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AMBIDENTATE LIGANDS, THE SCHIZOPHRENICS OF COORDINATION CHEMISTRY

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SUMMARY

Representative examples of ambidentate ligand chemistry, drawn primarily from studies published during the past decade, are presented. An overview of the physical methods used for structural elucidation is included, with major emphasis being placed on structures emanating from single crystal X-ray diffraction studies. A great variety of ambidentate ligands are covered, although the bulk of the review deals with the schizophrenic behaviour of the classic ambidentate ligands NO_2^-, CN^-, NCO^-, NCS^-, $NCSe^-$ and $NCTe^-$. As usual, the thiocyanate ion is accorded the most extensive coverage. Other ambidentate ligands discussed include CNO^-, CNS^-, azaphospholes, aminobenzonitriles, 4,4'-bipyrimidine, cyanoborohydrides, CCO, $ClC(CN)_3$, chloranilate ion, isonitroso(ß-ketoimine), nicotinate ion, nitramines, nitrosobenzenes and -anilines, $Ph_2PC(S)NHR$, phosphine/arsine, phosphine sulfide/methine, and phosphinethioamide hybrid ligands, pyridine-2-thione, N-(2-pyridyl)imidazole, 4,6-dimethylpyrimidine, saccharinate ion, $H_2NSO_3^-$, SO_3^{2-}, Me_2SO, SO_2, SO_2^-, SNO^-, NSO^-, $S_2O_3^{2-}$, S_2CO^{2-}, SeO_3^{2-}, $SC(O)NHR^-$, $OSNH^-$, dithioimidodiphosphinate ion, dithiosquarate ion, triphosphate ion, and ureas. Transition metal complexes of ambidentate ligands are emphasized throughout the review.

A. INTRODUCTION

Since the great patriarchs of coordination chemistry, Werner and Jørgensen, first attempted to elucidate the true nature of the reddish pink (O-bound nitrito isomer) and yellow-orange (N-bound nitro isomer) forms of $[Co(NH_3)_5NO_2]Cl_2$ a century ago [1], the coordination chemistry of ambidentate ligands has developed at an accelerating, albeit irregular, pace. Indeed, most of the published work has appeared during the past 30 years beginning, appropriately, with the first rational synthesis, by Basolo and Hammaker, of a linkage isomeric pair of coordination complexes [2]--also of the nitrite ion. My own enduring love affair with these schizophrenic ligands began shortly thereafter, when Basolo, Poë and I succeeded in synthesizing the first linkage isomers of a ligand other than the nitrite ion: the orange S- and yellow N-bound thiocyanato and isothiocyanato isomers of trans-$[Pd(AsPh_3)_2(NCS)_2]$ [3].

Explosive growth followed. This is graphically reflected in the three previous review articles that have appeared under my by-line [4-6], wherein the field of coverage narrowed (from ambidentate ligands to linkage isomerism to the thiocyanate ion), while the pages utilized for this purpose increased dramatically. It should be noted, in passing, that ref. 5 is the most cited paper ever published in this journal [7].

A substantial number of related review articles have been written by other authors, culminating in a comprehensive monograph by Golub, Köhler, and Skopenko [8], wherein references to these other reviews may be found. Although published fairly recently, its literature coverage extends only through 1980. [Notwithstanding this, and the fact that its subject matter is restricted to the chemistry of the pseudohalides, it contains an impressive total of 4217 references (up from the 2705 references in the German version of the text, which was originally published in 1979 and covered the literature through 1974).] Consequently, the primary emphasis in this paper will be directed toward work that has been published during the past decade, subject to the following biases and (largely space-induced) boundary conditions: this review will be critical, but not comprehensive; work emanating from my laboratory will be highlighted; pseudohalide chemistry (especially that involving the thiocyanate ion) will, as usual, be preeminent; the examples included in the potpourri of ambidentate ligand chemistry discussed in the final section will be largely a consequence of my own predilection, rather than an attempt to be encyclopedic.

B. PHYSICAL METHODS USED FOR STRUCTURAL ELUCIDATION

The development of so-called "sporting" methods to determine the bonding modes adopted by ambidentate ligands in coordination complexes, both in the solid state and in solution, was a major activity during the decades of the sixties and seventies. This was largely due to the fact that (the more definitive) structural characterization by means of single crystal X-ray diffraction had not yet become routine, given the relatively large expenditure of time, effort and money that it then required.

(i) Non-crystallographic methods

Not surprisingly, most of the early efforts were directed toward the discovery of frequency criteria, utilizing infrared, electronic, and Raman spectroscopy (in descending order of utility) to distinguish between/among the bonding modes adopted by a large variety of ambidentate ligands. Isotopic labelling was employed in the more sophisticated vibrational spectroscopic studies, e.g., the use of N-15 labelled thiocyanate in the infrared spectral characterization of the linkage isomers of pyridine(thiocyanato)cobaloxime [9]. Other refinements included the utilization of definitive ν(CN) integrated absorption intensity criteria for determining the bonding modes adopted by thiocyanate and selenocyanate complexes in solution [6]. Finally, these intensity criteria were extended to the solid state by the inclusion of internal standards such as salicylic acid and 1,4-dicyanobenzene, the latter being the standard of choice [10]. Recently, different subnanosecond transients were observed [11] for the linkage isomers of $[Co(NH_3)_5SCN]^{2+}$, following pulsed laser irradiation in the UV region.

The development of ever more easily accessed multinuclear NMR frequency measurements resulted in the technique's being applied, with increasing frequency, to structural problems involving ambidentate ligands during the past decade. Structural determinations have been made in solution that utilize the NMR spectra of both coordinating and non-coordinating atoms in the ambidentate ligands. Examples of the former include the use of N-15 NMR chemical shifts to distinguish between bent and linear nitrosyls, as well as N- and O-coordinated hyponitrites and nitrites [12], and the application of Se-77 NMR data in the determination of selenocyanate bonding modes [13]. Examples of the latter include the use of C-13 NMR spectra to characterize thiocyanate coordination behaviour, both in solution [14] and in the solid state [15].

Measurements involving the NMR frequencies of atoms remote to the ambidentate ligands have also proved to be sources of useful diagnostic information concerning the ligands' bonding modes. Representative examples include: the determination of Co-NCS/Co-SCN ratios in cobaloxime complexes utilizing proton NMR data for the hydrogen atoms in the dimethylglyoximate methyl groups [16]; the distribution of linkage isomers in $[Pd(diphosphine)(SCN)_2]$ and $[Pd_2(diphosphine)_2(SCN)_2]$ complexes inferred from P-31 NMR spectra [17]; Nb-93 NMR detection of thiocyanato and isothiocyanato niobium(V) complexes [18].

Other nuclear-centered probes have been employed, with some degree of success. Nitrogen-14 NQR measurements of coordinated thiocyanate have been shown [19] to be a definitive, albeit laboriously applied, means for determining the ion's bonding mode in the solid state. ESCA measurements have been successfully utilized as diagnostic sensors of the bonding modes of several ambidentate ligands, including thiocyanate [20], dimethylsulfoxide [21], isonitroso-ß-ketoimines [22], cyanide (F_3CNC vs. F_3CCN) [23], and sulfamidate [24].

(ii) Single crystal X-ray diffraction studies

Single crystal X-ray diffraction studies produced a tidal wave of structural information during the eighties, and the size of the wave continues to grow. As one very graphic measure of the impact the increased use of this technique has had on the structural aspects of ambidentate ligand chemistry, one need only compare the number of references (48) to single crystal X-ray structural determinations found in my 1975 thiocyanate review [6] to the number pertaining to thiocyanates (189) in the aforementioned circa 1980 monograph [8]. Indeed, one research group (that of Jan Reedijk at the University of Leiden) has published a series of 20 papers describing the structures, determined by single crystal X-ray diffraction, of 27 thiocyanate-containing complexes of Fe, Co, Ni, Cu, Zn, and Cd, as part of their extensive study of bioinorganically significant triazole, pyrazole, and imidazole complexes during a brief five-year period [25-33]. We are rapidly approaching the point where characterization by single crystal X-ray diffraction will be as commonplace as elemental analysis for non-trivial, non-repetitious compounds isolable as suitable single crystals. Exemplary are papers emanating from my department and my laboratory describing, respectively, the structures of seven ambidentate nitramine complexes of Cu(II) and Ni(II) [34] and seven thiocyanate-containing diphosphine complexes of Pd(II) [35].

Results emanating from this technique have had dramatic effects on structural chemistry and its practitioners. Although other examples will be cited in later sections of this review, it is revealing to consider several illustrative cases at this point. Most obvious are the corrections of structural mistakes, based on the use of so-called "sporting" methods, that have appeared in the earlier literature. Most, if not all, of these mistakes were honest, well-meaning, and, in some cases, unavoidable, given the information at hand. An excellent example of the last-named circumstance is found in a thiocyanate complex of Re, originally identified [36] as $[\underline{n}\text{-Bu}_4\text{N}]_3[\text{Re}_2(\text{NCS})_8(\text{CO})_2]$. A subsequent single crystal X-ray diffraction study [37] revealed that the complex actually is $[\underline{n}\text{-Bu}_4\text{N}]_3[\text{Re}_2(\text{NCS})_{10}]$, and that it contains the first examples ever observed of N,N-bridging thiocyanates. The very low ν(CN) stretching frequencies exhibited by the thiocyanate groups in this unusual bonding environment had been mistakenly identified as ν(CO) stretches in the earlier study (the two different formulations cannot be distinguished by C,H,N,S elemental analyses).

A second, related effect is found in the need to reevaluate qualitative, "hand-waving" explanations when faced with the hard(er) truths produced by single crystal X-ray analysis. For example, the switch from N- to S-bonding observed in the solid state [38] for the complex cation $[\text{Pd}(1,1,7,7\text{-tetraethyldiethylenetriamine})\text{NCS}]^+$ when the counter anion was changed from NCS^- or PF_6^- to BPh_4^- was initially ascribed [38] to crystal packing effects. However, the actual crystal structures [39] of five salts of this cation (N-bound as PF_6^- salt; N-bound as BPh_4^- salt, unsolvated; N-bound as BPh_4^- salt with acetone solvate; N-bound as BPh_4^- salt with CH_2BrCl solvate; S-bound as BPh_4^- salt with CH_3OH solvate) revealed that the S-bonding observed earlier was, instead, due to hydrogen bonding between the non-coordinated nitrogen end of the thiocyanate and the incorporated CH_3OH molecule. One is therefore led to wonder about the actual state of affairs that exists in the case of the analogous $NCSe^-$-containing cation (which has also been found to be Se-bound with the BPh_4^- counterion [38], based on spectroscopic evidence). A similar question arises in considering the more recent report [40] of another N- to S-bound switch for the $[Pd(N(CH_2CH_2NH_2)_3)NCS]^+$ cation when the counterion was switched from NCS^- to BPh_4^-.

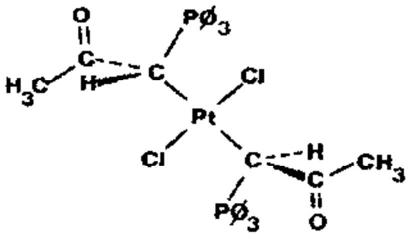
Thirdly, diffraction techniques provide structural solutions for the solid state that cannot be achieved, at least not with a comparable degree of certainty, by any other method. A prototypical example, in the present context, is found [41] in the complex $[Pt_2(PhNO)_3(PMe_3)_3]$, which contains *three* different linkage isomers of nitrosobenzene: simple N-coordination, η^1-bridging via N, and η^2-bridging via both the N and O atoms. A fourth bond type, simple O-coordination, has also been confirmed by X-ray diffraction in the complexes $[SnCl_2Me_2$(4-nitroso-N,N-dimethylaniline$)_2]$ [42a] and [Zn(4-nitroso-N,N-dimethylaniline$)_2Cl_2]$ [42b].

Lastly, the structural solutions produced by diffraction techniques tend to generate, in turn, bonding questions that are ever more sophisticated, subtle, and specific. The $[Pt_2(PhNO)_3(PMe_3)_3]$ complex noted above is a case in point. At first glance, it would appear to be a Pt(0) complex. However, consideration of the bond distances involved leads to the conclusion [41] that the platinum atoms are in the +2 oxidation state in a square planar, 16-electron environment, and that both bridging nitrosobenzenes are dianionic ligands.

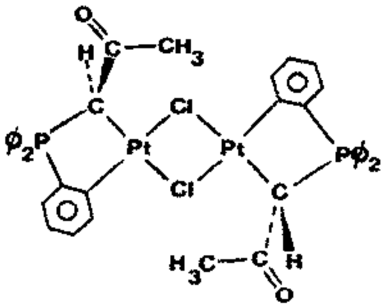
C. AN AMBIDENTATE LIGAND CASE STUDY: PHOSPHORUS YLIDES

Our initial interest in studying the coordination chemistry of ylides of the type $R_nZ\overset{*}{C}R'C(O)R''$ (Z = N,P,As,n = 3; Z = S,n = 2) was based on the presumption that their ambidentate bonding behaviour ($\overset{*}{C}$- *vs*. O-bonding) could be potentially controlled by a judicious choice of R, R', R" and/or Z, i.e., by variables *internal* to the ligand itself. Since the first reported structure [43] of a complex of this type, *trans*-$[Sn(CH_3)_3Cl(Ph_3PCHC(O)CH_3)]$ involved axial O-ligation of the ylide, acetyltriphenylphosphorane (henceforth, APPY), our first efforts [44] centered on the synthesis of a large series of C-bound ylides of the types $[Hg_2Cl_4$(ylide-C$)_2]$ and [M(ylide-C$)_2Cl_2]$ (M = Pd(II), Pt(II)). The C-bonding assignments were based on the observed (low resolution) methine proton chemical shifts and ν(C=O) stretching frequencies (complexed *vs*. free ylide).

In a subsequent multinuclear NMR study of one of these complexes, [Pt(APPY-C$)_2Cl_2]$, we were therefore somewhat surprised to find essentially two resonances for every atom in the proton, C-13, and P-31 NMR spectra [45], without any significant change in elemental analysis in the eight-year-old sample. We were even more surprised when the X-ray diffraction analysis of one of the crystals that grew in one of the NMR tubes produced [45] the ortho-metalated structure 2, instead of the anticipated structure 1:



(1)



(2)

We eventually discovered that 2 had actually been formed in the initial reaction between $PtCl_2$ and APPY in refluxing CH_3CN, but that the $APPYH^+Cl^-$ by-product had been mixed in a 2:1 ratio with 2 when the latter was isolated [44] by evaporating the solution to dryness. (A 2:1 ratio of $APPYH^+Cl^-$ to 2 produces the same elemental analysis as 1.)

Later studies [46] in our laboratory showed that $PdCl_2$ undergoes the same ortho-metalation reaction with APPY under the same conditions, that the arsenic and sulfur analogs of APPY also undergo ortho-metalation with $PdCl_2$, and that $PdCl_2$ will form an ortho-metalated ring with the ylide $(n\text{-Bu})_3PCHC(O)Ph$ (BBuPY), wherein the phenyl ring is bound to the carbonyl carbon. In our attempt to elucidate the mechanism of this ortho-metalation reaction, we were able to isolate and crystallographically characterize two intermediates in the reaction, simple C-bound trans-$[Pd_2Cl_4(BBuPY)_2]$, which contains two bridging chlorides [47], and its precursor, simple C-bound trans-$[Pd(BBuPY)_2Cl_2]$ [48]. Finally, we have come full circle with the synthesis and crystallographic characterization of the first transition metal complexes of these ylides that involve O-bonding: trans-$[MCl_4(\text{ylide-O})THF]$, where M = Ti(IV), Zr(IV), and Hf(IV) [49].

D. NITRITE (NO_2^-)-CONTAINING COMPLEXES

In retrospect, the central question (N- vs. O-bonding) inherent in the controversy between Jørgensen and Werner concerning the nature of the reddish-pink and yellow-orange forms of $[Co(NH_3)_5NO_2]^{2+}$ [1] seems pristine in its simplicity. In point of fact, as described by Hitchman and Rowbottom in their comprehensive review of transition metal nitrite complexes [50], there are nine different ways in which the nitrite ion might be expected to function as a ligand.

