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RECENT DEVELOPMENTS IN THE COORDINATION CHEMISTRY OF AMBIDENTATE LIGANDS

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The coordination chemistry of ligands possessing two different atoms capable of coordinating to metal ions has long been a subject of particular interest to both the synthetic and theoretical coordination chemist. The potpourri of ambidentate ligand chemistry which follows is not intended to be an exhaustive summary of recent developments in the field. It is, rather, a discussion of the results of current investigations being carried out in our laboratories concerning four such ligands, SCN^- $SeCN^-$, CN^-, and NO_2^-, with special reference to pertinent studies in the recent literature.

Thiocyanato and Isothiocyanato Complexes

Much of the current interest in ambidentate ligands in general, and thiocyanate complexes in particular, can be traced back to the discovery, by Turco and Pecile[1], that the presence of other ligands in the coordination sphere of a metal can affect the nature of the metal–thiocyanate bond (Table I). They pointed out that there are two sets of antibonding π-orbitals localized on the sulfur atom, which, along with the sulfur atom's vacant d-orbitals, can accept electron density from the metal's filled non-bonding d-orbitals (d_{xz}, d_{yz} and d_{xy}), resulting in addi-

TABLE I

EFFECT OF OTHER LIGANDS ON THIOCYANATE BONDING[1]

*Compound**	*C–N Stretch (cm^{-1})*	*C–S Stretch (cm^{-1})*
$K_2[Pd(SCN)_4]$	2118, 2086	703, 707 (sh), 696 (sh)
trans-$[Pd(NH_3)_2(SCN)_2]$	2116, 2100	701
$[Pd(P(C_2H_5)_3)_2(NCS)_2]$	2089	846, 842 (sh)
$K_2[Pt(SCN)_4]$	2120, 2089	697, 700 (sh), 690 (sh)
cis-$[Pt(NH_3)_2(SCN)_2]$	2116	703
$[Pt(P(C_2H_5)_3)_2(NCS)_2]$	2113	855

* Wherever shown, the symbols SCN and NCS denote S- and N-bonding, respectively; CNS denotes that either the bonding is not known or that the ion is not coordinately bound, as in KCNS.

tional stability of the M–S bond in palladium(II) and platinum(II) complexes. The importance of the additional stability will depend on the availability of the electrons of the metal and their relative energy as compared with that of the orbitals of the thiocyanate. Strong π-electron acceptors, such as trialkylphosphines, can make the metal d-orbital electrons less available for donation to the thiocyanate, removing the source of additional stability for the M–S bond and thereby enhancing M–NCS bonding. Stated in a somewhat different fashion[2], π-bonding ligands in these systems tend to reduce the electron density on the metal and thereby change class *b*, or soft (polarizable) metals, to class *a*, or hard (non-polarizable) metals. The bonding mode therefore changes from the soft sulfur atom to the hard nitrogen atom, in accordance with Pearson's soft–hard acid–base theory[3]. Indeed, the class *a* N-bonded, class *b* S-bonded bonding pattern is followed throughout the periodic table in complexes wherein thiocyanates are the only ligands present.

Turco and Pecile[1] were also among the first to demonstrate that the position of the thiocyanate C–S stretching frequency ν_1(SCN) can be used to determine the type of thiocyanate bonding[4,5]. This frequency is shifted to higher wave numbers (780–860 cm^{-1}) in the spectra of isothiocyanates (M–NCS), and to lower wave numbers (690–720 cm^{-1}) in the spectra of thiocyanates (M–SCN), both relative to the C–S stretching frequency of "ionic" thiocyanate, as in KCNS (749 cm^{-1})[6]. This has proved to be a very useful diagnostic tool, barring any interfering absorption bands due to other ligands present in the coordination sphere.

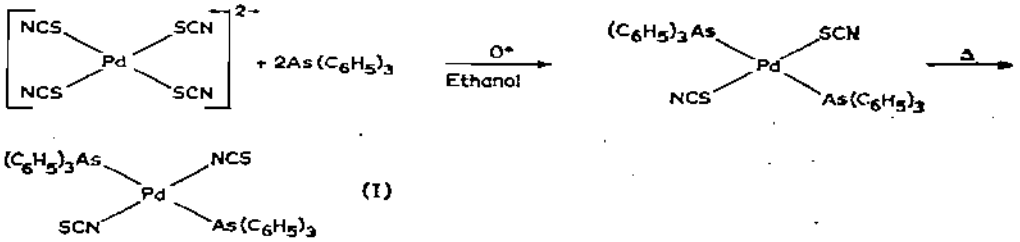
As a direct consequence of this work, Burmeister and Basolo[2] succeeded in synthesizing the first linkage isomers of the thiocyanate ion (reaction 1 and Table II).

