutral ligands from occupying positions mutually cis to each other.

b. Electronic Effects. Turco and Pecile (*745*) originally pointed out the cooperative effects of ligands with reference to the compounds $Pd(NH_3)_2(SCN)_2$ and $Pd(PEt_3)_2(NCS)_2$. They explained these findings by assuming that the Pd—NH_3 interaction was σ in character and resulted in a small further increase of electron density on the metal, which enhanced the covalency of the Pd—SCN bond. On the other hand, backbonding occurred between the filled metal and the empty phosphorous d orbitals, and this strengthened the Pd—P bond while at the same time reducing the electron density on the metal. The metal was thus assumed to be converted to a state where it had more ionic character and, hence, preferred to form the more ionic Pd—NCS linkage. The discussion on steric effects in the preceding section suggests that these effects could provide as valid an explanation for the behavior of the two compounds just cited as does the π-bonding hypothesis. It has been observed (*194*) that the recent preparation of *cis*-$Pd(Ph_2PC{=}CPPh_2)(SCN)_2$ involves a phosphine with better π-acceptor properties than that in *cis*-$Pd(Ph_2PCH_2CH_2PPh_2)(NCS)(SCN)$ (*102*), which, in turn, is contrasted with $Pd(PPh_3)_2(NCS)_2$ (*640*). Ignoring the electronic arguments and using the steric arguments cited previously, it is apparent that the P—Pd—P angle will decrease in the series $(Ph_3P)_2Pd$, $(Ph_2PCH_2CH_2PPh_2)Pd$, $(Ph_2PCH{:}CHPPh_2)Pd$, so that Pd—SCN bonding will become progressively more easy. The recent characterization of *trans*-$Pd(Ph_2PC{:}CBu^t)_2(SCN)_2$ and the careful study of the phosphine–thiocyanate interactions indicates that the N-bonded form would experience very similar steric interactions, so that the formation of the *S*-thiocyanate suggests that the electronic effects of $Ph_2PC{:}CBu^t$ on Pd(II) are insufficient to affect the mode of thiocyanate coordination (*101*). Such a conclusion is in agreement with the results of Venanzi (*605*, 766), who has argued against the idea of appreciable double-bonding between platinum(II) and phosphine ligands.

Whatever the final conclusions concerning the reasons for many phosphine complexes of palladium(II) forming *N*-thiocyanates, there are a number of amine complexes where electronic effects are apparent and the most satisfactory explanation does involve the π-bonding hypothesis. The presence of electron-withdrawing substituents such as the nitro group in phenanthroline increases the ability of the ligand to form π bonds, and this would account for the compounds $Pd(phen)(SCN)_2$ and $Pd(5\text{-}NO_2phen)(NCS_2)$. The same explanation serves for Pd(4,7-diph-phen)$(NCS)_2$ at low temperatures, while its isomerism at higher temperatures has been attributed to the increased thermal motion of the phenyl rings decreasing the intraligand conjugation (*103*). Similarly, the introduction of electron-donating substituents should decrease the ability of the ligand to form π bonds with the metal, and thus favor *S*-thiocyanato compounds. This is observed with the complexes Pd(bipy)$(NCS)_2$ (*143*) and Pd(4,4′-dimebipy)(NCS)(SCN) *103*). The phenanthroline and bipyridyl series of compounds each provide some evidence for the π-bonding hypothesis, whereas the inability of 4-CNpy to form a complex other than $Pd(4\text{-}CNpy)_2(SCN)$ has been attributed to its probable trans structure. It is not clear however, why the two parent chelate compounds should have different structures. Bertini and Sabatini (*103*) suggested that the σ-donor properties, as measured by the pK_a values, of the ligands were different and that this difference explained the different compounds formed. They therefore used 5Cl-phen which has a similar pK_a to bipy, but the former formed an *S*-thiocyanato complex so that pK_a alone does not provide a sufficient answer.

Electronic and steric effects have been compared and used to explain the mixed thiocyanate coordination when chelates with two different donor atoms are used (*526*), but it is now apparent that steric effects could be largely or even solely responsible.

It has been assumed that $M(PPh_3)_2CO(NCS)$ (M = Rh, Ir) have a trans configuration, and that the N bonding is a consequence of the strong π-bonding effect of the *trans*-CO group (*155*). In the similar $Rh(PPh_3)_3NCS$ (*35*), steric arguments could be used to explain the mode of coordination but there is no obvious reason why $Rh(PPh_3)_2CO(NCS)$ (*155*) or $Rh(PPh_3)_2L(NCS)$ (L = py, an, pip) should have different steric requirements from $Rh(PPh_3)_2L(SCN)$ (L = C_6H_6, MeCN, Me_2CO, Et_2O) (*35*). It has been widely assumed but rarely established that these compounds have trans geometry. Unless the formation of cis compounds could somehow provide an explanation for the foregoing results, it seems that the rhodium(I) complexes taken together provide a clear example of a cooperative ligand effect that is electronic in origin, but which is not easily explained in terms of π bonding: $Rh(PPh_3)_2pip(NCS)$ does not have the same π-bonding opportunities as $Rh(PPh_3)_2CO(NCS)$ even if the thiocyanate coordination is the same.

In octahedral cobalt(III) complexes there is a very clear illustration of cooperative ligand effect as exemplified by the ions $[Co(NH_3)_5NCS]^{2+}$ (*134*) and $[Co(CN)_5SCN]^{3-}$ (*139*). Each of these has a linkage isomer but the preceding are the stable forms. In contrast to the previous discussion on class b metals, cobalt is class a and the ligands with strong π-bonding ability modify the expected N bonding to give the preceding *S*-thiocyanato complex. Table XXX illustrates the point most emphatically and, although $[Co(bipy)_2(SCN)_2]^+$ (*513*, *570*) and $[Co(phen)_2(SCN)_2]^+$ (*513*) probably have a cis configuration (*505*), in which case steric effects may in some way influence S coordination, such an explanation does not apply to $[Co(CN)_5SCN]^{3-}$ (*139*) nor to the *trans*-$Co(DH)_2L(SCN)$ series of compounds (*572*). Thus, in these cobalt(III) complexes, there is clear evidence that ligands, such as CN^- and DH^-, which might be expected to take part readily in π bonding with the metal are the very ligands that encourage the formation of Co—SCN bonds. The effect is there, but the consequences are directly in opposition to that suggested first by Turco and Pecile.