(i) Structures determined by single crystal X-ray diffraction

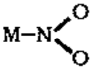
Of the nine structural types (**3** through **11**, shown in Fig. 1 on the next page) described by Hitchman and Rowbottom [50], eight (all except **10**) had been confirmed by X-ray crystallography by the time they wrote their review. The representative, crystallographically confirmed examples shown below each structural type, except for those pertaining to types **9** and **11**, have appeared in the literature since the publication of their article. In addition, an unanticipated bonding type (**12**) has also been observed. As should be obvious, deciphering this multitude of coordination environments without the aid of X-ray crystallography would be a hopeless task.

(ii) Linkage isomerization

Reactions involving linkage isomerism of the coordinated nitrite ion have been subjected to detailed scrutiny during the past decade. Van Eldik and his coworkers have studied the effect of pressure on the O- to N-bonded linkage isomerization reactions of cis- and trans-$[Co(en)_2(ONO)_2]^+$ in aqueous solution, both without [62] and with [63] base catalysis. In the former circumstance, they found that the linkage isomerization mechanism for the cis-isomer involves two reactions: a fast step, during which cis-$[Co(en)_2(ONO)NO_2]^+$ is produced, followed by a slower step to produce the final di-N-bound product. Although the same intermediate is formed in the linkage isomerization of the trans-isomer, the relative rates of the two steps are reversed. The observed negative volumes of activation suggest that the linkage isomerizations are intramolecular processes. In the presence of base, the results were interpreted in terms of a conjugate base mechanism, in line with earlier reported suggestions. The base hydrolysis of $[Co(NH_3)_3(NO_2)_3]$ has been studied by Singh and Shanker [64a]. Stochel and van Eldik have investigated [64b] the solvolysis reactions of $[Fe(CN)_5NO_2]^{3-}$ in a variety of solvents as a function of pH, temperature, and pressure.

Yoneda and his colleagues produced [65] a complementary report on the effect of the nature of other ligands on the rate of nitrito-to-nitro linkage isomerization of a variety of octahedral (nitrito)(amine)cobalt(III) complexes in aqueous solution. Their findings may be generalized as follows: (a) relative to that of $[Co(NH_3)_5ONO]^{2+}$, the isomerization is retarded by the presence of chelated amines trans to each other, but is accelerated by chelate rings in other forms; (b) an increase in the chelate ring size has little effect on the rate of linkage isomerization; (c) the isomerization rates of cis-$[Co(en)_2(X)ONO]^{n+}$ are relatively insensitive to the nature of the X ligands, whereas those of the trans isomers are greatly affected by changes in the X ligands; (d) a change in net charge on the complex has no appreciable effect on the rate constants.

(3)



$[Ni(NO_2)(NO)(PMe_3)_2]$ [51a]

$[Ni(NO_2)_2(Ph_2P(CH_2)_2PPh_2)]$ [51b]

$K_2[PtCl_4(NO_2)_2]$ [52a]
(cis and trans)

trans-[Pt(2,2'-bipyridyl)(N,N'-dinitroso-1,2-ethanediaminate)-$Cl(NO_2)$] [52b]

trans-$K[Co(NH_3)_2(NO_2)_4]$ [53a]

[Co(N-((2-pyridyl)methyl)-2-((2-aminoethyl)thio)acetamidate)-$(NO_2)_2$] [53b]

trans-$[Co(en)_2(NO_2)_2]NCS$ [53c]

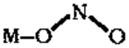
trans-$[Co(en)_2(NCS)(NO_2)][ClO_4]$
[53d]

trans-$[Co(en)_2(NCS)(NO_2)]I$ [53d]

cis-α-[Rh(triethylenetetramine)-$(NO_2)_2$]Cl [54]

[$Ru(PMe_3)_2$(2,2':6',2"-terpyridyl)-$(NO_2)][ClO_4]$ [55]

(4)

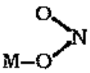


$[Ni(NH_2(CH_2)_2NH_2)_2ONO]_2[BPh_4]_2$
[56]

trans-$[Co(en)_2(NCS)(ONO)][ClO_4]$
[53d]

trans-$[Co(en)_2(NCS)(ONO)]I$
[53d]

(5)

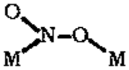


$[Ni(ONO)(NO)(Ph_2P(CH_2)_2PPh_2)]_2$
[52]

(6)

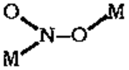
[Cu(2,2'-bipyridyl)ONO]$[NO_3]$ [57]

(7)



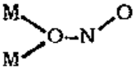
$[Cu_2(L\text{-}Et)NO_2][ClO_4]_2$ [58]
(HL-Et = N,N,N',N'-tetrakis-(2-(1-ethylbenzimidazolyl)-2-hydroxy-1,3-diaminopropane)

(8)



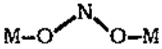
$[Ni(NH_2(CH_2)_2NH_2)_2NO_2][ClO_4]$ [59]

(9)



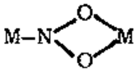
$[Co_4(NO)_8(NO_2)_2(N_2O_2)]$ [60]

(10)



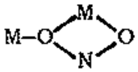
(no example known)

(11)



$K_2[Pb(NO_2)_3(NO_3)]\cdot H_2O$ [61]

(12)



$[Ni(NH_2(CH_2)_2NH_2)_2ONO]_2[BPh_4]_2$
[56]

Fig. 1. Types of metal-nitrite coordination, with examples.

Nitrite ion competition has been measured [66] for the base hydrolysis reactions of a series of $[Co(NH_3)_5X]^{n+}$ ions. Both O- and N-bonded $[Co(NH_3)_5NO_2]^{2+}$ ions are formed in the process, with an essentially constant (67%) predominance of the nitrito isomer. The total NO_2^- capture shows only a slight dependence on the over-all charge of the complex, and is even less dependent on the nature of X. The results are consistent with the formation of a common, reactive intermediate of reduced coordination number, $[Co(NH_3)_4NH_2]^{2+}$.

Jackson has found [67] that $[Co(NH_3)_5NO_2]^{2+}$ reacts rapidly and completely with neat anhydrous trifluoromethanesulfonic acid to generate $[Co(NH_3)_5OH_2]^{3+}$. The oxygen in the bound water is derived from the original nitro group, based on the results of O-17 NMR studies. A mechanism is suggested involving acid-catalyzed N- to O-bound nitrite rearrangement. Interestingly, the rapid nitrosation reaction of $[(H_3N)_5Co\text{-}^{17}OH]^{2+}$ in water leads [68] to the oxygen-bound nitrite ion product $[Co(NH_3)_5ONO]^{2+}$ having one O-17 per cobalt, but distributed *equally* between inner and outer sites.

The reversible red → blue color change exhibited by *trans*-$[Ni(en)_2(NO_2)_2]$ at ca. 120 °C has long been cited [69] as evidence for a reversible N- to O-bonded linkage isomerization. However, the results of more recent work by Hitchman and James [70] have shown that the blue isomer contains one O,O'-chelating nitrite and one ionic nitrite.

As part of their study of kinetic applications of chemically modified electrodes, Murray and his colleagues have discovered [71] that the oxidation of $[Ru(2,2'\text{-bipyridyl})_2(\text{isonicotinic acid})NO_2]^+$, attached to a silanized platinum electrode, produces a rapid, reversible linkage isomerization to the nitrito complex. On a much longer time scale, the complex reacts, irreversibly, by two competing reaction paths, to yield a mixture of nitrosyl and nitrato complexes, with the latter predominating.

E. INORGANIC LINKAGE ISOMERS OF THE CYANIDE ION

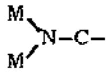
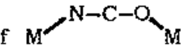
Although R-CN and R-NC linkage isomers are quite common in organic chemistry, virtually all of the cyano complexes of transition metals, wherein the cyanide ion is coordinated in a monodentate fashion, have been found to be C-bonded. The coordination chemistry of hydrogen cyanide, cyanogen, and cyanogen halides has been reviewed relatively recently [72]. Prior to the past decade, no crystallographically verified terminal transition metal M-NC bonds had ever been reported [73a], and a vanishingly small number had been claimed to have been verified by non-crystallographic techniques [73b]. By way of contrast, a vast number of M-CN-M and M-CN-M' bridged complexes have been synthesized and characterized, such as the series of $[(H_3N)_5Co\text{-}NC\text{-}Co(CN)_4X]$ complexes (X = CN, Cl, Br, I, NO_2, N_3), formed by the deaquation-anation of the double complex salts $[Co(NH_3)_5OH_2][Co(CN)_5X]$ by controlled heating in the solid state [74a], and a very recently crystallographically characterized trinuclear cyanide-bridged platinum-iron species [74b]. The reader is also referred to section G(iv) for an example of cyanide-bridged linkage isomers.

Relatively recently, however, Alvarez and Lopez [75] have synthesized the cyano and isocyano isomers of [Co(dimethylglyoximate)$_2$(OH$_2$)CN], and have characterized both by single crystal X-ray diffraction. The less stable isocyano (N-bound) isomer, which thermally isomerizes to the cyano isomer, was prepared by reacting [Co(dimethylglyoximate)$_2$(NH$_3$)$_2$]$^+$ with $[Ag(CN)_2]^-$ in water. The C-bound complex, which was first prepared in 1971 [76], also forms when the same diamine complex reacts directly with CN^-.

F. CYANATE (NCO^-)- AND FULMINATE (CNO^-)-CONTAINING COMPLEXES

The coordination chemistry of the cyanate and fulminate ions is similar to that of the cyanide ion in that, despite their potential for ambidentate behaviour, they tend to exhibit only one type of bond (N-bound for cyanates, C-bound for fulminates) when coordinated as monodentate ligands to a transition metal [77]. No crystal structures have been reported [77] that deviate from this pattern. Indeed, no M-ONC structures have been claimed on any basis, and only a few M-OCN structures have been reported on the basis of non-crystallographic evidence [77,78]. The only reported inorganic linkage isomers of the cyanate ion, the cyanato (O-bound) and isocyanato isomers of $[Rh(PPh_3)_3NCO]$ [79], fall into the latter category.

The coordination behaviour of the cyanate ion is entirely in accord with the results of calculations, based on fragment analysis of molecular orbital calculations, reported by Tuan and Hoffmann [78], which predict the greater stability of the M-NCO linkage. Their results also suggest that σ-bonding is the dominant factor in the metal-to-ligand bond.

The preference for N-bonding carries over to the bridged complexes of the cyanate ion, the vast majority of which involve  ${}^{M}_{M}\!\!>\!N{-}C{-}O$ bridging [78]. However, a few crystallographically confirmed examples of  $M{-}N{-}C{-}O{-}M$ bridges have been reported [78]. Another example, $[(H_3N)_5CrNCOCr(NH_3)_5]Cl_5$, has recently been claimed [80], based on a vibrational spectral analysis.

In this context, the strange behaviour of the pentafluorochalcogen cyanates provides a rather bizarre counterpoint [81,82]. As originally synthesized and characterized [81], all three F_5X-NCO (X = S, Se, Te) compounds were described as being isocyanates, as expected. However, a more recent review of the supporting IR and electron diffraction data, coupled with a comprehensive multinuclear NMR study, has led to the conclusion [82] that the selenium derivative actually involves the cyanato structure, F_5Se-OCN. The reason for this discontinuous bonding behaviour is unknown.

(i) Structures determined by single crystal X-ray diffraction

Several significant cyanate- and fulminate-containing structures were reported during the past decade. The presentation of the selected structural data shown in Table 1 follows that utilized by Golub, Köhler, and Skopenko in their monograph [8].

TABLE 1

Selected X-ray structural data for isocyanato and fulminato complexes

Compound	Bond angles (°)		Bond lengths (pm)			Ref.
	MNC	NCO	M-N	N-C	C-O	
[Mn(5,10,15,20-tetraphenylporphinate)$(NCO)_2$]	136.5 133.1	176.5 176.3	193.4 191.8	117.1 116.4	119.3 122.3	[83]
[Co(2,2':6',2"-terpyridyl)$(NCO)_2$]	160.9	178.3	194.9	112.6	119.7	[84]
[Cu(2,2':6',2"-terpyridyl)(NCO)(H_2O)]NO_3	163.1	176.9	NA	114.4	118.6	[85a]
[Cu(2,2':6',2"-terpyridyl)(NCO)(H_2O)]PF_6	153.6	177.0	336.8	115.4	120.4	[85a]
$[n\text{-}Bu_4N]_2$[Cu(4-chloro-1,2-benzoquinone-2-oximate)$_2$(NCO)]NCO	NA (no data given for uncoordinated NCO^-)	NA	185	109	127	[85b]
[Mo(PEt_2Ph)$_3$(O)$(NCO)_2$]	(data given only in supplementary material)					[86a]
[Mo_2(PMe_3)$_4$$(NCO)_4$]	169 172.7	179 179	208.1 206.3	113 121	122 112	[86b]
[$Ru_4(CO)_{12}H_3$(NCO)](N-bridging cyanate)	125.9 127.8	179.3	214.4 215.1	115.3	117.9	[87]
[Ru(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)O(NCO)] ClO_4	165.9	178.6	211.9	115.4	119.6	[88]

Compound	Bond angles (°)		Bond lengths (pm)			Ref.
	MNC	NCO	M-N	N-C	C-O	
$[Pt(CH_2CH_2NH-C{=}O)Cl(NCO)-(N,N,N',N'-tetramethylethylenediamine)]$	147	174	213	111	119	[89]
$[Pt(2,2'-bipyridyl)-(NCO)_2]$	147	170	200	113	123	[90]
$[Au(PPh_3)NCO]$	142.6	177.6	200.6	114.7	118.9	[91]
$[Au(PPh_3)CNO]$	162.9 (AuCN)	NA	193.9 (AuC)	115.4	127.2	[91]

The last two entries in Table 1 are of the greatest significance in the present context. They do not represent linkage isomers; rather, they are structural isomers. They are, in fact, the first pair of cyanate/fulminate structural isomers of a transition metal complex that have been characterized crystallographically. The fulminato complex was obtained [92] by reacting $[Au(PPh_3)NO_3]$ with CO in CH_2Cl_2. The isocyanato complex formed [92] when CO was reacted with solid $[Au(PPh_3)NO_3]$. The N-bridging cyanate group in the tetranuclear ruthenium cluster complex shown in Table 1 was prepared [87] by the reaction of N_3^- with $[Ru_3(CO)_{12}]$, via a rearrangement analogous to the Curtis reaction of acyl halides with azides. This represents the first extension of this reaction to a polynuclear metal carbonyl.

(ii) Cyanate-forming reactions and reactions of coordinated cyanate

Unlike the other pseudohalides, the primary source of which (for complexation purposes) is the free ion, the cyanate group can be introduced into metal complexes by a variety of reactions. Two examples are described in the preceding section. The complex $[LRe(NO)(CO)(NCO)][BF_4]$ (L = 1,4,7-triazacyclononane) is formed [93] when $[LRe(NO)(CO)_2][BF_4]_2$ reacts with a variety of nucleophiles ($N_2H_4 \cdot H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, H_2NOH, and N_3^-) in methanol. The isocyanate in the former complex, in turn, can be converted [93] into a variety of coordinated groups: NH_3, by reaction with HBr in methanol; HCO_2^- and $CF_3SO_3^-$, by reactions with the corresponding acids; methyl- or ethylcarbamates, by reaction with methanol or ethanol in the presence of I^-.

Both isocyanate and isothiocyanate complexes can be formed [94] by the following reaction sequence:

$$2[TiCl_3(THF)_3] + 5\,Mg + N_2 \rightarrow 2[TiNMg_2Cl_2THF] + [MgCl_2(THF)_2] + 2THF \qquad (1)$$

$$[TiNMg_2Cl_2THF] + CX_2 + 2THF \rightarrow [Ti(NCX)(X)Mg_2Cl_2(THF)_3]\ (X = O,\ S) \qquad (2)$$

Kohout and Hvastijová have succeeded [95] in converting [Cu(3-methylpyrazole)$_2$(NCO)$_2$] into its coligand (structural) isomer, [Cu(carbamoylmethylpyrazolate)$_2$].