TABLE II

EFFECT OF DECREASING π-BONDING[2]

Compound	*C–N Stretch, cm^{-1}*	*C–S Stretch, cm^{-1}*
$[Pd(P(C_6H_5)_3)_2(NCS)_2]$	2093 (s, br)	853 m
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	2089 (s, br)	854 m
$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	2119 (s, sp)	*
$[Pd(Sb(C_6H_5)_3)_2(SCN)_2]$	2115 (s, sp)	*

* No C–S stretching peak in N-bonded range; strong phenyl ring absorption in S-bonded range.



(I)

A second set of isomers was prepared[2] using the bidentate ligand 2,2′-bipyridine (Fig. 1).

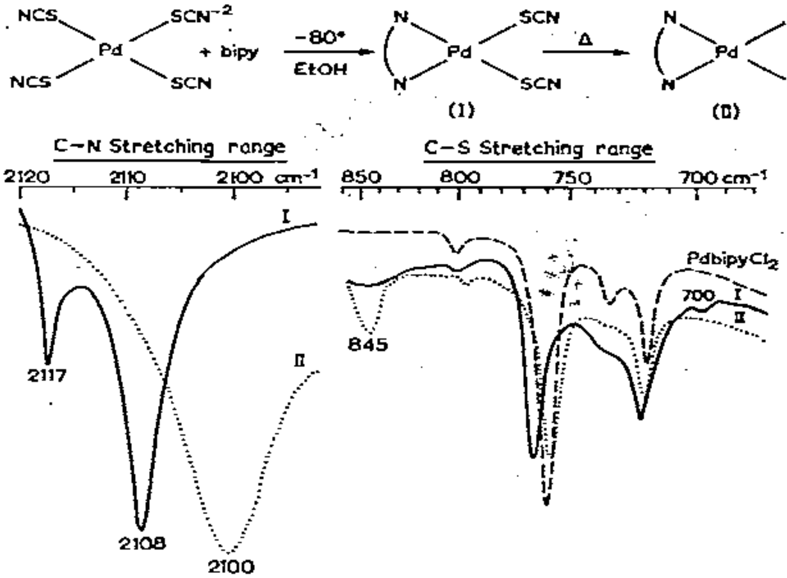
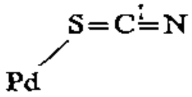


Fig. 1. Preparation and spectra of [Pd(bipy) $(SCN)_2$] and [Pd(bipy) $(NCS)_2$][8].

The trend shown in Table II might, at first glance, be used to further support the π-bonding hypothesis in that, concurrent with the decrease in π-bonding ability from triphenylphosphine to triphenylstibine, a change from N- to S-bonding occurs. However, it has recently been shown[7] that steric factors can alter the nature of thiocyanate honding in these systems. As would be expected, introduction of the non-π-bonding ligand diethylenetriamine, $NH_2C_2H_4NHC_2H_4NH_2$, yields a stable S-bonded complex, $[Pd(dien)SCN]^+$, exhibiting a C–S stretching frequency of 714 cm^{-1}. The tetraethyl-substituted ligand, $(C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$, yields instead a stable N-bonded complex, $[PdEt_4dien(NCS)]^+$ (C–S stretch at 832 cm^{-1}). The change from Pd–SCN to Pd–NCS bonding appears to be due to the steric hindrance caused by the four ethyl groups. Molecular models show that the angular[5]



$$\underset{Pd}{\diagup}S=C\equiv N$$

linkage would experience considerable steric strain in the latter complex, whereas the linear[5] (or nearly so) Pd—N≡C—S linkage is readily accomodated. It can then be seen that the steric factor is operating in the same direction as the π-bonding effect in the complexes listed in Table II. Because of the large size of antimony, the three phenyl groups are further removed from the palladium(II) in the complex containing triphenylstibine than in that containing triphenylphosphine. The steric hindrance encountered by a non-linear Pd–SCN linkage would, therefore, be less in the former complex.

Burmeister and Basolo[2] studied the effects of a large number of ligands on thiocyanate bonding and cited the change from Pd–NCS to Pd–SCN bonding in the complexes $[Pd(py)_2(NCS)_2]$ and $[Pd(\gamma\text{-pic})_2(SCN)_2]$ (py = pyridine, γ-pic = γ-picoline) as an unequivocal example, free of complicating steric effects, of the fact that electronic factors of coordinated ligands can alter the nature of thiocyanate bonding in metal complexes. However, it has been suggested very recently by Sabatini and Bertini[8] that the thiocyanate bonding assignment in the pyridine complex is incorrect. They concluded, from an examination of the infrared spectrum of the complex down to 400 cm^{-1}, that the band at 865 cm^{-1}, originally assigned to the C–S stretch of N-bonded thiocyanate, is, in actuality, the first overtone of an S-bonded SCN bend fundamental ν_2(SCN) at 436 cm^{-1}. The actual C–S stretching band would, therefore, be expected[1] to occur in the 680–720 cm^{-1} range, a region of the spectrum which is obscured by pyridine absorption.