The thiocyanate carbonyl compounds of manganese listed in Table XXIV follow a similar pattern to the cobalt(III) complexes. S Bonding occurs in $Mn(CO)_5SCN$ and in some tetracarbonyl derivatives (providing the ligand other than CO or SCN can play some part, which a second thiocyanate group apparently cannot) but is only present in those tricarbonyl compounds with the lopsided steric effect described in the previous section. Farona and Wojcicki (*280*) who first reported most of these compounds preferred to put the emphasis on Mn—CO π bonding and suggested that in $Mn(CO)_5SCN$ such π bonding is weak as a result of being spread over five CO groups so that the metal prefers the more polarizable sulfur atom which can, in turn, increase the negative charge and thus enhance π bonding between CO and Mn. As the extent of the participation of the metal in π bonding with its carbonyl groups increases (i.e., in the tricarbonyl compounds) the CO groups make less demand on the metal for negative charge, and the preference of the latter changes from the sulfur to the nitrogen atom.

The foregoing explanation, in which the extent of M—CO π bonding controls the polarizing ability of the metal and thus the preference of the metal for N or S coordination, can also be applied to cobalt(III) compounds, where ligands other than CO modify the polarizing power of the metal. These arguments, however, do not apply to the square planar palladium(II) case, just as the π-bonding arguments that appeared valid there do not apply for the class a metals.

There still remains the question, which is unanswered by either the π-bonding hypothesis or by the concept of metal polarizing power, as to why cobalt(III) and manganese(I) experience a cooperative ligand effect, whereas there is no evidence as yet for such an effect with chromium in various oxidation states [any Cr(III)—SCN compounds are purely kinetic in origin and thermodynamically unstable with respect to Cr(III)—NCS] with iron(II) or iron(III), cobalt(II), or nickel(II), even though the stereochemistries of these last two elements may be drastically modified by ligational effects (see Tables XXIX and XXXI).

An alternative approach was initiated by Jörgensen (*420*), who drew attention to the fact that $[Co(NH_3)_5X]^{2+}$ is better bound for $X = F$ than I and, thus, showed class a characteristics, whereas $[Co(CN)_5X]^{3-}$ is most stable with $X = I$, not known for $X = F$, and shows class b characteristics. The formation of $[Co(CN)_5SCN]^{3-}$ and $[Co(NH_3)_5NCS]^{2+}$, in which the soft cyanide and S coordinate together, and the hard NH_3 and N do likewise, may be regarded as a further illustration of this effect of the ligands, which Jörgensen had termed *symbiosis* or a flocking together of like ligands. [It has been pointed out (*150*) that symbiosis, as applied to biological systems, refers to the living together of *dissimilar* organisms, in contrast to its use to describe the behavior of similar ligands in inorganic chemistry. However, it seems probable that Jörgensen's definition has been assimilated into the vocabulary of chemists, and this review follows that definition.]

Symbiosis can be used to account for the general coordination behavior of the thiocyanate group toward cobalt(III) and manganese(I) compounds described in the previous paragraphs. The compound *cis*-$Co(DH)_2H_2O(NCS)$ (*3*) is an apparent exception, but it can be argued, notwithstanding steric effects, that destroying the $Co(DH)_2$ plane lessens the symbiotic effect of the dimethylglyoximato anions relative to that in *trans*-$Co(DH)_2(H_2O)(SCN)$. Similarly, $[Rh(NH_3)_5NCS]^{2+}$ (*659*, *660*) is accountably the more stable isomer because of the hardening effect of the amine ligands. However, when palladium(II) complexes are considered, as has been seen for the previous explanations, the arguments predict the wrong effects: soft phosphine ligands encourage interaction with the hard nitrogen atom. Also, $Rh(PPh_3)_2CO(NCS)$ (*155*) and $Rh(PPh_3)_2(MeCN)(SCN)$ (*35*) are not explicable, and pK_a changes of the ligands in the phenanthroline and bipyridyl complexes (*103*) have the opposite effects to those expected if symbiosis were to apply.

Pearson (*598*) has introduced the further idea of *antisymbiosis* by applying the original concept of Chatt and Heaton (*189*), "that groups of high trans-effect, as ethylene in $Pt(C_2H_4)Cl_3^-$, render the position in mutual trans-position more susceptible to bonding by what are now known as hard bases," to his principle of hard and soft acids and bases. Pearson put the idea in the form: "two soft ligands in mutual trans positions will have a destabilising effect on each other when attached to class 'b' metal atoms." This extension, which, like the original concept of symbiosis, has a wider chemical application than that of explaining thiocyanate coordination, would thus predict that *cis*-palladium–phosphine complexes would contain *N*-thiocyanato groups, whereas the corresponding trans compounds would be S-bonded. With $Rh(PPh_3)_2L(CNS)$ the same arguments are valid if it is assumed that all the compounds have trans geometry, in which case, for the stronger trans-directing ligands CO or piperidine, an *N*-thiocyanate is formed, whereas, for the weaker ligands MeCN and Et_2O, no antisymbiotic effect occurs and $Rh(PPh_3)_2L(SCN)$ is formed. It is not clear how this phenomenological approach should be applied to the bipyridyl and phenanthroline complexes, but it breaks down for the manganese carbonyl compounds. All the compounds in Table XXIV are assumed to have CO trans to the thiocyanate group, yet a variety of N- and S-bonded complexes are formed, so that, if antisymbiosis were to apply, a special explanation would be needed to account for the effects of the remaining four planar ligands: these range from four carbonyls in $Mn(CO)_5SCN$ to two carbonyls and a diphosphine in *fac*-$Mn(CO)_3$-diphosNCS via *fac*-$Mn(CO)_3py_2NCS$. The planar ligands in the dimethylglyoximatocobalt(III) compounds remain constant, but the ligand trans to the thiocyanate group varies considerably. Compounds $Co(DH)_2L(SCN)$ ($L =$ —SCN, Ph_3P, H_2O, NH_3) are all unaffected by the nature of the solvent (*572*), whereas both linkage isomers have been isolated for L = py (*574*) and detected in certain solvents for L = Me (*253*), substituted pyridines and anilines, and for $L = NO_2$ (*572*). Such behavior is not consistent with antisymbiosis following approximately the same sequence as trans-directing ligands.