Cooper and his colleagues have studied [96] the kinetics and mechanism of the acidolysis of the cyanate group in trans-[Co(en)$_2$(NCO)S$_2$O$_3$]. Cobalt(II)-substituted carboxypeptidase A has been found [97] to reversibly bind N_3^- and NCO^-, but not NCS^-, in the pH range 5-10 (including the pH range of activity of the enzyme).

G. THIOCYANATE (NCS^-)- AND THIOFULMINATE (CNS^-)-CONTAINING COMPLEXES

Cogener though it may be, the thiocyanate ion's coordination behaviour differs dramatically from that exhibited by the cyanate ion. Thiocyanate is truly ambidentate, in terms of both its monodentate and bridging bonding capabilities. In their review of the thiocyanate's coordination chemistry, Golub, Köhler, and Skopenko cite [98] ten potential bonding modes for an individual thiocyanate group (12 through 21 in Figure 2).

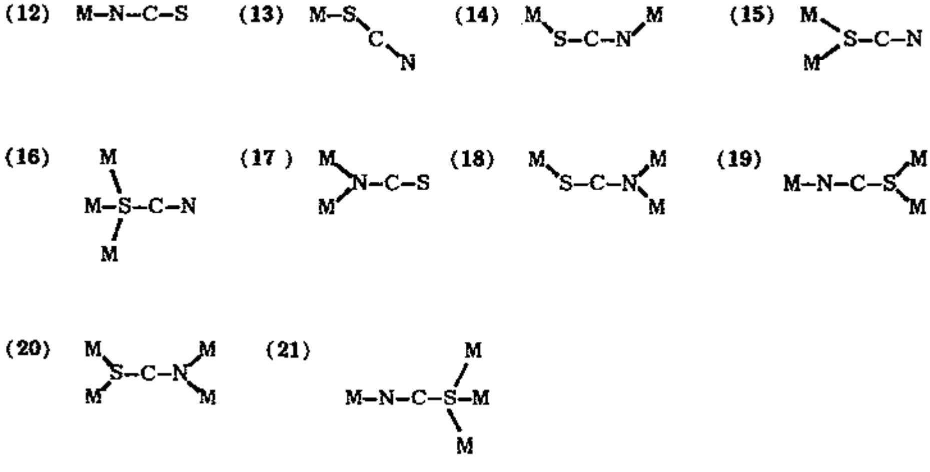


Fig. 2. Types of metal-thiocyanate coordination

If unencumbered by skewing extra-metal bonding mode controls (of which more will be said shortly), the thiocyanate dutifully follows an M(hard)-NCS, M(soft)-SCN monodentate bonding pattern. Consequently, it can function as a convenient test ligand for the relative hardness/softness [99-101] of a Lewis acid bonding site. As a bridging ligand, the thiocyanate ion adopts bond type (**14**) in the vast majority of cases.

Historically, the presence of a thiocyanate ion whose bonding mode is unknown or unspecified has been designated by the notation CNS. Although complexes containing the thiofulminate ion (CNS^-) are very rare, they are not non-existent, e.g., $K_3[Fe(CN)_4(CNS)_2]$, which was synthesized [102] by the reaction of $K_3[Fe(CN)_6]$ with molten sulfur at 200 °C. Consequently, the use of the CNS formalism should be restricted to thiofulminate complexes.

(i) Structures determined by single crystal X-ray diffraction

The relative numbers of M-NCS and M-SCN structures shown, respectively, in Tables 2 and 3, are a consequence of two factors: the substantially larger number of transition metal ions that function as hard Lewis acids and the ever-increasing interest in transition metal complexes that are of significance in the area of bioinorganic chemistry. Although restricted to representative examples that have appeared in the literature during the past decade, thiocyanate complexes of most transition elements are included in the Tables, as well as cases involving some representative elements, a lanthanide, and an actinide.

TABLE 2

Selected X-ray structural data for isothiocyanato complexes (structure type (**12**))

Compound	Bond Angles (°)		Bond Lengths (pm)			Ref.
	MNC	NCS	M-N	N-C	C-S	
$[(Ph_3P)_2N][B_3H_7(NCS)]$	173.7	178.1	152.0	115.4	160.0	[103a]
Cs[*nido*-7-(p-C_6H_4NCS)-9-I-7,8-$C_2B_9H_{11}$] (NCS bound to C in phenyl ring)	168.7	178.1	141.1	113.5	159.6	[103b]
KNCS ·[18]<O_5-(2,2')-benzophenono · 2_4-coronand-5>	NA	178.7	NA	115.3	162.6	[104]
KNCS · (2,3,11,12-(bis-1,2-acenaphtho)18-crown-6	NA	NA	272.7	NA	NA	[105]
KNCS · (dibenzo-18-crown-6)	135	165	280	122	153	[106]
	134	172	269	104	181	
$(KSCN)_3 \cdot 5(O{=}P(NMe_2)_3]$	NA	NA	269	114.2	162.5	[107]
trans-(R,S)-[Cr(1,4,8,11-tetraazaundecane)-$(NCS)_2$]NCS	NA	176.8	198.1	115.9	160.5	[108]
	NA	177.9	197.8	116.0	159.6	
	--	178.6	--	113.6	162.2	
[{Cr(tris(2-pyridylmethyl)-amine)(NCS)}$_2$O]-$[ClO_4]_2 \cdot 0.5H_2O$	168.3	178.6	200.4	NA	NA	[109]
cis-[Mn(2,2'-bipyridyl)$_2$-$(NCS)_2$]	170.7	178.7	207.5	114.4	163.0	[110]
	152.1	175.9	206.4	110.2	168.3	

Compound	Bond Angles (°) MNC	Bond Angles (°) NCS	Bond Lengths (pm) M-N	Bond Lengths (pm) N-C	Bond Lengths (pm) C-S	Ref.
cis-[Mn(N,N-bis(2-benzimidazolylmethyl)ethanolamine)(NCS)$_2$]	NA	NA	214.0	NA	NA	[111]
	NA	NA	210.7	NA	NA	
trans-[Mn(pyrazole)$_4$(NCS)$_2$]	145.2	178.7	220.2	114.1	166.3	[112]
trans-[Mn(H$_2$O)$_4$(NCS)$_2$]	171.9	178.5	213.8	114.6	163.7	[113]
trans-[Mn(2,6-diacetylpyridine-bis(semicarbazone))(NCS)$_2$]	NA	NA	220.9	NA	NA	[114]
trans-[Fe(pyridine)(m-tetraphenylporphinate)NCS]	155.6	177.0	194.2	114.4	160.6	[115]
trans-[Fe(pyridine)(octaethylporphinate)NCS]	176.0	179.6	203.1	115.3	162.6	[115]
trans-[Fe(4-acetylpyridine)$_2$(H$_2$O)$_2$(NCS)$_2$]	177.7	179.8	210.2	113.5	162.2	[116]
trans, cis, cis-[Fe(5-methyl[1,2,4]triazolo[1,5-α]-pyrimidine-N^3)$_2$(H$_2$O)$_2$(NCS)$_2$]	176.7	177.9	210.9	115.8	161.8	[28]
trans-[Fe([1,2,4]triazolo[1,5-α]pyrimidine)$_2$(NCS)$_2$]	158.4	179.0	205.6	115	162	[117]
cis-[Fe(2,2'-bipyrimidine)(NCS)$_2$]$_2$(2,2'-bipyrimidine)	158.2	178.2	207.8	116.8	162.3	[118]
	172.2	179.0	205.1	115.8	161.6	
cis-[Fe(2,2'-bi-2-thiazoline)$_2$(NCS)$_2$]						
(polymorph A)	163.3	177.2	207.9	114.0	160.7	[119]
	178.1	178.6	206.1	113.3	162	
(polymorph B)	160.4	179.6	208.2	115.6	162.1	
	159.8	179.2	208.2	116.3	162.0	
trans-[Co(en)$_2$(NO$_2$)(NCS)][ClO$_4$]	176.0	178.2	190.9	120	164	[53d]
trans-[Co(en)$_2$(NO$_2$)(NCS)]I	170.1	176.3	192.8	118	161	[53d]
trans-[Co(en)$_2$(ONO)(NCS)][ClO$_4$]	173.8	176.3	192.2	116	162	[53d]
trans-[Co(en)$_2$(ONO)(NCS)]I	175.8	178.3	190.3	115	162	[53d]
cis-[Co(2,2'-bipyridyl)$_2$(NCS)$_2$]	168.2	178.0	214.5	116.3	161.3	[110]
	178.1	178.1	216.9	115.7	161.7	
trans-[Co(4-vinylpyridine)$_4$(NCS)$_2$]	173.0	179.2	210.0	117	156	[120a]
	166.4	175.6	204.9	114	165	
cis-[Co(N$_2$H$_5$)$_2$(NCS)$_4$]·2H$_2$O	173.3	178.4	209.1	114.5	164.7	[120b]
	151.9	177.2	209.7	116.2	162.8	
trans-[Co(P(OEt)$_3$)$_4$(NCS)$_2$][BPh$_4$]	176.1	177.8	183.8	112	164	[121]
	178.8	178.4	187.4	113	167	
trans-[Co(2-aminothiazole)$_4$(NCS)$_2$]	158.5	177.9	211.9	116.4	162.6	[122]
	161.8	178.6	210.6	114.9	162.5	
trans-[Co(benzo(1,3)thiazole)$_2$(DMF)$_2$(NCS)$_2$]	155.7	179.4	208.2	114.7	163.3	[123]

Compound	Bond Angles (°)		Bond Lengths (pm)			Ref.
	MNC	NCS	M-N	N-C	C-S	
trans-[Co(4,4'-bis-1,2,4-triazole)$_2$(NCS)$_2$]H$_2$O	154.9	164.5	209.8	115.1	163.5	[26]
[Co$_2$(4-allyl-1,2,4-triazole)$_4$(H$_2$O)(NCS)$_4$]	167.7	179.2	206.9	111.8	163.6	[25]
	166.2	178.1	207.5	115.0	161.3	
	171.0	179.1	208.4	114.0	163.0	
	170.7	179.7	207.5	113.2	164.3	
[Co$_3$(4-t-butyl-1,2,4-triazole)$_8$(NCS)$_4$](NCS)$_2$(H$_2$O)$_9$	151.1	178	210	117	161	[124]
	158.1	177.5	209.1	117	159	
[Co$_3$(3,5-diethyl-1,2,4-triazole)$_6$F$_2$(NCS)$_4$](H$_2$O)$_2$	167.7	177.7	209.0	114.9	163.3	[125]
	168.4	177.9	209.6	114.7	165.0	
[Co$_3$(3,5-dimethyl-1,2,4-triazole)$_4$F$_2$(NCS)$_4$(H$_2$O)$_2$](H$_2$O)$_4$	169.1	NA	208.4	115.2	162.1	[27]
	168.3	NA	207.5	114.2	162.1	
mer-[Co(PMe$_3$)$_3$(NCS)$_3$]	176.2	178.3	196.5	114.7	162.4	[126]
	171.3	179.0	187.7	115.6	161.6	
	170.1	179.0	186.1	114.2	163.9	
trans, cis, cis-[Co(5-methyl[1,2,4]triazolo[1,5-α]pyridine-N3)$_2$(NCS)$_2$(H$_2$O)$_2$]	177.1	177.1	207.0	115.6	162.7	[127]
cis-[Co(1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane)(NCS)$_2$]	150.7	177.7	206.7	112.0	162.0	[31]
	172.9	177.6	204.3	113.6	160.6	
cis[Co(2-pyridinecarboxaldehyde 1-oxide-2'-pyridinylhydrazone)(NCS)$_2$]$_2$	167.5	176.5	204.5	117.4	163.3	[128]
	166.0	179.3	198.4	116.1	161.0	
trans-[Ni(2,6-diacetylpyridine-bis-(semicarbazone)(NCS)$_2$]	NA	NA	200.4	NA	NA	[114]
	NA	NA	201.1	NA	NA	
cis-[Ni(1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane)(NCS)$_2$]	174.1	179.5	202.1	116.0	162.7	[32]
trans-[Ni(4-vinylpyridine)$_4$(NCS)$_2$]·2CHCl$_3$	173.1	179.4	207.7	114.1	159.7	[129a]
	179.4	179.4	206.6	115.1	161.7	
trans-[Ni(o, o,-bis{(dimethylamino)methyl}phenyl)(pyridine)(NCS)$_2$]	168.7	178.3	196.5	116.9	160.0	[129b]
trans-[Ni(N$_2$H$_3$ · CS · NH$_2$)$_2$(NCS)$_2$]	178.1	177.4	207.1	115.8	164.3	[120b]
[Ni(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-N-acetate)(NCS)]H$_2$O	173.5	117.0(?)	209.2	115.8	162.9	[130a]
trans-[Ni$_2$(3-NH$_2$C$_5$H$_4$N)$_4$(H$_2$O)$_2$(NCS)$_4$]·2H$_2$O	NA	178.4	202	115	162	[130b]
	NA	179.0	203	115	164	
[Cu(6-methyl[1,2,4]triazolo[1,5-α]pyrimidine)$_2$(NCS)$_2$]	178.3	178.8	193.1	115.3	161.4	[33]
trans-[Cu(5-methyl[1,2,4]triazolo[1,5-α]pyrimi-	157.6	178.1	192.1	116.1	160.7	[33]

Compound	Bond Angles (°)		Bond Lengths (pm)			Ref.
	MNC	NCS	M-N	N-C	C-S	
dine)$_2$(NCS)$_2$]						
[Cu(2,2'-bipyridyl)$_2$NCS]-NCS	168	178	196.9	116.1	158.4	[131]
trans-[Cu(pyridine)$_2$(NCS)$_2$]	173.2	179.7	194	113	163	[132]
cis-[Cu(1,6-bis(3-5-dimethylpyrazol-1-yl)-2,5-dimethyl-2,5-diazahexane)(NCS)$_2$]	161.9	178.9	206.0	115.8	163.5	[133]
trans-[Cu([1,2,4]triazolo-[1,5-a]pyrimidine-N^3)-(NCS)$_2$]	162.5	179.8	193.5	114.9	161.5	[134]
[Cu(2,2':6',2"-terpyridyl)(NCS)$_2$]	156.6	178.4	202.0	115.7	163.1	[135]
cis-[Cu(1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)(NO$_3$)(NCS)]	NA	NA	196.8	NA	NA	[136]
[Cu(imidazolidine-2-thione)$_2$NCS]	151.9	177.4	195.6	116.1	162.5	[137a]
[Cu(N,N-bis(2-hydroxyethyl)glycinate)NCS]·H$_2$O	163	178	193	112	164	[137b]
[Zn(1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane)(NCS)$_2$]	158	176	201.8	NA	NA	[32]
[Zn(N,N,N-tris(1-pyrazolylmethyl)-amine)(NCS)$_2$]	174.6	179.8	192.7	115.6	162.6	[138]
	149.8	178.6	197.4	108.4	168.7	
[Zn$_2$(1,4,7,10,13,16,19,-22,25,28-decaaza-cyclotriacontane)NCS]-[ClO$_4$]}$_3$	NA	NA	198	NA	NA	[139]
[Zr(2,2'-bi-2-thiazoline)-(NCS)$_4$]	157.3	179.7	215.6	116.0	160.4	[140]
	149.9	178.8	218.3	113.9	161.7	
	174.0	179.1	218.2	116.6	161.1	
	153.6	179.0	216.7	116.2	160.8	
[PPh$_4$]$_2$[Mo(NO)(ONCMe$_2$)-(NCS)$_4$]	NA	NA	219.2 (ax)	NA	NA	[141]
			211.4 (eq)			
[{Mo(O)$_2$(DMSO)$_2$NCS}$_2$O]	NA	NA	209.4	NA	NA	[142]
K$_4$[Mo$_2$O$_3$(NCS)$_8$]·4H$_2$O	168.9	NA	210.4	NA	NA	[143]
	156.0	NA	226.2	NA	NA	
	169.6	NA	208.9	NA	NA	
	160.4	NA	209.7	NA	NA	
[pyridineH]$_5$[Mo$_3$O$_2$S$_2$-(NCS)$_9$]·2H$_2$O	NA	NA	NA	NA	NA	[144]
[Mo$_2$(PMe$_3$)$_4$(NCS)$_4$]	173.3	177.3	208.5	116	159.7	[86b]
	169.3	178.4	207.4	116	159.9	
[Mo$_2$(Ph$_2$Ppyridine)$_2$-(NCS)$_4$] ·2THF-·2 toluene	172.7	177.9	208.4	113.6	162.2	[145]
	172.8	178.9	208.6	114.2	162.7	
trans-[Tc(Ph$_2$P(CH$_2$)$_2$-PPh$_2$)$_2$(NCS)$_2$]	NA	NA	204.7	113	166	[146]
cis-[Ru(2,2'-bipyridyl)$_2$-(NCS)$_2$]·CH$_3$CN	168.2	177.5	205.5	112.4	165.4	[147]
[Pd(tris)(2-dimethyl-	170.7	176.7	198.7	115	164	[148]