Consequently, no change in the mode of thiocyanate bonding is expected or observed when γ-picoline is employed as the other ligand, since its greater basicity[9] and weaker π-bonding ability[9] should both serve to enhance Pd–SCN bonding. The possibility of effecting a change to M–NCS bonding therefore arises when a strongly electron withdrawing group is substituted in the para position of the pyridine ring (Table III). The change in bonding which occurs in going from the 4-cyanopyridine palladium(II) complex to that containing 4-nitropyridine vividly demonstrates that only the electronic factor is operative and, further, that only very small effects may be required to alter the nature of thiocyanate bonding in these systems.

The behavior of the SCN bending mode and the C–N stretching mode ν_3(SCN) upon coordination deserves some comment. Sabatini and Bertini[8,10] have noted that the former occurs as a single band at 460–490 cm^{-1} in the spectra of isothiocyanates, whereas thiocyanates exhibit a band at 410–440 cm^{-1}, with weaker satellites at higher frequencies, as shown in Table III. This behavior was also observed by Lewis, *et al.*[5] The ranges exhibited by the C–N stretching mode are much less well defined. Mitchell and Williams[11] studied a large number of thiocyanate-containing complexes and came to the conclusion that the frequency of this band varies in the order $CNS^- <$ M–NCS $\leqslant$ M–SCN $<$ M–SCN–M (bridged). Sabatini and Bertini[8] concluded, from their study, that the most reliable feature for diagnosing bond type in the complexes $[PdL_2(SCN)_2]$ is the C–N stretching band: it is sharp and above 2100 cm^{-1} in the S-bonded complexes and broad and below 2100 cm^{-1} in the N-bonded complexes. While there is as yet no evidence to the contrary as far as palladium(II) complexes are concerned (see, for example, Tables I, II, and III), it must be accepted with some reservation, for in two sets of thiocyanate linkage isomers recently prepared by Schmidtke[12], the relative positions of the C–N bands are reversed (Table IV). The bonding assignments are further supported by the visible and ultraviolet spectra of the isomers in that both S-bonded isomers exhibit band maxima which are shifted to longer wavelengths,

TABLE III

THIOCYANATE INFRARED FREQUENCIES FOR PALLADIUM(II) AND PLATINUM(II) COMPLEXES CONTAINING PARA-SUBSTITUTED PYRIDINES (cm^{-1})[a]

Complex	*Hammett substituent constant, σ_p*[b]	*C–N stretch*	*C–S stretch*	*NCS bend*	*Bending overtone*
[Pd(γ-pic)$_2$(SCN)$_2$]	−0.17	2112 s, sp	702 w	423 w	840 w
[Pd(py)$_2$(SCN)$_2$]	0.00	2112 s, sp	d	424 w, (436 s)?	865 w
cis-[Pt(py)$_2$(SCN)$_2$][c]	0.00	2120 s, sp	d	480 w, 465 mw, 430 sh, 425 m	848 w
trans-[Pt(py)$_2$(SCN)$_2$][c]	0.00	2115 s, sp	d	426 mw, 418 sh	855 w
[Pd(4-acpy)$_2$(SCN)$_2$]	0.52	2117 s, sp	706 w	422 mw, 430 sh 465 w	d
cis-[Pt(4-acpy)$_2$(SCN)$_2$]	0.52	2116 s, sp; 2131 m, sp[e]	697, w, br	418 w, 427 w, 450 vw	d
trans-[Pt(4-acpy)$_2$(SCN)$_2$]	0.52	2130 s, sp[e]	703 w	412 w, 465 vw	d
[Pd(4-cypy)$_2$(SCN)$_2$]	0.63	2111 s, sp	698 w	425 w, 460 w	d
[Pd(4-nitropy)$_2$(NCS)$_2$]	0.78	2097 s, br	d	455 w	d
[Pd(phen) (SCN)$_2$][c]	—	2116 s, sp	697 w	418 m, 460 mw	d
[Pd(5-nitrophen) (NCS)$_2$][c]	—	2090 s, br	d	458 w	

[a] Complexes held in Nujol suspension.

[b] Values taken from H. H. Jaffé, *Chem. Rev.*, 53 (1953) 191.

[c] Frequencies taken from ref. 8.

[d] Band masked by absorption of the organic ligand.