A further, semiquantitative approach has been made to the problem of providing a consistent explanation for the behavior of mixed-ligand thiocyanate complexes for both classes a and b metals (*567*). The distribution of electrons in the two most energetically available orbitals of the thiocyanate ion is unequal, being concentrated more on the nitrogen atom in σ_4 and on the sulfur atom in σ_3 (*249*). It was argued that both these orbitals would play an important part in any thiocyanate complex, and the hardness or softness of each donor atom in each orbital was calculated (*567*) according to the polyelectron perturbation treatment developed by Klopman (*454*). The treatment takes account of the varying dielectric constant of the solvent in which the reaction takes place, and the results are presented in Fig. 6 which shows how these hardness or softness parameters vary with $1-(1/\epsilon)$ (Klopman's equations contain the dielectric constant in this form and it is retained in order to give a convenient linear plot). Inspection of Fig. 6 reveals that the hardest center available is the nitrogen atom of σ_4, so that this is the most likely donor to the hardest Lewis acid, namely, a class a metal surrounded by hard ligands (e.g., $[Co(NH_3)_5NCS]^{2+}$). The softest center is also a nitrogen atom but this time of σ_3, and it will bond to the softest Lewis acid available which this time would be a class b metal surrounded by soft ligands [e.g., $Rh(PPh_3)_2CO$-(NCS) or Pd(II) surrounded by phosphine or arsine ligands]. Intermediate situations involving class a metals with soft ligands or class b metals with hard ligands would each prefer to coordinate with the sulfur atom, as has often been observed in the previous pages. The arguments can be extended to discuss solvent effects also, as will be described in the next section.

The advantage of this explanation of thiocyanate coordination is that it does allow a description that fits both classes a and b metal complexes, although there are some examples that do not fit. It is not clear why in $Rh(PPh_3)_2L(CNS)$ the *N* isomer should be obtained for L = pip, and the S isomer for L = MeCN (*35*). Manganese(I) has to be treated as a class a acid, the same approach as is used for it to fit with cobalt(III) in the discussion of π-bonding effects. Since neither of these metals exist as the hydrated species, they cannot be classified in the same way as the other metals, but only in their commonly ligated forms, such as $Mn(CO)_5^-$ or $[Co(NH_3)_5\text{-}]^{3+}$, where a different situation prevails. The treatment is not supported by recent, X-ray, electron spectroscopy measurements (*384*) on the $Pd(3d_{3/2})$ electrons of $Pd(AsPh_3)_2(NCS)_2$ and $Pd(AsPh_3)_2(SCN)_2$, with binding energies of 6.5 and 5.8 eV, respectively. These results imply that the electrons on the metal are less tightly held for $Pd(AsPh_3)_2(SCN)_2$, but care must be excercised in the use of such data, and the fact that the valence electrons $Pd(4d_{3/2})$ have identical binding energies in the two compounds may also be significant.

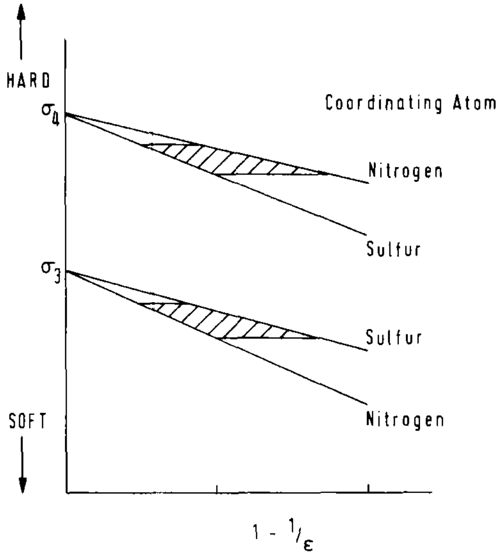


FIG. 6. Variation in softness character of donor centers on CNS$^-$ with dielectric constant.

The major disadvantage of this semiquantitative approach, of the π-bonding treatment of Turco and Pecile, and the qualitative soft and hard acids and bases treatment is that any π bonding between the thiocyanate group and the metal is neglected. Gutterman and Gray (*359*) have assigned the electronic absorption spectra of the series $[Co(CN)_5X]^{3-}$ (X = $—SCN^-$, NCS^-, $NCSe^-$, and N_3^-) in terms of a molecular orbital scheme for the complex anion. They obtain no evidence for the participation of thiocyanate π-acceptor orbitals in the metal–ligand bonding, but they do find that the highest filled orbital, the 2π, contributes significantly to the absorption spectrum. The distribution of electrons in this orbital is particularly sensitive to bond distances. There is an approximately equitable distribution in the free ion, but when the group is N-bonded the 2π electrons are concentrated more on the sulfur atom. From the position of —SCN at the low field end of the spectrochemical series, and from the preceding results, the authors conclude that —NCS behaves essentially as a σ donor, whereas the often bent M—SCN bond results from the overlap of these 2π electrons with an empty metal orbital, in addition to the normal σ overlap.

c. Solvent Effects. Burmeister *et al.* (*154*) originally observed that the nature of the solvent may modify the mode of thiocyanate coordination of certain complexes in solution. They studied the behavior of $Pd(AsPh_3)_2(NCS)_2$ and its linkage isomer in a number of different solvents, and concluded that Pd—SCN bonding was promoted by solvents with high dielectric constants, whereas solvents with low dielectric constants resulted in a mixture of Pd—NCS, Pd—SCN, and Pd—SCN—Pd bonding modes. An extension of the work (*155*) revealed that the compounds $M(PPh_3)_2CO(NCS)$ (M = Rh, Ir) were not susceptible to these solvent effects but that $PdL_2(NCS)_2$ (L = Ph_3P, Ph_3As, $\frac{1}{2}$bipy) isomerized to $PdL_2(SCN)_2$ completely in DMF, DMSO, py, Me_2CO, MeCN, $PhCH_2CN$, or adiponitrile ($NC(CH_2)_4CN$)—solvents that were referred to as group A. In group B solvents (C_6H_6, CCl_4, $CHCl_3$, CH_2Cl_2, cyclopentanone, cyclohexanone, $PhNO_2$, 2-butanone, 3-pentanone), the experimental behavior was rationalized in terms of equilibria involving the bridged species as follows:

$$2Pd(AsPh_3)_2(SCN)_2 \rightleftharpoons [Pd_2(AsPh_3)_2(SCN)_4] + 2Ph_3As \rightleftharpoons 2Pd(AsPh_3)_2(NCS)_2$$