Compound	Bond Angles (°)		Bond Lengths (pm)			Ref.
	MNC	NCS	M-N	N-C	C-S	
aminoethylamine)-NCS]SCN						
[Pd(1,1,7,7-tetraethyl-diethylenetriamine)-NCS]X						[39]
X = PF_6^-, unsolvated	173.3	177.0	201.9	114.2	160.8	
X = BPh_4^-, acetone solvate	167.8	179.8	201.9	109.0	164.0	
X = BPh_4^-, unsolvated	164.7	179.0	200.3	114.4	163.2	
X = BPh_4^-, CH_2BrCl-solvate	162.4	178.6	202.6	113.9	162.4	
trans-[Cd(α, α'-bipyridyl)$_2$-(NCS)$_2$]	168.6	178.3	223.9	116.7	161.5	[149]
	153.3	177.7	226.0	115.7	160.7	
[SnMe$_2$(OH$_2$)$_2$(NCS)$_2$]·18-crown-6	163.7	158.2	227.0	111.8	162.8	[150a]
[SnPh$_3$(NCS)(1-[4'-methyl-phenylimino)-methyl]-2-naphthol)]	161.6	178.1	223.0	114.4	160.5	[150b]
[SnPh$_3$(picolinic acid)-NCS]·H$_2$O	172.2	178.2	228.4	115.5	161.0	[151]
[Ba(5,8,11-trioxa-2,14,-dithia[15](2,6)pyridino-phane)(NCS)$_2$]·H$_2$O	155.8	179.2	280.2	115.1	164.1	[152]
	176.3	178.6	280.4	113.6	162.3	
Cs$_3$NH$_4$[W$_4$O$_8$(NCS)$_{12}$]·6H$_2$O	165	172	221	110	160	[153]
	154	173	228	112	168	
	162	172	201	113	170	
	160	174	208	113	163	
	167	176	207	120	157	
	164	171	210	122	153	
	169	174	207	125	155	
	143	156	210	140	162	
	173	168	207	129	146	
	172	170	224	111	161	
	168	168	241	108	147	
	155	167	211	123	155	
[AsPh$_4$]$_2$[Re$_2$(NCS)$_8$]-·2Me$_2$CO	172	178	200.3	112	161.6	[154]
	174	179	200.5	114.7	161.1	
	173	179	201.3	118	156.0	
	171	179	199.4	115	160.9	
[AsPh$_4$]$_2$[Re$_2$(NCS)$_8$]-·2C$_5$H$_5$N	168.4	178	200.5	113	162	[154]
	162	180	198.6	116	160.3	
	174	179	200.0	116	160	
	166	179	199.2	115	160.4	
[Dy(O$_2$P(OCH$_3$)CH$_2$C(O)N-(C$_2$H$_5$)$_2$)$_2$(NCS)]	164.6	178.1	243.3	116.4	162.4	[155]
[U(N,N-diisopropyl-acetamide-O)$_4$(NCS)$_4$]-·CH$_2$Cl$_2$	168	177	244.4	113	162	[156]
[NEt$_4$][U(2,2'-bipyridyl)$_2$-(NCS)$_5$]	155	178	235	113	172	[157]
	174	174	238	115	164	
	161	178	240	115	159	
	163	177	236	117	161	
	165	179	247	110	160	

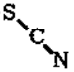
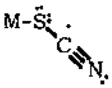
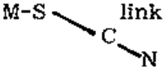
The data shown for the isothiocyanate complexes in Table 2 are remarkably homogeneous, considering the wide range of metals, oxidation states, coordination numbers, and coordination geometries involved. Indeed, the M-N bond length is the only property that exhibits significant variation throughout the entire compilation. (The strange NCS bond angle shown for the sixth Ni complex must be a misprint in the original paper.) Otherwise, each of the metal-thiocyanate structures involved can be reasonably well represented by the simple canonical structure $\mathrm{M{-}N{\equiv}C{-}\overset{..}{\underset{..}{S}}}$:. The palladium complexes shown represent the only deviations from the M(hard)-NCS bonding pattern in the entire Table. In these cases, the thiocyanates are being forced to adopt the linear Pd-NCS bonding mode (rather than the normal non-linear Pd(soft)-  bonding mode) by the steric hindrance created by the terminal alkyl groups on the amine ligands. This effect will be addressed in greater detail in a later section of this paper.

TABLE 3

Selected X-ray structural data for thiocyanato complexes (structure type (**13**))

	Bond angles (°)		Bond lengths (pm)			
Compound	MSC	SCN	M-S	S-C	C-N	Ref.
[Fe(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)$(SCN)_2$]-$[PF_6]$	104.0	179.7	232.8	167.7	114.8	[158]
[Co(pyridine)-(phthalocyaninate)(SCN)]	106.9	175.6	226.9	163.6	115.2	[159]
$[N(PPh_3)_2]_2[Rh_5(\mu\text{-}CO)_6(CO)_8(SCN)]$	NA	NA	258.2	160	121	[160]
[Pd(1,1,7,7-tetraethyldiethylenetriamine)(SCN)]-$[BPh_4]\cdot HOCH_3$	100.7	178.1	232.8	166.2	114.8	[39]
trans-[Pd(N-methyl-O-ethylthiocarbamate)$_2$-$(SCN)_2$]	109.7	176.0	233.1	166.9	114.7	[161a]
trans-$[Pd(Te(CH_2CH_2CH_2SiMe_3)_2)_2(SCN)_2]$	110.4	176	231.0	158	116	[161b]
$[N(PPh_3)_2][Ir_4(\mu\text{-}CO)_3(CO)_8(SCN)]$	106.0	172.2	242.2	158	109	[162]
$[Pt_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3(SCN)][PF_6]\cdot 2\text{-}Me_2CO$	111.5	179.8	265.6	155.3	118	[163a]

	Bond angles (°)		Bond lengths (pm)			
Compound	MSC	SCN	M-S	S-C	C-N	Ref.
[Pt(5,7-dimethyl-[1,2,4]triazolo-[1,5-α]pyrimidine-N^3)][Pt(SCN)$_6$]	94.6	173	231	170	108	[163b]
	92.1	178	235	167	109	
	95.5	170	237	166	118	
[Pt{PhTe(o-(PPh$_2$-C$_6$H$_4$))}$_2$][Pt(SCN)$_4$]·2DMF	107.3	172.2	232.3	166.1	113	[163c]
	110.2	166.6	231.2	165.9	110	
[Au(PPh$_3$)$_2$SCN]	NA	NA	234.8	NA	NA	[164]
[Au(PPh$_3$)$_3$SCN]·-H$_2$O						
(orthorhombic)	99.7	174.0	293.8	170.1	120.3	[165]
(monoclinic)	105.2	175.4	279.1	157.7	119.9	[164]

In like manner, the variation in the metal-thiocyanate bond lengths excepted, the thiocyanate bonding environments compiled in Table 3 can also reasonably be represented by one simple cannonical structure:  . As already has been noted, the dichotomy between the linear (or almost linear) M-N-C-S linkage and the sharply bent  linkage produces a steric sensitivity that has long been known to be sufficient to alter the normal M(soft)-thiocyanate-S bonding pattern, e.g., [Pd(diethylenetriamine)SCN]$^+$ versus [Pd(1,1,7,7-tetraethyldiethylenetriamine)NCS]$^+$ [166]. The reason for the latter cation's crystallizing as an S-bound species as a tetraphenylborate salt solvated by methanol has already been described in Section B.

The iron and cobalt complexes deviate dramatically from the normal M(hard)-NCS bonding pattern. The S-bonding observed for both cannot be ascribed in any reasonable way to steric factors within the coordination spheres of the metals. Electronic control by the macrocycles is most probably operative in both cases, although it should be noted that the synthesis of the iron complex is facilitated by the use of an acidic medium, which would tend to stabilize the formation of the Fe-SCN bond by hydrogen-bonding to the nitrogen [158].

Half of the eight possible thiocyanate bridging bonding modes shown in Fig. 2 are exemplified by the structures cited in Table 4, with the vast majority involving μ-S,N-two metal atom bridging (structure type **14**).

TABLE 4

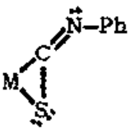
Selected examples of thiocyanate-bridged complexes, confirmed by X-ray diffraction studies

Compound	Structure type	S-bound metal atom(s)	N-bound metal atom(s)	Terminal thiocyanates	Ref.
[(DMF)$_2$Co(NCS)$_4$Hg]	14	Hg	Co	-	[167]
[Ni(2-aminopyridine)$_2$(NCS)$_2$]•Et$_2$O	14	Ni	Ni	-	[130b]
[Cu$_2$(catena(1,6-bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane-2N^{3}S^{2}S^5)(NCS)$_3$]	14	Cu	Cu	-	[30]
ß-[CuNCS]	14	Cu	Cu	-	[168]
[Cu$_2$(PPh$_3$)$_4$(NCS)$_2$]	14	Cu	Cu	-	[169]
[Cu(2,6-dimethylpyridine)-NCS]	14	Cu	Cu	-	[170]
[CuL$_2$NCS]					[170]
(L = 2-methylpyridine)	14	Cu	Cu	-	
(L = 3-methylpyridine)	14	Cu	Cu	-	
(L = 4-methylpyridine)	14	Cu	Cu	-	
(L = 2,4-dimethylpyridine)	14	Cu	Cu	-	
(L = quinoline)	14	Cu	Cu	-	
[Cu$_2$(N,N-bis(3,5-dimethyl-1-pyrazolylmethyl)-aminobenzene)(NCS)$_3$]	14	Cu	Cu	-	[171]
[Cu(4-bromopyridine)$_2$(NCS)$_2$]	14	Cu	Cu	-	[172]
[Cu(tetrathiafulvalene)(NCS)$_2$]	14	Cu	Cu	-	[173]
ß$_m$-[Cu$_2$(bis(ethylenedioxy)-tetrathiafulvalene)$_3$(NCS)$_3$]	14	Cu	Cu	-	[174]
[(5,7-dimethyl[1,2,4]triazolo-[1,5-*a*]pyrimidine)$_2$-Cu(NCS)$_3$Hg]	14	Hg	Cu	-	[175]
[Cd(trans-(6,8-dimethyl-[1,2,4]-triazolo[3,4-b]-pyridazine-N^2)$_2$(NCS)$_2$]	14	Cd	Cd	-	[29]
[Cd$_2$(1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithia-octane)(NCS)$_4$]	14	Cd	Cd	-	[32]
[Cd(P(m-tolyl)$_3$)(NCS)$_2$]	14	Cd	Cd	-	[176]
[Hg$_2$(hexamethylenetetramine)(SCN)$_4$]	14	Hg	Hg	-	[177]
[Hg(hexamethylenetetramine)-(SCN)$_2$]	14	Hg	Hg	-	[178]
[Pb(2,2':6',2''-terpyridyl)-(NCS)$_2$]	14	Pb	Pb	-	[179]

Compound	Structure type	S-bound metal atom(s)	N-bound metal atom(s)	Terminal thio-cyanates	Ref.
[{Cu_2(5,7-dimethyl[1,2,4]-triazolo[1,5-α]-pyrimidine-N^3)$_4$(NCS)$_4$]	14, 12	Cu	Cu	Cu-NCS	[163b]
ß-[Cu-(bis(5,7-dimethyl-[1,2,4]triazolo[1,5-α]-pyrimidine)$_2$(NCS)$_2$]	14, 12	Cu	Cu	Cu-NCS	[180]
[(5,7-dimethyl[1,2,4]triazolo-[1,5-α]pyrimidine)$_3$-Co(NCS)$_4$Hg(H_2O)]$_2$	14, 13	Hg	Co	Hg-SCN	[181]
[(5,7-dimethyl[1,2,4]triazolo-[1,5-α]pyrimidine)$_2$-Fe(NCS)$_4$Hg(H_2O]	14, 13	Hg	Fe	Hg-SCN	[182]
[NEt_4]$_3$[Cu_4(NCS)$_5$$WS_4$]	14 19	Cu Cu, Cu	Cu Cu	-	[183]
[N(n-Bu)$_4$]$_3$[Re(NCS)$_{10}$]	17, 12	-	Re, Re	Re-NCS	[37]
[24<O_5-$2_{4\bullet}$[(4',4")-1,8-diphenylnaphthalenol]-coronand-5>•KNCS]$_2$	17	-	K, K	-	[184]
[Ni_3(3,5-diethyl-1,2,4-triazole)$_6$(NCS)$_6$(H_2O)]$_2$	17, 12	-	Ni, Ni	Ni-NCS	[185]
[Co_2L(OEt)(NCS)$_3$] (see ref. 186 for structure of L)	17, 12	-	Co, Co	Co-NCS	[186]
[Cu_2L(SCN)$_2$] (see ref. 186 for structure of L)	15	Cu, Cu	-	-	[187]
[Cu(2-methylpyridine)NCS]	19	Cu, Cu	Cu	-	[170]
[Pb(1,10-phenanthroline)-(NCS)$_2$]	19	Pb, Pb	Pb	-	[179]

It should be noted, in passing, that the $ß_m$[Cu_2(bis(ethylenedioxy)tetrathiafulvalene)$_3$(NCS)$_3$] complex shown in Table 4 is the first ambient pressure organic superconductor containing oxygen in the donor molecule ever discovered [174].

In addition to the ten anticipated [98] bonding modes for the thiocyanate ligand shown in Fig. 2, a new bonding mode has been discovered during the past decade: η^2-C,S (sidewise) bonding. Thus far, this type of bonding has not yet been observed for the thiocyanate ion itself. The examples shown in Table 5 all involve phenyl isocyanate (Ph-NCS) molecules bonded to metals in this manner:



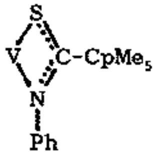
(22)

TABLE 5

Examples of η^2-C,S (sidewise, structure 22) bonded thiocyanate complexes confirmed by X-ray diffraction studies

Compound	Bond angles (°)		Bond distances (pm)				Ref.
	CMS	NCS	MC	MS	NC	CS	
[Ni(1,1,1-tris((diphenylphosphino)methyl)ethane)(SCNPh)]•0.5 CH_2Cl_2	46.9	141.8	188	225.9	126	168	[188]
[Co(tris(2-(diphenylphosphino)ethyl)amine)(SCNPh)]•1.33 C_4H_9OH	48.9	141.1	187	222.0	127	172	[188]
[V(η^5-C_5Me_5)$_2$V(SCNPh)]	44.7	138.6	204.2	244.4	126.5	174.5	[189]

The vanadium complex is thermally labile, and undergoes [189] a thermal transformation with the migration of the thiocyanate carbon atom to one of the C_5Me_5 rings, yielding a four-membered ring:



(23)

As expected, the NC bond lengths in the complexes shown in Table 5 are significantly longer than those observed for M-NCS or M-SCN complexes (Tables 2 and 3).

(ii) <u>The electronic/steric controversy in thiocyanate bonding mode control</u>

There yet remains one group of thiocyanate-containing complexes whose structures have been confirmed by single crystal X-ray diffraction: the geminites. For reasons which will become apparent, this group will be spotlighted in this section.

As noted in the previous section, the existence of steric control of the thiocyanate's bonding mode is incontrovertible [166], and numerous, clear-cut examples have surfaced since the effect was first discovered. Likewise, the existence of electronic thiocyanate bonding mode control, both by metals (as noted in the previous section) and by other ligands is equally certain, e.g., $[Co(NH_3)_5NCS]^{2+}$ versus $[Co(CN)_5SCN]^{3-}$ [190], and both symbiotic [191] and anti-symbiotic [192] trends have been confirmed. Ironically, the first discovery [193] of the fact that the normal M(hard)-NCS/M(soft)-SCN bonding pattern could be altered by the presence of other ligands in the coordination sphere is still the subject of debate, insofar as the precise nature of the bonding mode control is concerned. The problem stems from the fact that the S- to N-bound switch observed by Turco and Pecile for trans-$[Pd(NH_3)_2(SCN)_2]$ versus trans-$[Pd(PEt_3)_2(NCS)_2]$ could be explained either on the basis of the greater steric crowding created by the PEt_3 groups or (as Turco and Pecile did initially) on the basis of the greater π-acidity of the PEt_3 molecules (as compared to -SCN). The same dichotomy exists in the series (all trans) $[Pd(ZPh_3)_2(\text{thiocyanate})_2]$ (Z = P, As, Pd-NCS; Z = Sb, Pd-SCN) that led to our synthesis [3,194] of the first linkage isomers of the thiocyanate ion. The $SbPh_3$ molecule creates the largest amount of space for the bent M-SCN linkage and is, presumably, the weakest π-acid of the three ZPh_3 ligands.

The problem has been compounded by a growing realization that PPh_3 is most probably not the strong π-acid type ligand that it was originally thought to be. For example, a recent photoelectron spectroscopic study [195] of the complexes $[W(CO)_5(PMe_nPh_{3-n})]$ has revealed that PPh_3 is a stronger Lewis base than PMe_3.

In 1975, Palenik, et al. published the results of a single crystal X-ray diffraction study [196] that appeared to settle the controversy on the side of steric control by the phosphines. They argued, convincingly, that the thiocyanate bonding mode changes observed [196] in the series $[Pd(Ph_2P(CH_2)_nPPh_2)(\text{thiocyanate})_2]$ were attributable solely to the increasing steric hindrance of the phenyl groups that accompanied the widening of the P-Pd-P angle: n = 1, 73.3°, $(SCN)_2$; n = 2, 85.1°, (SCN)(NCS) geminite; n = 3, 89.3°, $(NCS)_2$. In retrospect, these results appear to have been too true, i.e., ideal, to be good.

We have recently completed a major X-ray crystallographic study [35] of complexes of this type. The results are shown in Table 6, along with pertinent additional data drawn from the recent literature.

TABLE 6

Selected X-ray crystallographic data for <u>cis</u>-[Pd(diphosphine)(thiocyanate)$_2$] complexes

Diphosphine	Bonding modes	Bond angles (°)				Ref.
		PPdP	MNC	SCN	MSC	
$Ph_2PCH_2PPh_2$	S,S	73.3	-	177.8	108.0	[196]
			-	177.6	108.5	
$Ph_2P(CH_2)_2PPh_2$	N,S	85.1	163.5	178	-	[196]
			-	175	115.5	
$Ph_2PCH{=}CHPPh_2$	S,S	85.4	-	177.4	117.0	[35]
			-	174.1	107.6	
$Ph_2PCH{=}CHPPh_2$	N,S	85.4	167.5	175.9	-	[35]
			-	174.1	107.6	
o-bis(diphenyl-phosphino)-benzene	N,S	86.0	162.1	176.0	-	[35]
			-	179.4	103.2	
o-bis(diphenyl-phosphino)-benzene	S,S	86.2	-	176.9	102.6	[35]
			-	176.1	106.2	
$Ph_2P(CH_2)_3PPh_2$	N,S	89.0	171.2	179.0	-	[35]
			-	173.1	107.3	
$Ph_2P(CH_2)_3PPh_2$	N,N	89.3	165.0	179.4	-	[196]
			165.0	179.4	-	
$Ph_2PCH_2C(CF_3){=}CHPPh_2$	S,S	90.6	-	NA	NA	[197]
			-	NA	NA	
(1,3,4-trimethyl-phosphole)$_2$	S,S	91.3	-	176.9	105.9	[198]
			-	176.9	105.9	
$Ph_2P(CH_2)_3NMe_2$	N,S	92.4	177.7	NA	-	[199]
			-	NA	NA	
$Ph_2P(CH_2)_4PPh_2$ (grown from CH_3NO_2)	N,S	92.8	163.8	178.1	-	[35]
			-	176.0	104.1	
$Ph_2P(CH_2)_4PPh_2$ (grown from CH_2Cl_2	N,S	92.9	163.6	179.0	-	[35]
			-	173.1	107.3	
(1-phenyl-3,4-dimethyl-phosphole)$_2$	N,S	94.5	171.0	178.8	-	[200]
			-	176.3	102.8	
(α,α'-bis(diphenyl-phosphino)-o-xylene	N,S	100.7	155.7	178.5	-	[35]
			-	173.7	101.3	

Diphosphine	Bonding modes	Bond distances (pm) M-N	N-C	C-S	M-S	Ref.
$Ph_2PCH_2PPh_2$	S,S	-	113.5	167.2	236.6	[196]
		-	113.4	163.6	236.2	
$Ph_2P(CH_2)_2PPh_2$	N,S	206.2	107.8	164.5	-	[196]
		-	116.0	165.3	236.4	
$Ph_2PCH{=}CHPPh_2$	S,S	-	113.0	163.8	244.8	[35]
		-	113.1	164.2	236.9	
$Ph_2PCH{=}CHPPh_2$	N,S	191.3	113.0	164.1	-	[35]
		-	113.1	164.2	236.9	
o-bis(diphenylphosphino)-benzene	N,S	202.0	114.4	164.0	-	[35]
		-	110.7	168.1	238.6	
o-bis(diphenylphosphino)-benzene	S,S	-	116.5	162.3	240.2	[35]
		-	115.5	165.2	237.9	
$Ph_2P(CH_2)_3PPh_2$	N,S	203.6	114.6	161.9	-	[35]
		-	113.7	165.0	237.0	
$Ph_2P(CH_2)_3PPh_2$	N,N	205.5	115.1	161.6	-	[196]
		205.5	115.1	161.6	-	
$Ph_2PCH_2C(CF_3){=}CHPPh_2$	S,S	-	NA	NA	237.1	[197]
		-	NA	NA	236.9	
(1,3,4-trimethylphosphole)$_2$	S,S	-	114	167.7	238.2	[198]
		-	114	167.7	238.2	
$Ph_2P(CH_2)_3NMe_2$	N,S	206.3	NA	NA	-	[199]
		-	NA	NA	229.5	
$Ph_2P(CH_2)_4PPh_2$ (grown from CH_3NO_2)	N,S	204.5	114.6	162.3	-	[35]
		-	113.5	167.3	236.8	
$Ph_2P(CH_2)_4PPh_2$ (grown from CH_2Cl_2)	N,S	203.6	114.6	161.9	-	[35]
		-	113.7	165.0	237.0	
(1-phenyl-3,4-dimethylphosphole)$_2$	N,S	203.0	115.1	161.9	-	[200]
		-	113.7	165.1	238.5	
(α,α'-bis(diphenylphosphino)-*o*-xylene)	N,S	206.1	114.4	162.9	-	[35]
		-	115.1	159.4	238.0	

An extrapolation of the trend observed by Palenik, *et al*. [196] leads to the prediction that, for similarly constituted *cis*-diphosphines, as the PPdP angle is increased beyond the 89.3° observed for the $Ph_2P(CH_2)_3PPh_2$ derivative, both thiocyanates should remain N-bonded. The data in Table 6 clearly show that this is *not* the case. Indeed, the di-N-bound complex reported by Palenik, *et al*. is the *exception*, not the rule. In fact, as shown in Table 6, we have synthesized and characterized the geminite complex of $Ph_2P(CH_2)_3PPh_2$ as well, and it is the *geminite* structure (mono-S-, mono-N-bound) that is the *rule*, rather than the exception, for the vast majority of the complexes shown. This has led us to the conclusion [35] that there is a *conjunctive response* of the two thiocyanate groups to steric hindrance. The N,S-geminite configuration minimizes interaction with bulky substituents on other ligands *and* with each other. The S-bound thiocyanates in the geminites are almost invariably tilted toward the isothiocyanate, and often use the angular nature of the Pd-SCN bond to tilt up to 73° out of the coordination plane to further minimize steric interactions. Since electronic effects on the thiocyante's bonding mode would be even less important in *trans*-diphosphine complexes, whereas steric effects would be more important (since each thiocyanate is flanked by the other ligand), it seems reasonable to conclude, in agreement with Palenik [196], that the latter is dominant in the first series of complexes [193,194] that spawned the controversy.

The impact of steric hindrance in *cis*-[Pd(diamine)(thiocyanate)$_2$] complexes has also been delineated more clearly by our group [201]. A nitrogen-bonded thiocyante can even be forced [202] on the very soft Au(III) center by steric constraints, e.g., $[Au(S_2CN(CH_2CH_2N(C_2H_5)_2)_2)(SCN)_2]$ (di-S-chelated dithiocarbamate, di-S-bound thiocyanates) *versus* $[Au\{((C_2H_5)_2NCH_2CH_2)_2NCS_2\}NCS]SCN$ (triply-N-chelated dithiocarbamate, one N-bound thiocyanate, one ionic thiocyanate).

(iii) Electronic bonding mode control by other ligands in the coordination sphere and solvent bonding mode control

Two different families of complexes have proved to be fertile proving grounds for measuring the type and extent of electronic bonding mode control of the thiocyanate ion by other ligands in the coordination sphere: *trans*-[Co(dimethylglyoximate)$_2$L(thiocyanate)] [16] and [LAu(thiocyanate)] [203]. The mutual *trans*-disposition of the L ligands and the thiocyanate, with a sterically constant intervening barrier (the hydrogen-bonded dimethylglyoximate rings in the cobaloximes, nothing (except solvent molecules) in the linear Au(I) complexes) permits the isolation of electronic effects.

A symbiotic [191] bonding trend was observed [16] for the cobaloximes, the Co-SCN/Co-NCS ratio *decreasing* as the *trans*-influence of L decreased. As expected, an anti-symbiotic [192] bonding trend was noted [203] for the Au(I) complexes, the Au-SCN/Au-NCS ratio *increasing* as the *trans*-influence of L decreased. Solvent effects on the M-SCN/M-NCS ratio were noted [16,203] in both studies, as well as in a more recent study of ours [204] involving $[Pd(diphosphine)(thiocyanate)_2]$ complexes. Unfortunately, an over-all rationale of the observed solvent-dependent behaviour remains elusive.

(iv) Molecular engineering utilizing the μ^2-N,S bridging capability (structure type 14) of the thiocyanate

The ability of the thiocyanate ion to simultaneously bond to two metals via its terminal atoms, coupled with the disparate soft/hard bonding propensities of, respectively, the S and N atoms, has been utilized to produce a kaleidoscopic array of polynuclear complexes. Both the cyanide and selenocyanate ions have been employed in like manner. The research groups of P. P. Singh and Uson have been particularly active in this area.

Singh has written a comprehensive review [205] of the synthesis, characterization, and reactivity of these heteronuclear, polymetallic, pseudohalide-bridged complexes. The simplest of these complexes [205] are of the type $>M(NCS)_2M'(SCN)_2<$, where M is a hard Lewis acid, e.g., Co(II); M' is a soft Lewis acid, e.g. Hg(II); and no other ligands are present. Starting from this prototype, the subsequent synthetic evolution has followed several paths, including these recent examples: reaction of the complexes of the type shown with a variety of neutral Lewis bases [206,207], mixed pseudohalide bridges, e.g., $>M(NCS)(NCSe)M'(SCN)(SeCN)<$ [208] and $>M(N_3)_2M'(SCN)_2<$ [209] and their reaction with Lewis bases; replacement of terminal pseudohalides by alkyl groups on the M' atom [210,211]; extension to trimetallic compounds, e.g., $[Fe(C_5H_4HgSCN)_2M(NCS)_2]$ [212].

Uson and his colleagues have concentrated their efforts in the area of single-bridged polynuclear pseudohalide complexes of the noble metals. For example, by reacting $[MR_2(THF)_2]$ or $[PtR_2(CO)_2]$ (M = Pd, Pt; R = C_6F_5) with monomeric Pd(II) complexes containing one potentially bridging ligand (CN^-,SCN^-), homo- or hetero-, bi- or trinuclear single bridged complexes can be synthesized [213].

Utilizing this chemistry, they have succeeded [213] in synthesizing bridged linkage isomers of the cyanide ion:

$$\textit{cis}\text{-}[\mathrm{Pd(C_6F_5)_2(THF)_2}] + 2\ \textit{trans}\text{-}[\mathrm{Pd(CN)(C_6F_5)(PPh_3)_2}] \xrightarrow{-2\mathrm{THF}} \textit{cis}(\mathrm{C_6F_5})_2\mathrm{Pd}[(\mu\text{-NC})\textit{trans}\text{-}\mathrm{Pd(C_6F_5)(PPh_3)_2}]_2 \qquad (3)$$

$$[\mathrm{NBu_4}]_2[\textit{cis}\text{-}\mathrm{Pd(CN)_2(C_6F_5)_2}] + 2\ \textit{trans}\text{-}[\mathrm{Pd(OClO_3)(C_6F_5)(PPh_3)_2}] \longrightarrow \textit{cis}\text{-}(\mathrm{C_6F_5})_2\mathrm{Pd}[(\mu\text{-CN})\textit{trans}\text{-}\mathrm{Pd(C_6F_5)(PPh_3)_2}]_2 \qquad (4)$$

In our laboratory, single-bridged complexes of the type *trans*-[(L)Co(dimethylglyoximate)$_2$-X-Co(dimethylglyoximate)$_2$X] have been synthesized [214] by the reaction between *trans*-[Co(dimethylglyoximate)$_2$(L)Y] and X in a variety of solvents (L = PPh_3, $AsPh_3$, $SbPh_3$; X = SCN^-, $SeCN^-$; Y = Cl^-, Br^-). The magnetic properties of both linear chain, e.g., [Mn(pentane-2,4-dionate)$_2$NCS] [215] and zig-zag chain, e.g.,[M(2,2'-bipyridyl)$(NCS)_2$] (M = Mn, Co, Fe) [216] thiocyanate-bridged polymers have been studied extensively.

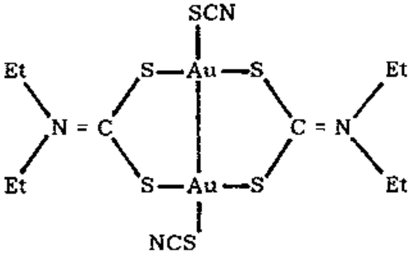
(v) Other factors initiating linkage isomerization of the thiocyanate ligand

Studies carried out during the past decade have revealed or expanded upon a number of additional thiocyanate bonding mode controls. Mares, Palmer, and Kelm [217] investigated the linkage isomerization of [Pd(1,1,7,7-tetraethyldiethylenetriamine)SCN]$^+$ as a function of pressure in both water and DMF. The negative activation volumes observed (-10.1 cm^{3}mol^{-1} and -9.5 cm^3 mol^{-1}, respectively) are in accord with the expectations derived from the mechanism previously proposed for this reaction [218, 219].

Wei and Ho [220] induced partial linkage isomerization in a unique manner by irradiating $[Fe(NCS)_4]^{2-}$ with γ-rays. Some Fe-SCN bonding was also observed [220] to form when $[^{57}Co(NCS)_4]^{2-}$ undergoes electron capture. Photolysis of $[Co(CN)_5X]^{n-}$ (X = CN^-, N_3^-, Cl^-, Br^-, I^-, OH^-, H_2O) in slightly acidic aqueous thiocyanate solution has been found [221] to produce the linkage isomers of $[Co(CN)_5\text{thiocyanate}]^{3-}$, with a ca. nine-fold excess of the Co-SCN isomer. Thermal anation produces only a ca. four-fold excess of this isomer.