The possible existence of the mixed compound $Pd(AsPh_3)_2(NCS)(SCN)$ was also considered, but could not be confirmed in solution. Similar behavior was observed for the analogous Ph_3Sb complex, but no bridged intermediate was observed for the Ph_3P complex. A third group of solvents (MeOH and EtOH) showed intermediate behavior for $Pd(AsPh_3)_2(SCN)_2$, and solubility difficulties prevented further studies of this system. The induction period before changes occurred, which was observed only for this group of solvents, was attributed to the necessity of breaking hydrogen bonds.

The authors drew attention to the fact that group A solvents had generally larger dielectric constants, dipole moments, and internal pressures than those in group B, although exceptions did occur: acetone and py belong to group A, whereas 2-butanone and $PhNO_2$ belong to group B. They then argued that the results were consistent with the conclusions of Klopman (*454*) that solvents with high dielectric constants tend to enhance frontier-controlled (largely covalent) reactions, whereas those with low dielectric constants favor charge-controlled (largely ionic) reactions. Thus, group A and B solvents should encourage Pd—SCN and Pd—NCS bonding, respectively, as is observed, and the implication of this interpretation is that a similar effect should be observed in other systems.

However, the behavior of $Co(DH)_2py(SCN)$ shows the opposite effect to that observed for the palladium complexes and the solvent dependence of this compound may be represented (*571*):

$$Co(DH)_2py(SCN) \underset{\text{low } \epsilon}{\overset{\text{high } \epsilon}{\rightleftharpoons}} Co(DH)_2py(NCS)$$

Burmeister and co-workers (*155*, *370*) challenged these results and suggested that they were due to kinetic rather than thermodynamic effects—the activation energy for the isomerization being lowered by high dielectric solvents. However, Marzilli *et al.* (*269*, *519*) studied the behavior of the compound $Co(DH)_2(t\text{-Bupy})(SCN)$ in solution, using the proton NMR spectrum of the *t*-butyl group as a probe. They found that an equilibrium to type reported did indeed exist, and that Burmeister's results and, hence, conclusions were invalidated by the presence of traces of cobalt(II) that catalyze the isomerization.

The observation (*571*) that class a metals apparently show a different solvent dependence of thiocyanate coordination to class b metals was discounted by Marzilli (*519*) on the grounds that cobalt(III) in these systems has become sufficiently soft for it to be regarded as similar to palladium(II). The problem of the relative hardness or softness of metals was discussed in the previous section of this review from which it is clear that the association of cobalt(III) with palladium(II) in these terms must be viewed with extreme caution.

Further experimental evidence for a solvent effect is limited. The compound $Mn(CO)_5SCN$ is stable as a solid, but forms the N-isomer in acetonitrile (*277*). This, the isomerization of $Pd(AsBu_3)_2(SCN)_2$ on melting (*640*) and the partial isomerization of $Pd(Ph_2AsCH_2CH_3AsPh_2)(SCN)_2$ in dichloromethane (*526*) all involve changes of state and are not comparable with the previous results where an equilibrium exists between the two forms in solution. The stability of $[Co(CN)_5SCN]^{3-}$ in water and the N-bonded isomer in CH_2Cl_2 (*368*, *369*) is, however, a further example of an equilibrium situation, but it is not yet clear whether arguments that apply for aprotic solvents may be used when hydrogen bonding is also present. It does seem reasonable that, if the factors modifying the coordination behavior of the thiocyanate group are in approximate balance and linkage isomerism is observed, then the fine balance of ligational effects may be perturbed by the nature of the solvent. Although too few compounds have been studied for a firmly based generalization, it begins to appear that, for linkage isomers in aprotic solvents, M—NCS bonding is favored for class a metals in solvents with high dielectric constants and for class b metals for solvents with low dielectric constants. In addition, M—SCN bonding is promoted under the opposite conditions (class a and b metals in the presence of solvents with low and high dielectric constants, respectively).

TABLE XL

SUMMARY OF COOPERATIVE LIGAND AND SOLVENT EFFECTS ON THIOCYANATE COORDINATION

Metal	σ-Donor ligand	Solvent		π-Acceptor ligand
		High ϵ	Low ϵ	
Class a	—NCS	—NCS	—SCN	—SCN
Class b	—SCN	—SCN	—NCS	—NCS

There is some parallel in the effects caused by ligands, where soft or π-bonding ligands favor M—NCS bonds for class b metals and M—SCN bonds for class a metals, and hard ligands have the opposite effect. The situation may be summarized tentatively using Table XL where the solvent effect is apparent only for intermediate ligand situations, and the use of the terms σ donor and π acceptor is in a descriptive sense rather than necessarily implying an understanding of the nature of the effect. It is also assumed that, under certain conditions, steric effects could override the solvent or even the ligand effects (see Section, V, A, 3, a).

Figure 6 may be used (*567*) to provide a self-consistent explanation for the behavior summarized in Table XL if it is assumed that the metal is unaffected by changes in the solvent, but that the hardness and softness of the electrons in σ_4 and σ_3 on nitrogen and sulfur do change. As the dielectric constant of the solvent increases, the class a metal, which had previously preferred to form an M—SCN bond, gradually changes its preference until an M—NCS bond is preferred (see areas with diagonal lines on Fig. 6). If, however, a class b metal is considered, then the opposite effect is observed in agreement with the observed experimental situation.

d. Counterion Effects. Solid [PtEt$_4$dien(SCN)]NCS isomerizes completely in 3 days, but under the same conditions there is no isomerization of [PdEt$_4$dien(SCN)]PF$_6$ (*78*). The steric effects that favor formation of the [PdEt$_4$dien(NCS)]$^+$ cation have been detailed in Section V, A, 3, so that the stability of the hexafluorophosphate salt just mentioned is of interest. This apparent reversal of stability is illustrated more strikingly by the solid state isomerization of [PdEt$_4$dien(NCS)]BPh$_4$ to give [PdEt$_4$dien(SCN)]BPh$_4$ in which the interaction of the sulfur atom with the phenyl groups of the anion in the crystal overrides its interaction with the ethyl groups of the coordinated amine (*156*).