(vi) Reactions with thiocyanogen, $(SCN)_2$

Although the source of thiocyanate is usually a salt of the ion, the ligand can also be introduced into the coordination sphere by oxidative addition reactions with thiocyanogen. We have used this to good advantage with a variety of metal substrates, most recently with complexes of Au(I), e.g., $[Au(PMe_3)(CN)]$ [222] and $[Au_2$(N,N-dialkyldithiocarbamate)$_2]$ [223]. The former reaction produced the square planar Au(III) complex *trans*-$[Au(PMe_3)(CN)(SCN)_2]$. The latter reaction yielded the first example of a completely S-bound complex of Au(II):



(24)

Compound (**24**) thermally disproportionates [223] to form the Au(III)/Au(I) salt $[Au$(N,N-diethyldithiocarbamate)$_2][Au(SCN)_2]$. Benzyl and *para*-substituted benzylcobaloximes react [224] with $(SCN)_2$ in the dark under anaerobic conditions to give a variety of organic products: thiocyanates, isothiocyanates, bibenzyl, and the benzyl ether of dimethylglyoxime.

(vii) Reactions of bound thiocyanate

The reaction of KNCS and 48% HF with $Fe(OH)_3$ in the presence of H_2O_2 has been found [225] to produce $K_3[Fe(SO_4)F_4]$. In a quite different series of reactions, Balch and his colleagues [226] have shown that phenyl and methyl isothiocyanate react with $[Pd_2(Ph_2PCH_2PPh_2)_2Cl_2]$ to yield $[Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}CNR)Cl_2]$; some $[Pd_2(Ph_2PCH_2PPh_2)_2\ (\mu\text{-}S)Cl_2]$ is formed in the process. Dash, *et al*. have studied [227,228] the thermal decomposition of cobaloximes containing imidazoles and thiocyanate as the axial ligands. House and Jepsen [229a] have carried out a similar study with $[Co(NH_3)_5H_2O][Cr(NCS)_6]$, as has Brown [229b] with $[Ti(C_5H_5)_2(NCS)_2]$.

The products of photolysis reactions of coordinated thiocyanate are markedly solvent-dependent. Both $[Cr(NCS)_6]^{3-}$[230] and *trans*-$[Cr(NH_3)_4(CN)NCS]^+$ [231] undergo photolytically-induced aquation in water, whereas the photolysis of $[Co(CN)_5NCS]^{3-}$ in CH_2Cl_2 produces [232] the thiocyanate-bridged complex $[Co_2(CN)_{10}NCS]^{5-}$.

(viii) *Kinetics and mechanisms of reactions involving the thiocyanate ion*

Kinetic studies executed during the past decade have produced a huge amount of detailed information pertaining to reactions involving the thiocyanate group. Although theoretically within the scope of this review, spatial constraints preclude an analysis of the results and the voluminous mechanistic interpretations they have spawned. Instead, I shall have to content myself with a representative listing of the various reactions, by type, that have been studied, thereby providing the reader with facilitated access to the literature covering this fascinating, albeit complicated, subject. In so doing, I am ignoring a sizable number of papers involving reactions wherein thiocyanate is merely a passive participant.

(a) *Substitution reactions: thiocyanate as leaving group*. Alkaline hydrolysis of *cis*- and *trans*-$[Co(H_2NCH_2CH_2NH_2)_2(NCS)X]^{n+}$ [233], as well as *p*- and *t*-$[Co(N(CH_2CH_2NH_2)_3)(NH_3)SCN]^{2+}$ [234]; Hg(II)- and Ag(I)-catalyzed reactions of *t*-$[Co(N(CH_2CH_2NH_2)_3)(NH_3)SCN]^{2+}$ [235].

(b) *Substitution reactions: thiocyanate as entering group*. Substrates: $[M($*meso*-tetrakis(*p*-sulfonatophenyl)porphine$)(H_2O)_2]^{3-}$ (M = Cr(III) [236], Rh(III) [237]), $[Pd($*o*-$MeXC_6H_4PPh_2)Y_2]$ (X = S, Se; Y = SCN^-, I^-; reaction involves demethylation to form MeSCN as byproduct) [238], [Co(*meso*-tetrakis(N-methyl-4-pyridyl)-porphine) $(H_2O)_2]^{5+}$ [239], $[Fe(H_2O)_6]^{3+}$ [240], $[Mo_2(H_2O)_8]^{4+}$ [241], $[Mo_3O_4(H_2O)_9]^{4+}$ [242,243], $[V(H_2O)_6]^{2+}$ [244], $[FeX_4]^-$ (X = Cl^-, Br^-) [245], $[Co(NH_3)_5X]^{n+}$ (base hydrolysis; X = OSO_3^{2-}, I^-, ONO_2^-,

$O_3SCH_3^-$, $O_3SCF_3^-$, $OClO_3^-$, $OS(CH_3)_2$, $OP(OCH_3)_3$, $OC(NH_2)_2$, $OC(NH_2)N(CH_3)_2$) [246], $[Co(NH_3)_5OH_2]^{3+}$ [247], $[Co(NH_3)_5X]^{n+}$ (acid hydrolysis; X = fourteen different ligands) [248], (μ-peroxo)bis[(bis(salicylaldehyde)ethylenediiminato)-Co(III)] [249], $[Au(NH_3)_4]^{3+}$, trans-$[Au(NH_3)_2Cl_2]^+$, and trans-$[Au(NH_3)_2Br_2]^+$ [250].

(c) Redox reactions: inner sphere pathways with bridging thiocyanates. Oxidant/reductant: $[Co(NH_3)_5NCS]^{2+}$/Pt, Au, Ag, and Hg electrodes [251], cis-$[Co(H_2NCH_2CH_2NH_2)_2(NCS)_2]^+$ (dibridged)/Pt, Au, Ag, and Hg electrodes [251], $[Cr(NH_3)_5NCS]^{2+}$/Ag and Hg electrodes [252], $[Cr(OH_2)_5NCS]^{2+}$/Ag and Hg electrodes [252], cis-$[Cr(OH_2)_4(NCS)_2]^+$ (dibridged)/Ag and Hg electrodes [252], fac-$[Cr(OH_2)_3(NCS)_3]$ (dibridged)/Ag and Hg electrodes [252], $[Cr(NCS)_6]^{3-}$/Ag and Hg electrodes [252], cis-$[Cr(H_2NCH_2CH_2NH_2)_2(NCS)_2]^+$/Ag and Hg electrodes [252], $[Co(dimethylglyoximate)_2(thiocyanate)_2]^-$/Fe(II) (aq.) and V(II) (aq.) [253], $(SCN)_2^-$ (radical formed by pulse radiolysis)/various Ni(II) macrocyclic complexes [254].

(d) Redox reactions: outer-sphere pathways. Oxidant/reductant: $[Co(NH_3)_5NCS]^{2+}/I^-$-coated Pt electrode [251], cis-$[Co(H_2NCH_2CH_2NH_2)_2(NCS)_2]^+/I^-$-coated Pt and Au electrodes [251], $[IrCl_6]^{2-}$/SCN^- [255], $(SCN)_2^-$ (radical formed by pulse radiolysis)/[M(2,2'-bipyridyl)$_3]^{n+}$(M = Os(II),Os(III)) [256], $[Co(CN)_5NCS]^{3-}/[Ru(NH_3)_6]^{2+}$ [257].

(ix) Other studies involving the thiocyanate group

Literally dozens of studies have been published during the past ten years involving various other aspects of thiocyanate chemistry. Some of these only involve the thiocyanate peripherally; others focus on the thiocyanate, but yield no new insights into its chemical behaviour. Papers falling into either of these categories will not be cited in this review, although interested readers are invited to request a supplementary list of these references from the author. The remaining papers constitute several different motifs, which will be mentioned briefly at this point.

(a) Complexes with biologically important substrates. Examples include thiocyanate binding to Cu(II) in bovine plasma amine oxidase [258], bovine copper-zinc superoxide dismutase [259], and Fe(II), Co(II), Ni(II), and Cu(II) complexes with bromazepan [260], an anxiolytic drug.

(b) Equilibrium constants for thiocyanate complexes. The methods used for determining the stability constants have been varied: $[Zn(NCS)_n]^{2-n}$ in methanol, using a thiocyanate-sensitive electrode [261]; $[Cd(thioacetamide)_m(NCS)_n]^{2-n}$ in water using a polarographic method [262]; [Ni(S-methyl-N-(2-pyridyl)methylenehydrazinecarbodithioate)NCS] with pyridine and 4-methylpyridine, spectrophotometrically [263]; $[Co(NCS)_n]^{2-n}$ in aqueous methanol, spectrophotometrically [264]; $[\mathrm{Co(NCS)}_n]^{2-n}$ in micellar solutions of a nonionic surfactant, calorimetrically [265]; $[\mathrm{Au(SCN)}_n]^{1-n}$ in pyridine and acetonitrile, potentiometrically and calorimetrically [266].

(c) Ion-pairing with thiocyanate. A wide range of salts and solvents have been investigated: CuSCN in N,N-dimethylthioformamide, tetrahydrothiophene, dimethylsulfoxide, and hexamethylphosphoric triamide [267]; LiNCS, mixed with LiCl and LiBr in cyclopentanone, dimethyl- and diethylcarbamate, isopropyl acetate, tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane, dimethylformamide, tetramethylurea, propylene carbonate, and various ethers [268], $\mathrm{NH_4NCS}$, $\mathrm{Me_4NNCS}$, KNCS, and NaNCS in liquid ammonia [269].

(d) Magnetic studies, especially those involving spin-crossovers. Most of these studies have involved thiocyanate complexes of iron: [Fe(1,10-phenanthroline)$(\mathrm{NCS})_2$] [270]; $[\mathrm{Fe}_x\mathrm{M}_{1-x}$(1,10-phenanthroline)$_2(\mathrm{NCS})_2]$ (M = Mn,Co,Ni,Zn) [271]; [Fe(4,7-dimethyl-1,10-phenanthroline)$_2(\mathrm{NCS})_2]\cdot$α-picoline [272]; [Fe(1,10-phenanthroline)$_2(\mathrm{NCX})_2]$ (X = S,Se) [273]; $[\mathrm{Fe}_p\mathrm{Zn}_{1-p}$(1,2,4-triazole)$_2(\mathrm{NCS})_2]$ [274]; [Fe(2,2'-biquinoline)$_3](\mathrm{NCS})_2$ [275]; [Fe(pyrazine)$_2(\mathrm{NCX})_2]$ (X = O,S) [276]; trans-[Fe(4,4'-bi-1,2,4-triazole)$_2(\mathrm{NCS})_2]\cdot \mathrm{H_2O}$ [277]; [Fe(2,2'-bi-2-thiazoline)$_2(\mathrm{NCX})_2]$ (X = S,Se) [278].

(e) Molten thiocyanate salts. Studies have included: the coordination chemistry of $\mathrm{UO_2}^{2+}$ and VO^{2+} in KSCN-KF [279]; Ag(I)/SCN^- coordination in KNCS, KNCS-KCN and KNCS-KI [280]; and the complexation of Al(III) and V(III) by F^- in KSCN [281]. Related to this area is the solid (not molten) phase synthesis of $[\mathrm{S(CN)}_2]_n$ by the reaction of KNCS with ICN [282].

(f) New/improved synthetic methods/preparations. Examples include the direct electrochemical synthesis of thiocyanate complexes of Zn, Cd, Ge, Sn, Co, and Au [283] and the improved synthesis of salts of the linkage isomers of $[\mathrm{Co(CN)}_5$thiocyanate$]^{3-}$ [284a] and of $[\mathrm{Co(NH_3)}_5$ thiocyanate$]^{2+}$ [246]. A discovery having environmental significance is exhibited by the photocatalyzed transformation of CN^- to SCN^- by rhodium-loaded CdS in alkaline aqueous sulfide media [284b].

(g) Optically active complexes. DL-phenylalanine has been resolved by reacting it with [Cr(L-phenylalaninate)$_2$(NCS)$(\mathrm{OH_2})]$ in ethanol [285]. Potassium antimony-(+)-tartrate has been used to resolve cis-[Cr((RR),(SS)-C(5,12)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-$(\mathrm{NCS})_2$]NCS [286]. Three optically active antipodes ((+)$_D$-(ethylenediamine)$_2$-, (+)$_D$-α-triethylenetetraamine, and (+)$_D$-ß-triethylenetetraamine mixed ligand complexes (with acetylacetonate) of Co(III)) have had the methine hydrogen of the coordinated acetylacetonate ion substituted with a thiocyanate group with retention of configuration [287].

(h) Photochemical studies. Krause and Wasgestian [288] have reported an increased reactivity of SCN^- in the photoanation of $[Cr(NH_3)_6]^{3+}$. Walker and McCarthy [289] have studied the CT spectra and photochemistry of $[Fe(NCS)_6]^{3-}$ at cryogenic temperatures in diluent crystals of $R_3[Ln(NCS)_6]$ (R = large organic cation, Ln = lanthanide cation).

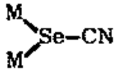
(i) NCS· and $(SCN)_2^-\cdot$ radicals and polythiocyanogen. Rehorek and Janzen [290] have succeeded in spin trapping thiocyanatyl (NCS ·) radicals using nitrone spin traps. Itabashi [291], using a gold-minigrid optically transparent thin-layer-electrode cell, has shown that the oxidation of SCN^- by Fe(III), as well as the electrooxidation of SCN^- in acidic thiocyanate solution, yields $(SCN)_3^-$. He has proposed [291] that the formation of $(SCN)_3^-$ proceeds through the anion radical $(SCN)_2^-\cdot$, produced by the oxidation of SCN^- by Fe(III), and is followed by the disproportionation of $(SCN)_2^-\cdot$ into $(SCN)_3^-$ and SCN^-. Beck and his colleagues have prepared [292] photoactive polythiocyanogens, $(SCN)_x$, via the oxidation of thiocyanates by iodine in water.

(j) Compounds with representative elements. Including the potassium complexes already cited in Table 2, examples from every A group in the periodic table have been reported during the past decade, with the exception of VIA and VIIA: [Ba(7,16-dihydroxy-bis[1'(pyridinyl-2''-methyl)[10,9-a][1,18-a]imidazolidine-bis[5'-chloro[6,8-1',3'][15,17-1',3']phenylene]1,4,10,13-tetraazacyclooctadeca-4,13-diene)$(NCS)_2$] [293], $R_{3-n}H_nNH\cdot BH_2(NCS)$ [294a], (3- or 4-)(alkyl or amino)pyridine$\cdot BH_2NCS$ [294b], Ga(III)/NCS^- equilibria [295a], $[Tl(SCN)]^{2+}$, $[Tl_2(SCN)]^{5+}$, and $[HTl(SCN)_2]^{2+}$ [295b], $CH_3SiH_2(X)$ (X = CN,NCO,NCS,NCSe) [296], $[SnL_2X_n(NCS)_{4-n}]$ (L = chelating N-donor ligand, X = Cl,Br,I) [297], $[Sn(NCS)_2(\text{Schiff base})_2]$ [298], $K_2[SbCl_3X_2]$ (X = CN^-, NCO^-,SCN^-,N_3^-), $SbClX_2$(X = CN^-,NCO^-,NCS^-) and $[Sb(C_5H_5)X_2]$ (X = CN^-, NCO^-,SCN^-,N_3^-) [299], SbF_3/NH_4NCS mixtures (mass spectral study) [300], BiL$(\text{thiocyanate})_3$ (L = tridentate N-donor ligand) [301].

(k) Unusual bonding behaviour. In addition to the examples cited in Table 5, Ashton and Manning [302a] have reported the synthesis of $[Fe(PPh_3)_2(CO)_2(RNCS)]$ (R = Ph,Me) complexes, wherein the RNCS molecules are η^2-C,S (sideways) bound, based on IR spectral evidence. An unusual sequence of reactions involving the thiocyanate group has been observed by Gibson and Cowie [302b]. The reactions of $[Rh_2Cl_2(\mu\text{-}CO)(dpm)_2]$ (dpm = $Ph_2PCH_2PPh_2$) with the isothiocyanate molecules RC(O)NCS (R = EtO, Ph) yield the complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)R)(dpm)_2]$, in which the metals are bridged by the carbonyl ligand and the isothiocyanate molecule, with no accompanying Rh-Rh bond. The EtO derivative, in turn, reacts further with isothiocyanates to yield $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(R)C(O)OEt)(dpm)_2]$ (R = Me,Ph,C(O)OEt,C(O)Ph). An X-ray structure [302b] of the R = Ph derivative indicates that condensation of the isothiocyanate molecules has occurred with C-N bond formation, accompanied by migration of the C(O)OEt moiety to the nitrogen atom of the PhNCS group. The unusual tridentate ligand which results can be viewed as a new isothiocyanate group, RNCS, with R = C(S)N(Ph)C(O)OEt. This group bridges the metals, bound to one via the sulfur and to the other via the carbon of the isothiocyanate group, and is additionally coordinated to one metal center by the thiocarbonyl moiety.

The first dichromium complex containing axially bonded anions, $[NEt_4]_2[Cr_2(O_2CCH_3)_4(NCS)_2]$, has been reported by Larkworthy and Roberts [303]. Ahuja and Yadava [304] have claimed the synthesis of an extremely unusual N-bound Hg(II)-thiocyanate complex, $[Hg_4$(hexamethylenetetraamine)-$(NCS)_8]$. Most thiocyanate linkage isomerizations that have been reported are of the M-SCN → M-NCS variety. We have observed a rare example [305] of a thiocyanate linkage isomerization in the reverse direction, when [Pd(5-nitro-1,10-phenanthroline)$(NCS)_2$] is heated.

H. SELENOCYANATE ($NCSe^-$)-CONTAINING COMPLEXES

In principle, the selenocyanate ion should be capable of forming all of the bond types shown in Fig. 2 for the thiocyanate ion. In practice, relatively few studies have dealt with its coordination chemistry [306]. The toxicity of selenium and the ghastly smell of some of its compounds, most notably that of H_2Se, probably have been major contributing factors to this lack of interest. Nonetheless, like thiocyanate, selenocyanate is a functional ambidentate ligand, although its bonding behaviour is much less varied, being limited, thus far, to the M-SeCN, M-NCSe, and M-SeCN-M bond types. (One example of  $\begin{matrix}M\\ M\end{matrix}\!\!>\!Se{-}CN$ bridging has been reported [307], in the complex $[Cu(H_2NCH_2CH_2NH_2)_2H_2O]$-$[Cu_2(CN)_3SeCN]$.) It follows an analogous M(hard)-NCSe, M(soft)-SeCN bonding pattern at coordination sites that are not altered by steric and/or electronic factors created by other ligands in the coordination sphere.

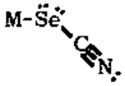
(i) Structures determined by single crystal X-ray diffraction

Studies involving crystallographic characterization of selenocyanate complexes have been few and far between, as shown in Table 7.

TABLE 7

Selected X-ray structural data for isoselenocyanato (M-NCSe) and selenocyanato (M-SeCN)complexes

	Bond angles(°)			Bond lengths(pm)				
Compound	MNC	SeCN	MSeC	M-N	N-C	C-Se	M-Se	Ref.
$[N(PPh_3)_2]$-$[B_3H_7NCSe)]$	174.1	178.1	-	152.4	115.6	174.2	-	[103]
[Cu(2,2':6'2"-terpyridyl)-$(NCSe)_2]$	158.9	179	-	204	114	175	-	[308]
$[Pd(Ph_2PCH_2P$-$(Se)Ph_2)(CN)$-(SeCN)](SeCN <u>trans</u> to P)	-	176.5	105.8	-	114.2 109.7 (CN^-)	181.6	245.0	[309]
$[Pd(Ph_2P$-$(CH_2)_2PPh_2)$-$(SeCN)_2]$	- -	177.1 177.5	109.1 105.0	- -	114.2 113.6	183.7 182.0	247.8 247.6	[310]
$[Pd(Ph_2P$-$(CH_2)_3PPh_2)$ $(SeCN)_2]$	- -	172.1 177.3	106.6 94.2	- -	114.3 114.8	183.4 182.1	245.8 248.8	[310]

The two monodentate bonding modes shown in Table 7 are adequately represented by the simple canonical structures $M-N\equiv C-\ddot{S}e:$ and 

The first palladium complex listed in Table 7 is of particular interest, since it is a structural isomer of $[Pd(Ph_2PCH_2PPh_2)(SeCN)_2]$ [309].

(ii) Comparison of the coordination behaviour of the selenocyanate and thiocyanate ligands

There is, to be sure, a significant degree of "me-tooism" in the coordination chemistry of selenocyanate. In situations which are not sterically or electronically complicated by the presence of other ligands, $SeCN^-$ tends to mimic SCN^- in its coordination behaviour, e.g., $[MnL(NCSe)_2]$(L = EtOH,PPh_3,$PPhMe_2$), $[MnL_2(NCSe)_2]$ (L = THF), and $[MnL_4(NCSe)_2]$ (L = $OPPh_3$) [311]; $[Ru(2,2'\text{-bipyridyl})_2(NCSe)X]$ and $[Ru(2,2'\text{bipyridyl})_2(NCSe)X]Y$ (X = $NCSe^-$,Cl^-; Y = PF_6^-,BPh_4^-) [312]; $[NEt_4][U(AA)_2(NCX)_5]$ (AA = 2,2'-bipyridyl, 1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridyl; X = S,Se) and $[AsPh_4]_4[U(NCX)_8]$(X = S,Se) [313].

Likewise, its sensitivity to steric and electronic bonding mode control by other ligands tends to follow the same pattern as that delineated by the thiocyanate ion. Here, however, there is a difference in degree, if not in kind. Thus, the steric hindrance created by the ligand 1,1,7,7-tetraethyldiethylenetriamine is sufficient to destroy the normal Pd(soft)-XCN (X = S,Se) bonding preference in both $[Pd(Et_4dien)NCX]^+$ complexes [314], for the reason already discussed in section G(ii). However, the selenocyanate exhibits considerably greater resistance to having its normal M(soft)-SeCN bonding mode changed in this manner. None of the $[Pd(Ph_2P(CH_2)_nPPh_2(SeCN)_2]$ (n = 1,2,3) complexes, for example, contain any N-bound groups [309,310], despite their having very similar P-Pd-P bond angles to those exhibited by their thiocyanate analogs (Table 6), which contain at least one N-bound thiocyanate for n = 2 and 3. In the same vein, *trans*-$[Pd(PPh_3)_2X_2]$ is N-bound for X = NCS^- [194] and Se-bound for X = $SeCN^-$ [315].

Electronic control of the selenocyanate's bonding mode, like that of the thiocyanate, can either be symbiotic or anti-symbiotic. A recent example [316] of the former is found in the series of cobaloxime complexes with Se-bound selenocyanate *trans* to imidazole ligands in the axial positions. An excellent example of the latter, *trans*-$[Rh(PPh_3)_2(CO)NCSe]$, was first reported [317] quite some time ago.

The utilization of the selenocyanate as a bridging ligand has been much less extensive, and its bridging behaviour much less varied, than that already described in sections G(i) and (iv) for the thiocyanate. In those instances where bridged selenocyanate complexes have been prepared, they have been found (with the one exception already cited [307]) to be of the μ^2-N,Se-bound type. Recent examples, in addition to those already cited in section G(iv), include: single-bridged: *trans*-[LCo(dimethylglyoximate)$_2$-NCSe-Co(dimethylglyoximate)$_2$SeCN] (L = PPh_3,$AsPh_3$,$Sb(C_4H_9)_3$) [214], [Cl(2,2'-bipyridyl)$_2$-RuNCSeRu(2,2'-bipyridyl)$_2$Cl]$^{n+}$ (n = 1,2,3) [312], $[(NC)_5FeNCXFe(CN)_5]^{n-}$ (X = S,Se; n = 5,6,7) [318]; double-bridged: $[(SCN)_2M(NCSeHgR)_2]$(M = Co(II), Ni(II)) [319], $[(SeCN)_2M(NCSeHgR)_2]$(M = Co(II), Ni(II)) [320], $[(Fe(C_5H_4Hg\text{-}SeCN)_2)M(NCSe)_2]$ (M = Co(II), Ni(II)) [321].

Finally, Walker and his colleagues have reported [322] that reaction of $[Pt(PPh_3)_2C_2H_4]$ with p-tolyl-NCSe yields a unique example of η^2-N,Se (sideways) bonding of the NCSe group in the complex $[Pt(\eta^2\text{-}SeCNC_7H_7)(PPh_3)_2]$ (η^2-N,Se structure comparable to that (**22**) shown earlier for NCS). Potassium selenocyanate has been found [323] to be an active catalyst in the carbonylation of nitrobenzene. Selenocyanogen, $(SeCN)_2$, is also capable of oxidizing Au(I) (in the complex [Au_2(N,N-dialkyldithiocarbamate)$_2$]) to Au(II) [223]. The structure of the Au(II) product complex is analogous to that shown earlier (**24**) for the product of the comparable reaction with $(SCN)_2$. The Au(II)-selenocyanate complex also disproportionates to [Au^{III}(N,N-diethyldithiocarbonate)$_2$][$Au^I(SeCN)_2$].

I. TELLUROCYANATE ($NCTe^-$) - CONTAINING COMPLEXES

The title of this Section is, admittedly, somewhat misleading. To the best of my knowledge, no stable tellurocyanate-containing transition metal complex has ever been isolated and characterized. The ion has a nasty habit of breaking its Te-C bond when placed in contact with transition metal ions. Indeed, ref. 8 does not contain a section dealing with $TeCN^-$. However, the general ligand chemistry of tellurium has been thoroughly reviewed within the past decade [324], including a description of the synthesis and crystallographic structural characterization of stable salts of the $TeCN^-$ ion.

By way of contrast, the organic chemistry of the TeCN group has been reasonably well-developed. Although a thorough discussion of this area would stray beyond the scope of this review, inclusion of several points of comparison is appropriate. Chief among these is the structural comparison (Table 8) made possible by the single crystal X-ray diffraction studies of 4-nitrobenzylthiocyanate, -selenocyanate and -tellurocyanate carried out by Maartmann-Moe, Sanderud, and Songstad [325].

TABLE 8

Selected X-ray structural data for 4-X-benzylthiocyanate, selenocyanate, and tellurocyanate (all bound via chalcogen atom Z) [325]

X	Pseudohalide	Bond angles(°)		Bond lengths(pm)		
		ZC^aN	C^bZC^a	$N\text{-}C^a$	$C^a\text{-}Z$	$C^b\text{-}Z$
NO_2	-SCN	175.9	100.3	113.8	168.0	182.2
NO_2	-SeCN	179.5	94.0	112.9	184.4	197.2
H	-SeCN	177.6	96.0	113.2	182.9	197.1
NO_2	-TeCN	179.3	90.6	114.1	206.0	216.7

[a] Pseudohalide carbon atom

[b] Benzyl carbon atom

The $C^a{\equiv}N$ bond lengths all three pseudohalides are quite similar whereas, as expected, their C^a-Z bond lengths are quite different. The latter are considerably shorter than the C^b-Z bonds to the benzyl groups. Maartmann-Moe and Songstad have also determined [326] the crystal structures of $[N(PPh_3)_2][4\text{-nitrobenzyl-}Te(CN)X]$(X = Cl, Br, I), where the X atom is bound to the tellurium.

Songstad and his group have studied the reactions of a variety of 4-substituted benzylic compounds, 4-X-$PhCH_2Z$ with several nucleophiles, Y^-(X = NO_2, H, Me; Z and Y = Cl, Br, I, SCN, SeCN, TeCN) [327]. They found an average carbon basicity order (which is essentially the reverse of the average leaving group ability) of $TeCN^- \gg SeCN^- \sim SCN^- \sim Cl^- \gg Br^- > I^-$ [327]. They also investigated [328] the reactions of CH_2Cl_2 with <u>all</u> of the common pseudohalides (N_3^-, NC^-, NCO^-, NCS^-

, NCSe⁻, NCTe⁻). The reactivity order found was $N_3^- > CN^- > NCTe^- > NCS^- > NCO^-$ [328].

J. COMPLEXES CONTAINING OTHER AMBIDENTATE LIGANDS

With very little space left, but with a great deal of chemistry yet to be covered, brevity will have to be the order of the day. I hope that the buffet of ambidentate ligand chemistry presented will serve to stimulate the interest of the reader into pursuing it further while, at the same time, providing useful access to the greater body of literature involved.

(i) Structures determined by single crystal X-ray diffraction

The ligands and complexes shown in Table 9 give some measure of the considerable variety of ambidentate ligands that have been studied recently, above and beyond the work already described involving the classic nitrite and pseudohalide ions.

TABLE 9

Complexes of other ambidentate ligands whose structures have been determined by single crystal X-ray diffraction

Ambidentate ligand(s)	Compound	Bonding mode(s)	Ref.
cyanoborohydrides	$[Pt(Ph_2PCH_2PPh_2)(CNBH_2CN)]_2 \cdot CHCl_3$	one cyanide C bound to Pt, N of second CN is uncoordinated	[329]
	$[Pt(Ph_2PCH_2PPh_2)(CNBH_3)]_2 \cdot H_2O$	C-bound to Pt	[329]
nitramines	trans-$\{Cu(NH_3)_2[N(NO_2)CH_3]_2\}$	N-bound to Cu	[34]
	$\{Cu(en)[N(NO_2)CH_3]_2\}$	N-bound to Cu	[34]
	trans-$[Cu(NH_3)_2(\mu$-N,N'-ethylene dinitraminate$)]_n$ (ligand = EDNA-2H)	N,N'-bridged to Cu's	[34]
	$[Ni(H_2O)_4(EDNA\text{-}2H)]$	N,N'-chelated to Cu	[34]
	$[Ni(NH_3)_3(N_4CNNO_2)]_2$	N,O chelated to each Cu, N,N' bridging both Cu	[34]
	$[Cu(en)_2][Cu_2(en)_2(EDNA\text{-}2H)_3] \cdot 2H_2O$	two N,N'chelated to Cu, one N,N' bridging both Cu	[34]
nitrosobenzenes and -anilines	$[Pt_2(PhNO)_3(PMe_3)_3]$	one N-bound to Pt, one N-bridging two Pt, one N,O-bridging two Pt	[41]
	trans,trans-,trans-$[SnCl_2Me_2$(4-nitroso-N,N-dimethylaniline$)_2]$	O-bound to Sn	[42a]
	[Zn(4-nitroso-N,N,-dimethylaniline$)_2$-	O-bound to Zn	[42b]