A similar type of effect has been observed with cations: K$_3$[Co(CN)$_5$SCN)] is the stable form in the solid state (*139*) although its linkage isomer is also known (*708*). When the cation was replaced by (n-Bu$_4$N)$^+$ it was apparently impossible to isolate the pure, solid, S-bonded compound, and the mixed solid product isomerized to give (n-Bu$_4$N)$_3$[Co(CN)$_5$(NCS)] in 3 days (*358*). It was suggested (*358*) that the stabilization of the N-bonded isomer is due to an electronic effect by which the polarizable end of the thiocyanate group is better accommodated by the soft nonpolar environment of the (n-Bu$_4$N)$^+$ cation, whereas the hard K$^+$ undergoes a more favorable interaction with the hard nitrogen atom. This explanation would predict the wrong result if applied to the palladium example in the previous paragraph.

By way of contrast, the study of a series of compounds CuL$_n$(CNS)$_x$(ClO$_4$)$_{2-x}$ (x = 0, 1, 2; n = 1, 2; L = bi-, ter-, and quadridentate amines) suggests that, whatever the coordination in the bisthiocyanato complexes, the substitution of a perchorate ion for a thiocyanate ion favors the coordination of the remaining thiocyanate by the nitrogen atom when the resulting complexes are five-coordinate (i.e., when L$_n$ = bisdiamine or a tetramine); for tridentate ligands, five coordination is achieved by Cu—NCS—Cu bridging (*72*, *124*).

There are too few examples of the effect of the counterion on the coordination of the thiocyanate group for any generalization to be apparent. Detailed crystal structure determinations are required in order to reveal whether any effects other than those associated with crystal packing are occurring.

B. SELENOCYANATES

1. *Homogeneous Anionic Selenocyanate Complexes*

Table XLI summarizes the structures of known, homogeneous, anionic selenocyanate complexes. Although fewer examples exist than for the corresponding thiocyanate complexes, it is apparent that a similar pattern exists for the two sets of complexes. Class a metals are coordinated by the nitrogen atom, whereas selenium is the donor for the class b metals. In mixed metal complexes containing bridging selenocyanate groups the nitrogen atom coordinates to the harder or class a metal, and the selenium atom bonds to the softer or class b metal, as was observed with the corresponding thiocyanate complexes.

2. *Mixed-Ligand Selenocyanate Complexes*

Table XLII summarizes the different types of coordination behavior for the selenocyanate group. Relatively few examples were cited in Section IV so that, like Table XXXIX, which contains the corresponding data for thiocyanate complexes, Table XLII is likely to alter considerably in the ensuing years.

3. *Nature of Cooperative Effects in Mixed-Ligand Selenocyanate Complexes*

Of the data leading to Table XLII, the results for the copper(II) complexes are complicated by long and short or weak and strong bonds as indicated in Section IV, J, 1, c and will not be discussed further; similarly, the iron(II) examples are the linkage isomers cpFe(CO)$_2$NCSe and cpFe(CO)$_2$SeCN (*410*). Because the remaining compounds are few

TABLE

HOMOGENEOUS ANIONIC

	Ti(NCSe)$_6{}^{2-}$	VO(NCSe)$_4{}^{2-}$ V(NCSe)$_6{}^{3-}$	Cr(NCSe)$_6{}^{3-}$	Mn(NCSe)$_6{}^{4-}$ Mn(NCSe)$_4{}^{2-}$
Y(NCSe)$_6{}^{3-}$	Zr(NCSe)$_6{}^{2-}$		Mo(NCSe)$_6{}^{3-}$	
	Hf(NCSe)$_6{}^{2-}$			Re$_2$(NCSe)$_8{}^{2-}$
Pr(NCSe)$_6{}^{3-}$	Nd(NCSe)$_6{}^{3-}$		Sm(NCSe)$_6{}^{3-}$	
Pa(NCSe)$_8{}^{4-}$	U(NCSe)$_8{}^{4-}$			

and because the nature of the ligational effect is even less clear than for thiocyanates, no attempt has been made to divide the following discussion into subsections.

Most palladium(II) selenocyanate complexes have a Pd—Se bond, but the compound $[Pd(Et_4dien)(SeCN)]BPh_4$, isolated at low temperatures, isomerizes in a number of different solvents via a dissociative process, whereas $[Pd(dien)(SeCN)]BPh_4$ shows no signs of such isomerization. Further, if $[Pd(Et_4dien)NCSe]BPh_4$ is isolated it reisomerizes to the Se-bonded form at room temperature in the solid state (*153*, *156*). This behavior parallels that of the thiocyanate group under similar circumstances and provides evidence for a steric effect modified by the nature of the anion.

Electronic effects account for the variations in selenocyanate coordination toward cobalt(III) recorded in Section IV, H, 3, and again the pattern is similar to that for the corresponding thiocyanate complexes. The pentamine cobalt(III) moiety bonds with nitrogen, but *trans*-cobaloxime complexes are S- or Se-coordinated: *cis*-$[Co(DH)_2(H_2O)(NCSe)]$ having a structure affected by steric hindrance (*3*). The explanations that have been put forward for cobalt(III) thiocyanates could, therefore, apply here where complications due to palladium(II) complexes do not exist. There is, however, one example of cooperative ligand effects with a class b metal in the form of the compounds $Rh(PPh_3)_2CO(NCSe)$ (*150*) and $Rh(PPh_3)_2MeCN(SeCN)$ (*36*). Thus, there are indications that a very similar set of arguments to those given for the thiocyanate group may be rehearsed for the selenocyanate group also, including a similar lack of definite conclusions.