Ambidentate ligand(s)	Compound	Bonding mode(s)	Ref.
	$Cl_2]$		
phosphine/arsine	$[Au\{(Ph_2PCH_2)_2AsPh\}_2][Au(CN)_2]$	P,P' chelated to Au	[330]
	trans-$[Ru\{(Ph_2PCH_2)_2AsPh\}_2Cl_2]$	one P,P'-chelated to Ru one P,As-chelated to Ru	[330]
phosphine sulfide/methine	$[PtCl(PEt_3)(CH(PPh_2S)_2)]$	C,S-chelated to Pt	[331]
phosphinethioamide	*trans,trans*-$[Mo_2(Ph_2PC(S)NMe)_4]$	two N,S-bridging to Mo's two N,P-bridging to Mo's	[332a]
	$[Mo_2(Ph_2PC(S)NMe)_4]$	all N,S-bridging to Mo's	[332a]
pyridine-2-thione	$[Ag(PPh_3)_2$(pyridine-2-thione)Cl]	S-bound to Ag	[332b]
saccharinate ion	[Cu(2-formylpyridinethiosemicarbazonate)(saccharinate)$(H_2O)]\cdot 0.5H_2O$	N-bound to Cu	[332c]
sulfite ion	αα[Co(tetraethylenepentamine)$SO_3][ClO_4]$	S-bound to Co	[333a]
sulfur dioxide	$[Fe(P(OPh)_3)_2(CO)_2(SO_2)]$	S-bound to Fe	[333b]
	$[Fe(P(OC_6H_4Me$-*o*$)_3)_2(CO)_2(SO_2)]$	S-bound to Fe	[333b]
sulfoxides	$[Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-}Ph_2PCH_2PPh_2)_2]$	S-bridged to Pd's	[334]
	$[\{Mo(O)_2(NCS)(Me_2SO)_2\}O]$	O-bound to Mo	[142]
	mer-$[Rh(Me_2SO)_2(DMF)Cl_3]$	S-bound to Rh	[335]
	$[Rh_2(O_2CC_2H_5)_4(Me_2SO)_2]$	S-bound to Rh	[336a]
	$[Rh_2(O_2CCF_3)_4(Me_2SO)_2]$	O-bound to Rh	[336a]
	$[Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2]$	O-bound to Rh	[336b]
	$[OsCl_2($*p*-$MeC_6H_4CHMe_2)(Me_2SO)]$	S-bound to Os	[337]
	$[Pt(Me_2SO)_4][F_3CSO_3]$	two *cis*-S-bound to Pt two *cis*-O-bound to Pt	[338a]
	cis-$[Pt(Me_2SO)(H_2O)Cl_2]$	S-bound to Pt	[338b]
	[Pt(2,2,2,2',2',2'-hexachlorodiacetamidate)$(Me_2SO)Cl]$	S-bound to Pt	[338b]
	$[Pd(Me_2SO)_4][BF_4]_2\cdot Me_2SO$	two *cis*-S-bound to Pd two *cis*-O-bound to Pd	[339]
	cis-$[Pt(Me_2SO)(CH_3CN)Cl_2]$	S-bound to Pt	[340,341]
	$[Pt_2(\mu$-acetamido$)_2Cl_2(Me_2SO)_2]$	S-bound to Pt	[340]
	cis-$[Pt(Me_2SO)(CH_3CN)Br_2]$	S-bound to Pt	[341]
	cis-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$	S-bound to Pt	[341]

Ambidentate ligand(s)	Compound	Bonding mode(s)	Ref.
	cis-[Pt(Me_2SO)(pyridine)Cl_2]	S-bound to Pt	[341]
thiazate ion (NSO^-)	[(η^5-C_5H_5)$_2$Ti(NSO)$_2$]	N-bound to Ti	[342]
thiocarbonate ion	[PPh_4]$_3$[Cr(S_2CO)$_3$]	S,S'-chelated to Cr	[343]
dithioimidodiphosphinate ion	[$AuCl_2$($SPPh_2NPPh_2S$)]	S,S'-chelated to Au	[344a]
thionyl imide	cis-[Pt(PPh_3)$_2$(OSNH)$_2$]	O-bound to Pt	[344b]
dithiosquarate ion	[PPh_4]$_2$[Pd(dithiosquarate)$_2$]	S,S'-chelated to Pd	[345]

Technically, the cyanoborohydride ligands shown in Table 9 are not ambidentate - the CN group is the ambidentate species. Although the precursor isomer has not been characterized crystallographically, Fackler and his colleagues have reported [329] the linkage isomerization of trans-[Pt($Ph_2PCH_2PPh_2$)($NCBH_2CN$)]$_2$ to trans-[Pt($Ph_2PCH_2PPh_2$)($CNBH_2CN$)]$_2$. It should be noted that the structures of the [M(Me_2SO)$_4$]$^{2+}$(M = Pd(II), Pt(II)) complexes represent excellent examples of antisymbiotic behavior [192].

(ii) Miscellaneous studies involving other ambidentate ligands

A representative sampling of studies involving other ambidentate ligands that have appeared in the literature during the past decade is shown in Table 10.

TABLE 10

Non-crystallographic studies of other ambidentate ligands

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
di-and triazaphospholes (P=C(H)C(Me)=NNMe) [L_A] (P=NC(Ph)=NNMe)[L_B]	trans-[$PdCl_2$(PEt_3)L] (σ-N-bound) [$PtBr_2$(PEt_3)L] (mixture of cis-σ-P and trans-σ-N-bound)	Synthesis by reaction of L with [MX_2(PEt_3)]$_2$; characterization by multi-nuclear NMR	[346]
(P=NN(Me)C(Me)=N)[L_C]	cis-[$PtCl_2$(PEt_3)L_A] (σ-P-bound) (dinuclear, with L_B,L_C)		
aminobenzonitriles(L)	cis-[PtL_2X_2](X=Cl,Br) trans-[PdL_2X_2] (amino-N-bound)	Synthesis by reaction of L with K_2[MX_4]; IR	[347]

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
		characterization	
4,4'-bipyrimidine(L)	$[\{(OC)_5W\}_2L\text{-}\{W(CO)_4\}]$ ($W(CO)_5$ fragments-$N^1,N^{1'}$; $W(CO)_4$ fragment-$N^3,N^{3'}$)	Synthesis by reaction of L with $[W(CO)_5THF]$; IR, electronic, ESR, cyclic voltammetry characterization	[348]
ketenylidene(CCO)	$[N(PPh_3)_2]_2[Ru_3(CO)_6\text{-}(\mu_3\text{-}CCO)]$ (μ_3-C-bound)	IR, Raman characterization	[349]
chlorotricyanomethane ($ClC(CN)_3$)	$[ClC(CN)_3{\cdot}SbCl_5]$ (Cl-bound, some ionization to $[C(CN)_3]^+[SbCl_6]^-$)	Mass spectral, IR, Raman, UV, NMR, conductimetric titration characterization	[350]
chloranilate dianion(CA^{2-}) (2,5-dioxo-3,6-dichloro-1,4-benzoquinone)	$[Pd(CH_3CN)_2CA]$ (di-C-bound) $[Pd(PPh_3)_2CA]$ (di-π-bound)	NMR, UV-visible, IR characterization; kinetic study of linkage isomerization	[351,352]
isonitroso (ß-ketoimine) (L)	$[PdL_2]$ (N,N'-chelated) $[NiL_2]$ N,O-chelated)	X-ray photoelectron spectroscopic study	[22]
nicotinate(L) (3-carboxypyridine)	[Cr(N,N'-ethylenebis-salicylideneaminate)(L)H_2O] (O-bound)	IR characterization; determination of equilibrium quotients	[353]
$Ph_2PC(S)NHR$ $Ph_2PC(S)NR^-$	$\{Rh(CO)Cl[Ph_2PC\text{-}(S)NHPh]\}_2$ (P-bound modentate, P,S-bound chelate) $\{Rh(CO)[Ph_2PC(S)\text{-}NPh]\}_4$ (N,S,P-bridged) $\{RhCl(CO)[Ph_2PC(S)\text{-}NHPh]_2\}$ (P-bound monodentate) $\{Rh(CO)[Ph_2PC(S)\text{-}NPh][Ph_2PC(S)\text{-}NHPh]\}$ (P-bound monodentate, P,S-chelate) $\{RhH(CO)[Ph_2PC(S)\text{-}NPh]_2\}$ (P,S chelate)	IR, NMR characterization	[354]
N-(2-pyridyl)imidazole(L)	$[MeHgL]NO_3$ (imidazole N-bound)	IR, NMR characterization	[355]

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
4,6-dimethylpyrimidine-2-one (L)	$[ML_2X_2]$(M=Mn,Fe, Co,Ni,Cu,Zn,Cd; X=Cl,Br) (N-bound) $[ML_4X_2]$(M=Mn,Co, Ni; X=I, NO_3,ClO_4) (O-bound)	UV-visible, IR characterization	[356]
sulfamidate($NH_2SO_3^-$)	large number of complexes (some N-bound, some O-bound, some mixed bonding modes)	ESCA study	[24]
dimethylsulfoxide (Me_2SO)	$[Ru(NH_3)_5(Me_2SO)]^{2+}$ (S- to O-bound isomerization when Ru oxidized to 3+ state; O- to S- bound reisomerization when 3+ Ru reduced to 2+)	Kinetic study	[357]
	cis-$[Pt(L_2)X_2]$ (L_2=$(NH_3)_2$,en; X=Cl,Br,I)	Kinetic study of solvolysis in Me_2SO	[358]
	$[Pt_2Cl_2(\mu\text{-}Cl)_2(Pcyclohexyl_3)_2]$	Study of bridge cleavage reactions in Me_2SO and dibenzylsulfoxide	[359]
sulfur dioxide molecular ion (SO_2^-)	MO_2S (M=Cs,K,Na) (O,O'-chelate)	IR and Raman study, with isotopic substitution, of matrix isolated MSO_2	[360]
	$[Ru(NH_3)_4Cl(SO_2)]Cl$ (S-bound)	UV-visible and IR (with isotopic substitution) of photochemical linkage isomerization to μ_2-S,O)	[361]
sulfite(SO_3^{2-})	$[Co(AA)_2O_2SO]$ (AA=2,2'-bipyridyl; 1,10-phenanthroline) (O,O'-chelate) cis-$[Co(AA)_2(CN)SO_3]$ (S-bound)	IR characterization	[362]
	Various Pd,Ir,Rh,Pt, Os complexes (S-bound) $[Fe(OSO_2)_6]^{9-}$ (O-bound)	Raman and IR characterization	[363]
	$[Co(NH_3)_5\,SO_3]^+$ trans-$[Co(NH_3)_4(SO_3)_2]^-$ (both complexes	Kinetic study of formation, substitution, and aquation reactions	[364]

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
	S-bound)		
	cis-$[Co(en)_2(OH_2)SO_3]^+$ (S-bound)	Synthesis and kinetic study of *cis* to *trans* isomerization	[365]
	cis-$[Co(en)_2Cl(SO_3)]$ (S-bound)	Synthesis, kinetics and stereochemistry of aquation	[366]
	cis-$[Co(phen)_2(OH_2)SO_3]^+$ $[Co(bipy)_2(OH_2)SO_3]^+$ *cis*-$[Co(phen)_2(SO_3)_2]^-$ *cis*-$[Co(bipy)_2(SO_3)_2]^-$ (all four complexes S-bound)	Kinetic study of formation and redox reactions	[367]
	$[Cr(OH_2)_5OSO_2]^+$ (O-bound)	Kinetic study of formation, acid-catalyzed decomposition, and intramolecular isomerization	[368]
	$[Co(NH_3)_5OSO_2]^+$ [O-bound]	Oxygen-17 NMR study	[369]
		Effect of pressure on intramolecular electron transfer reaction	[370]
	trans-$[Co(NH_3)_4(CN)OSO_2]$ (O-bound)	Kinetic study of formation, substitution, isomerization, and acid-catalyzed aquation	[371]
	$[Co(tren)(OH_2)OSO_2]^+$ (O-bound)	Kinetic study of formation and aquation	[372]
	$(\alpha,\beta,\underline{S})$-[Co(tetraethylenepentamine)$OSO_2]^+$ (O-bound)	Kinetic study of formation, acid-catalyzed decomposition and intramolecular isomerization	[373]
	(S-bound isomer)	Kinetic study of hydrolysis	[373]
	trans-$[Co(en)_2(OH_2)OSO_2]^+$ (O-bound)	Kinetic study of formation, aquation and intramolecular electron-transfer	[374]
	[Pd(1,1,7,7-tetraethyldiethylenetriamine)$SO_3]$ (S-bound)	Kinetic study of formation and reactivity	[375]
	$[Pt(NH_3)_5OSO_2]^{2+}$ (O-bound)	Kinetic study of formation, isomerization, and sulfite addition reactions	[376]
	cis-$[Pt(NH_3)_4(SO_3)_2]$ (S-bound)	Kinetic study of intramolecular redox reactions	[376]
SNO	$[Co(P(OPh)_3)_2Cl_2(N(O)S)]$(N (thionitro)-bound)	Infrared characterization, synthesis by reaction of $(NSCl)_3$	[377]

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
		with[CoH(P(OPh)$_3$)$_4$]	
thiosulfate ($S_2O_3^{2-}$)	trans-[Co(en)$_2$(OH$_2$)S$_2$O$_3$]$^+$ (S-bound)	Study of kinetic trans effect induced by $S_2O_3^{2-}$	[378]
	trans-[Co(en)$_2$(S$_2$O$_3$)$_2$]$^-$(S-bound)	HPLC investigation of nucleophilic substitution reactions	[379]
	[Co(NH$_3$)$_5$(S$_2$O$_3$)]$^+$ (S-bound)	Kinetic study of oxidation of coordinated $S_2O_3^{2-}$ to $S_2O_5^{2-}$	[380]
	[Co(NH$_3$)$_5$(thiosulfate)]$^+$ (both S- and O-bound)	Kinetic study of base hydrolysis of [Co(NH$_3$)$_5$X]$^{n+}$ in presence of $S_2O_3^{2-}$	[381]
	[Co(en)$_2$S$_2$O$_3$]$^+$ (O,S-chelated)	IR and UV-visible characterization	[382]
selenite (SeO_3^{2-})	[Pt(diamine or (NH$_3$)$_2$)O$_2$SeO] (O,O'-chelated)	Synthesis and study of antitumor activity	[383]
thiocarbamates (SC(O)NHR$^-$)	[Co(NH$_3$)$_5$SC(O)NHR]$^{2+}$ (R=Me,Ph,benzyl, 4-CN-C$_6$H$_4$) (S-bound) [Co(NH$_3$)$_5$OC(S)NHR]$^{2+}$ (R=CH$_3$,benzyl) (O-bound)	Kinetic study of Cr(II) reduction reactions	[384]
thionyl imide (OSNH$^-$)	[Pt(S$_2$N$_2$H$_2$)(OSNH)$_2$] (O-bound)	Synthesis by reaction of K$_2$[PtCl$_4$] with S$_4$N$_4$H$_4$ in acetone; IR, UV-visible, and NMR characterization	[385]
triphosphate	β,γ-[Co(NH$_3$)$_4$(H$_2$P$_3$O$_{10}$)] (O,O'-chelate,6-membered ring) α,γ-[Co(NH$_3$)$_4$(H$_2$P$_3$O$_{10}$)] (O,O'-chelate, 8-membered ring)	Study of bidentate linkage isomerization and phosphate hydrolysis; characterization by UV-visible and NMR	[386]
dimethylurea	[(H$_3$N)$_5$Co(NHC(O)N(CH$_3$)$_2$)]$^{2+}$ (N-bound) [(H$_3$N)$_5$Co(OC(NH$_2$)N(CH$_3$)$_2$)]$^{3+}$ (O-bound)	Kinetic study of base-catalyzed hydration of [(H$_3$N)$_5$Co(NCN(CH$_3$)$_2$)]$^{3+}$ to form N-bound dimethylurea complex; study of linkage isomerization of N-bound dimethylurea complex	[387]
urea	[Ru(NH$_3$)$_5$(NH$_2$C(O)NH$_2$)]$^{3+}$ (N-bound) [Ru(NH$_3$)$_5$(OC(NH$_2$)$_2$)]$^{3+}$ (O-bound)	Kinetic study of linkage isomerization (N→O at pH<2,O→N at pH>pKa) and substitution	[388]

Ambidentate ligand(s)	Compound(s) (Bonding mode(s))	Nature of study	Ref.
		reactions	
	$[Ru(NH_3)_5(O\text{-ligand})]^{3+}$ (O-ligand=$OCHNH_2$, $OCHN(CH_3)_2$, $OC(CH_3)$-$N(CH_3)_2$)	Kinetic study of aquation reactions	[388]
	$[Co(NH_3)_5(OC(NH_2)_2)]^{3+}$ (O-bound) $[Co(NH_3)_5(NH_2C(O)NH_2)]^{3+}$ (N-bound)	Kinetic study of reversible linkage isomerization	[389]
	$[Cr(NH_3)_5(OC(NH_2)_2)]^{3+}$ (O-bound) $[Cr(NH_3)_5(NH_2C(O)NH_2)]^{3+}$ (N-bound)	Kinetic study of base hydrolysis and base-prompted linkage isomerization; similar study also carried out with O-coordinated formamide complex	[390]

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