XLI

SELENOCYANATE COMPLEXES

$Fe(NCSe)_6^{3-}$ $Fe(NCSe)_6^{4-}$ $Fe(NCSe)_4^{2-}$	$Co(NCSe)_6^{4-}$ $Co(NCSe)_4^{2-}$	$Ni(NCSe)_6^{4-}$		$Zn(NCSe)_4^{2-}$
	$Rh(SeCN)_6^{4-}$	$Pd(SeCN)_4^{2-}$		$Cd(SeCN)_4^{2-}$ $Cd(SeCN)_6^{4-}$
		$Pt(SeCN)_6^{2-}$ $Pt(SeCN)_4^{2-}$	$Au(SeCN)_4^-$	$Hg(SeCN)_4^{2-}$
		$Dy(NCSe)_6^{3-}$	$Ho(NCSe)_6^{3-}$	$Er(NCSe)_6^{3-}$

TABLE XLII

COORDINATION OF THE SELENOCYANATE GROUP IN MIXED-LIGAND COMPLEXES[a]

Ti(IV)–N	V(IV)–N V(III)–N	Cr(III)–N Cr(II)–N	Mn(II)–N Mn(I)–N	Fe(III)–N Fe(II)–N/Se	Co(III)–N/Se Co(II)–N	Ni(II)–N	Cu(II)–N/Se	Zn(II)–N
Zr(IV)–N		Mo(III)–N Mo(II)–Se		Ru(III)–Se	Rh(I)–N/Se	Pd(II)–Se/N		Cd(II)–Se
Hf(IV)–N		W(II)–Se	Re(IV)–N		Ir(III)–N Ir(I)–N	Pt(IV)–Se Pt(II)–Se	Au(III)–Se	Hg(II)–Se

[a] M–N implies *N*-selenocyanato coordination. M–Se implies *Se*-selenocyanato coordination. M–N/Se implies ambidentate behavior of $NCSe^-$ to the metal in that oxidation state.

C. CYANATES

1. *Homogeneous Anionic Cyanate Complexes*

The homogeneous cyanato anions are presented in Table XLIII. Although the majority are *N*-cyanato complexes, $[Mo(OCN)_6]^{3-}$, $[Re(OCN)_6]^{2-}$, $[Re(OCN)_6]^-$ (*56*), and $[Hg(OCN)]_4]^{2-}$ (*724*) have been characterized by the positions of the fundamental cyanate vibrations; only for the last compound has any confirmatory measurement been attempted, in which case ^{14}N NMR showed a relatively small upfield shift, characteristic for an N-bonded compound (*192*).

2. *Mixed-Ligand Complexes*

Only one pair of linkage isomers has been reported in the solid state, and here the compounds $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$ are characterized by differences in the positions and intensities of the infrared peaks (*37*). The possibility is that *trans*-$PtH(PEt_3)_2NCO$ has a linkage isomer in solution, but only ^1H NMR shifts are available for this compound (see Section IV, I, 3, a).

No mixed-ligand cyanate complexes of molybdenum(III), rhenium(IV), rhenium(V), or mercury(II) are known, but a large number of mixed ligand *N*-cyanato complexes involving a variety of metals have been reported, including the compounds *mer*-$MoO(NCO)_2L_3$ (L = Et_2PhP, Me_2PhP) (*166*). These suggest that an investigation of cooperative ligand effects in molybdenum cyanate complexes would be interesting. The few reported mixed ligand *O*-cyanates are $K[Cupic_2 \cdot (OCN)]$ (*321*) and $cp_2M(OCN)_2$ (M = Ti, Zr, Hg) (*145*, *146*), and the situation regarding the latter series well illustrates the complexity and difficulty of determining whether or not such compounds do exist. The series was reported in 1969 on the basis of mass spectroscopic and infrared shifts even though $cp_2Ti(OCN)_2$ had a rather different infrared spectrum to the others. Subsequent ^{14}N NMR shifts were in accord with the proposed structure for the titanium compound which was the only one measured (*93*). However, Burmeister *et al.* (*411*), who originally reported the compounds, later found that dipole moment measurements on the titanium and zirconium compounds (the hafnium compound being insufficiently soluble for useful measurements) were incompatible with both being *O*-cyanates. These workers favored $cp_2Zr(OCN)_2$ which would be in agreement with the homogeneous anionic complexes but casts doubt on the use of ^{14}N NMR for diagnostic purposes and also on the claim of linkage isomers. However, the alternative choice of $cp_2Ti(OCN)_2$ also presents its own problems. All that can be said at present is that there

TABLE XLIII

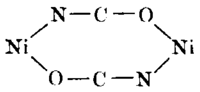
HOMOGENEOUS ANIONIC CYANATE COMPLEXES

$Cr(NCO)_6^{3-}$	$Mn(NCO)_4^{2-}$	$Fe(NCO)_4^-$ $Fe(NCO)_4^{2-}$	$Co(NCO)_4^{2-}$	$Ni(NCO)_4^{2-}$	$Cu(NCO)_4^{2-}$	$Zn(NCO)_4^{2-}$
$Mo(OCN)_6^{3-}$				$Pd(NCO)_4^{2-}$	$Ag(NCO)_2^-$	$Cd(NCO)_4^{2-}$
	$Re(OCN)_6^{2-}$			$Pt(NCO)_4^{2-}$	$Au(NCO)_2^-$	$Hg(CNO)_4^{2-}$[a]

[a] See Text.

is an urgent need for some X-ray structure determination of *O*-cyanato complexes. (See Appendix, p. 382.)

Two types of bridging cyanate have been confirmed by X-ray crystallography. In AgNCO only the nitrogen atom is involved (125) but in $[Ni_2tren_2(NCO)_2](BPh_4)_2$ the bridge is of the type,



thus establishing unequivocally the involvement of the cyanate oxygen in coordination for the first time (*265*).

In view of the foregoing situation and the uncertainties of whether or not *O*-cyanates do indeed exist or whether all the many *N*-cyanato complexes have been correctly characterized, any explanations concerning the behavior of the cyanate group would be premature. INDO calculations showed that almost equal electron densities existed at nitrogen and oxygen (*383*), so there is no apparent reason why both ends should not be involved in coordination. Attention has been drawn (*86*) to the fact that many of the metals found to form *O*-cyanates have vacant or only partly filled $d\pi$ orbitals to interact with filled π orbitals of the cyanate group. Whether these are centered on the oxygen or whether that atom forms the better σ bond with these mostly class a metals remains to be seen.

VI. Comparative Coordination Chemistry of the Chalcogenocyanate Groups

The preceding sections have shown that the behavior of the thiocyanate and selenocyanate groups in homogeneous complex anions is identical: in both cases the nitrogen atom coordinates to the class a metal, and the sulfur or selenium atoms coordinate to the class b metal. Although fewer comparable cyanate complexes are known, it is quite clear that the coordination of the cyanate group is not governed by the same factors.

Similarly, with mixed-ligand complexes it is apparent that selenocyanate complexes do follow similar patterns of behavior to thiocyanate complexes [e.g., with cobalt(III); see Section IV, B, 3] although ligational changes have a smaller effect. Thus, the pentacyanocobaltate(II) moiety forms linkage isomers with the thiocyanate group, but the N-bonded $[Co(CN)_5NCSe]^{3-}$ is the only selenocyanate species. Similarly the palladium complexes listed in Table XLIV show the sensitivity of the thiocyanate group to ligational change to be much greater than that of the cyanate and selenocyanate groups. At the time of writing there are no reported tellurocyanate complexes for further comparisons.

When the bridging behavior of these groups is compared, another difference emerges. Generally, thiocyanate and selenocyanate bridges have the form M—NCX—M, whereas cyanate forms M—N(CO)—M bridges in most cases, although the three-atom bridge is known. Further, the cyanate group does not form analogous compounds to the extensive series of M(NCX)Hg reported for X = S, Se.

These facts, together with the remarkably few *O*-cyanato complexes reported, suggest that the oxygen atom of the cyanate group is involved in coordination only with reluctance. Although there are obvious differences in the systematic chemistry of oxygen, sulfur, and selenium which will contribute to the differences in the coordination behavior of the chalcogenocyanate ions, it is not clear whether any overall explanation can, or should, be offered. Indeed, it has been pointed out that, when the donor properties of sulfur and oxygen in ambidentate ligands containing both these elements are compared, the preferred donor atom depends on the particular ligand. Thus, dimethyl sulfoxide coordinates through sulfur or oxygen, depending on the metal, $S_2O_3^{2-}$, SO_3^{2-}, SO_2, and RSO_2^- all prefer to coordinate through sulfur, and the sulfinate group shows a strong tendency to form M—O bonds (see Ref. *576* for further details and references).

TABLE XLIV

CHALCOGENOCYANATE COORDINATION IN SOME $PdL_2(CNX)_2$ COMPLEXES

L	NCO^- (*575*)	NCS^- (*143*)	$NCSe^-$ (*152*)
NCX	N	S	Se
NH_3	N	S	Se
py	N	S (*640*)	Se
γ-pic	N	S	Se
$\frac{1}{2}$bipy	N	N	Se
$\frac{1}{2}$phen	—	S	Se
$\frac{1}{2}5NO_2$-phen	—	N (*640*)	Se
Ph_3P	N	N	Se
Ph_3As	N	N	—
Ph_3Sb	—	S	—

It may be concluded, therefore, that attempts to provide too detailed a comparison of the coordination behavior of the chalcogenocyanate ions are not useful until a better understanding is obtained of the differing effects of the cyano group on the atom X in NCX^-. Such an interaction may, and probably does, modify the comparative chemistry that might be expected for the oxygen, sulfur, or selenium atoms in these ions. Similarly, the coordination properties of the nitrogen atom will also depend, to some extent, on the particular Group VI atom in the ion; the nucleophilicity of NCO^- toward organic substrates is appreciably different from that of NCS^- and of $NCSe^-$ (*43*). If the gross coordination behavior of these ions is difficult to understand, it is not surprising that the accurate description of the processes modifying the behavior of any one of the ions also provides difficulties. These difficulties reach a maximum for any two linkage isomers that do not owe their existence to kinetic factors since, by definition, the energy difference between the isomers will be very small, and, thus, very difficult to account for in detail.

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APPENDIX

The following represents a brief outline of the more important of the many papers published since this review was completed. The references cited are only those which have a direct bearing on the more general themes discussed previously.

A. CYANATES

The crystal standard of $(\pi\text{-cp})_2\text{Ti(NCO)}_2$ has been determined and confirms that, in the solid state, the cyanate group is here N-bonded; it was only in the last stages of the analysis that the O-bonded alternative could be finally eliminated (*1*). Hexa-*N*-cyanato complexes of ytterbium, erbium, and neodymium have been reported as quaternary onium salts (*16*) and reference made to the series of tetraethylammonium salts of $[\text{Ln(NCO)}_6]^{3-}$ (Ln = Eu–Yb) (*22*); these results extend Table XLII. The ESR spectra of series of complexes $\text{CuL}_2\text{(NCO)}_2$ (L = an, or substituted an) have been interpreted to show Cu—N(CO)—Cu bridges with no indication of any Cu–O interactions (*19*). The ESCA spectra of $[\text{M(NCO)}_4]^{2-}$ (M = Mn, Co, Zn) have been recorded (*12*).

B. THIOCYANATES

Crystal structures have been determined by X-ray methods for a number of compounds, among the more important being the following:

the dimer $[CoPPQ(NCS)_2]_2$ (PPQ = 2-(2′-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline) in which each cobalt exists in a distorted octahedron of five nitrogen atoms, three from the organic ligand, and two from thiocyanate groups, and a sulfur atom from a bridging thiocyanate group (*20*); the different salts of the linkage isomers $[Ir(NH_3)_5(SCN)](ClO_4)_2$ (*14*) and $[Ir(NH_3)_5(NCS)]Cl_2$ (*13*); the complex $NiL_2(NCS)_2$ (L = thiosemicarbazide) where the ligand is bidentate and the thiocyanate groups complete octahedral coordination around the nickel atom by forming two Ni–NCS linkages (*10*); the phosphite complex $Pd(P(OPh)_3)_2(SCN)_2$ unlike the corresponding phosphine, contains only Pd–SCN linkages (*18*); analysis of repulsive contacts in *cis*-$Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2(NCS)(SCN)$ leads to the conclusion that the mixed bonding is mainly due to steric inhibition of dithiocyanato coordination (*28*); the series of polyamine copper(II) complexes has been extended with $[Cu(H_2NCH_2CH_2CH_2NH_2)_2(NCS)]ClO_4$ in which the metal has trigonal bipyramidal coordination (*5*), $[CuHN(CH_2CH_2NH_2)_2(NCS)_2]$ in which the metal has tetragonal pyramidal coordination (*6*), and $[CuHN(CH_2CH_2NH_2)_2(NCS)]_2(ClO_4)_2$ in which Cu—NCS—Cu bridges lead to a tetragonally distorted octahedron with a long copper–perchlorate interaction (*7*).

Various geometric isomers can be obtained in the chromium(III)–amine–thiocyanate system. The isothermal decompositions of $[Cr(NH_3)_6](NCS)_3$ and $[Cr(NH_3)_5(NCS)](NCS)_2$ both proceed via *trans*-$[Cr(NH_3)_4(NCS)_2]NCS$ to give *mer*-$[Cr(NH_3)_3(NCS)_3]$ (*24*), while the aqueous photolysis of *trans*-$[Cren_2(NCS)_2]^+$ gives a mixture of *cis*-$[Cren_2(H_2O)(NCS)]^{2+}$ and $[Cren(enH)(H_2O)(NCS)_2]^{2+}$, where the thiocyanate groups are still trans to each other (*2*). Similarly, aqueous photolysis of *trans*-$[Cren_2Cl(NCS)]^+$ leads to the aqueous replacement of either anion, while use of the corresponding cis-isomer gives initially $[Cren(enH)(H_2O)Cl(NCS)]^{2+}$ (*15*).

The ESCA spectra of $[M(NCS)_4]^{2-}$ (M = Co, Ni, Zn), $[Ni(NCS)_6]^{4-}$ (*12*), $[Re(NCS)_6]^{2-}$, and $[Re_2(NCS)_8]^{2-}$ (*27*) have been recorded. Further details have been published on the compound $(Me_4N)_2[Tc(NCS)_6]$ together with the new compound $(Me_4N)[Tc(NCS)_6]$ which extends Table XXXVIII. The two anions form a redox system with $E^\circ = 0.53$ V in 1*M* H_2SO_4, and their infrared spectra support their formulation as *N*-thiocyanates (*26*).

The complex $(Ph_4As)[Co(DH)_2(SCN)_2]$ has been obtained in three forms, and the S,S-, N,S-, and N,N-isomers all characterized (*11*). Spectrophotometric measurements on the equilibrium

$$Co(DH)_2py(SCN) \rightleftharpoons Co(DH)_2py(NCS)$$

indicate that in chloroform at 298°K, $\Delta G = 3.1$ kJ mol^{-1}, $\Delta H = 26.4$ kJ mol^{-1}, and $\Delta S = -78$ J K^{-1} mol^{-1} (*23*); energy differences which are so small that they more than adequately illustrate the force of the closing sentence of the main body of this review. The consequences of modifying the activation energy for the isomerization by adding cobalt(II) species to similar systems and the relative importance of adjacent and remote attack during the electron transfer reaction have been discussed (*21*).

The recognition of the importance of steric effects in determining thiocyanate coordination to palladium(II) and platinum(II) continues to gain ground. Thus, the mixed complexes *cis*-$Pt(Ph_2PC{\equiv}CR)_2(NCS)(SCN)$, (R = Ph, Et, *i*-Pr, *t*-Bu) have been characterized by infrared spectroscopy and, when R = *t*-Bu, by X-ray crystallography, and the authors suggest, on the basis of a careful analysis of intermolecular repulsions, that these results are consistent with the reduced steric demands of the phosphinoacetylene increasing the possibility of S-coordination (*28*). Similarly, X-ray crystallography showed that *trans*-$Pd[P(OPh)_3]_2(SCN)_2$ is S-bonded as a solid while infrared measurements showed no evidence for complete isomerization in solution. These results are in important contrast to the behavior of $Pd(PPh_2)_2(NCS)_2$ since $P(OPh_3)_3$ is the better π-acceptor and would be expected to promote *N*-thiocyanate coordination if the π-bonding hypothesis were of major importance (*18*). The solid state isomerization of the unstable linkage isomers *cis*-$PtL_2(SCN)_2$ (L = Ph_3P, Ph_3, As) is not accompanied by any geometric isomerization (*17*). The steric effects which encourage the isomerization of $[PdET_4dien(SCN)]^+$ in solution to give the N-bonded isomer, which in turn reisomerizes as the solid S-bonded tetraphenylborate have been described previously, and these have been reiterated with further examples. Interestingly though the corresponding platinum(II) complex exists only as the *S*-thiocyanate in solid and solution (*3*).

Electronic effects of one sort or another do, however, appear to have some part to play in certain complexes as indicated previously. Recent examples are $[Pdtripy(NCS)]BPh_4$ which exists only in the N-bonded form (*3*), whereas steric effects of the compact tripy ligand might be expected to be less than of ET_4dien. Similarly, the steric effects of $Ph_2PCH{:}CHPPh_2$ and $Ph_2PCF{:}CFPPh_2$ would appear to be comparable yet with the former ligand $PdL(SCN)_2$ exists while the latter gives $PdL(NCS)(SCN)$ (*8*). In contrast, the formation of a series of isonitrile complexes $Pd(CNR)_2(SCN)_2$ (R = Ph, C_6H_{11}), $Pd(CNR)(PPh_3)(SCN)_2$ (R = Ph, C_6H_{11}, *p*-NO_2–C_6H_4), and $Pd(CNPh)(AsPh_3)(SCN)_2$ lead to the suggestion that the isonitriles function only as σ-donors in this case, and that their trans influence is insufficient to modify the mode of coordination of the thiocyanate group (*9*), whereas the reduced steric effects of the linear isonitriles appear to offer an explanation which is more consistent with the larger body of data.

The Au–NCS/Au–SCN ratios of a series of LAu (thiocyanate) complexes in solution have been measured and the authors (*4*) claim that their results support Pearson's concept of antisymbiosis (*25a*), but it has been pointed out that the ligands used give ratios in an order which does not follow that accepted for the trans effect (*18*).

C. SELENOCYANATE

The crystal standard of bis(*N*,*N*-dimethylethylenediamine)-copper(II) selenocyanate has been determined (*25*). The ESCA spectra of $[M(NCSe)_4]^{2-}$ (M = Co, Zn) and $[M(NCSe)_6]^{4-}$ (M = Co, Ni) have been measured (*12*).

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