[e] Both the in- and out-of-phase C–N and C–S stretching modes are active in the *cis*-isomer. Only the out-of-phase mode is active in the *trans*-isomer of a square planar complex. Abbreviations: γ-pic = γ-picoline(4-methylpyridine), py = pyridine, 4-acpy = 4-acetylpyridine, 4-cypy = 4-cyanopyridine, phen = 1,10-phenanthroline, s = strong, m = medium, w = weak, sp = sharp, br = broad, sh = shoulder.

TABLE IV

INFRARED SPECTRA OF THIOCYANATE LINKAGE ISOMERS OF RHODIUM(III) AND IRIDIUM(III) (cm^{-1})[12]

Complex	*C–N Stretch*	*C–S Stretch*
$[Rh(NH_3)_5NCS]^{2+}$	2145 s, br	815 s
$[Rh(NH_3)_5SCN]^{2+}$	2115 s, sp	730 w, br
$[Ir(NH_3)_5NCS]^{2+}$	2140 s, br	825 s
$[Ir(NH_3)_5SCN]^{2+}$	2110 s, sp	700 m

in accordance with the lower position of –SCN in the spectrochemical series.

The 4-cyanopyridine complex of palladium(II) shown in Table III presents a special problem in that, in addition to coordination *via* the pyridine nitrogen, coordination *via* the nitrile group is a reasonable possibility. The former bonding mode is that actually observed, as demonstrated by the data shown in Table V.

TABLE V

INFRARED FREQUENCIES OF FREE AND COORDINATED 4-CYANOPYRIDINE (cm^{-1})

Compound	*Nitrile stretching*	*C–C and C–N stretching*				*Ring breathing*	
		(1)	*(2)*	*(3)*	*(4)*	*1st*	*2nd*
4-cyanopyridine*	2240	1591	1535	1490	1408	985	1078
$[Pd(4\text{-}cypy)_2(SCN)_2]$	2240	1620	1545	1495	1422	1043	1072
$[Pd(4\text{-}cypy)_2Cl_2]$	2240	1615	1553	1495	1423	1052	1075

* Values taken from F. FARHA, JR. AND R. T. IWAMOTO, *Inorg. Chem.*, 4 (1965) 844.

The CN group is not conjugated with the lone electron pair on the pyridine nitrogen and, therefore, coordination through the latter should not change the nitrile stretching frequency from that of the free base. Gill, *et al.*[13], and Greenwood and Wade[14] have noted that, upon pyridine coordination, the four principal bands of pyridine between 1430 and 1600 cm^{-1} (ring C–C and C–N stretching vibrations) undergo a blue shift, as do the ring breathing frequencies in the 985 to 1250 cm^{-1} region.

Selenocyanato and Isoselenocyanato Complexes

The coordination chemistry of the selenocyanate ion was, until this decade, an area almost completely devoid of research. Recent studies[15–18] have emphasized the analogous coordination behavior of the thiocyanate and selenocyanate ions. However, complexes containing selenocyanates as the only ligands had been prepared for only five different transition metal ions: $[(CH_3)_4N]_2[Co(NCSe)_4]$ (ref. 15,17), $K_3[Cr(NCSe)_6]$ (ref. 18), $K_2[Pt(SeCN)_6]$ (ref. 15), $K_2[Hg(SeCN)_4]$ (ref. 15), and AgSeCN (bridged)[15]. The shifts of the selenocyanate C–Se stretching frequency ν_1(SeCN) upon N- or Se-coordination were found to parallel those exhibited by the C–S stretching frequency of the thiocyanate group upon N- or S-coordination, *i.e.*, relative to that of uncoordinated selenocyanate, as in potassium selenocyanate (558 $\mathrm{cm^{-1}}$)[19], the C–Se stretching frequencies of M–NCSe complexes are shifted to higher wave numbers, while those of M–SeCN complexes are shifted to lower wave numbers[15].

In an effort to obtain a more complete picture, we have synthesized a number of hitherto unknown simple selenocyanate complexes. The basic preparative technique involves the reaction of the appropriate metal nitrate or complex metal chloride with potassium selenocyanate and tetra-*n*-butylammonium selenocyanate in absolute ethanol. The pertinent infrared absorption bands of the new selenocyanate complexes, along with those of their known thiocyanate analogs, are shown in Table VI. In those cases where comparisons are possible, the similarity in behavior, both with respect to the mode of bonding and to the spectra, is rather remarkable. Most of the complexes exhibit a simpler C–N stretching spectrum in solution due to the disappearance of solid state splitting effects. The nickel(II) complex is an exception, and the appearance of the band at 2070 $\mathrm{cm^{-1}}$ (the C–N stretching frequency of "ionic" selenocyanate[19]) indicates that some dissociation of the complex is taking place in acetone solution. The off-white iron(II) and reddish

TABLE VI

C–N, C–S, AND C–Se STRETCHING FREQUENCIES OF SOME THIOCYANATE AND SELENOCYANATE COMPLEXES ($\mathrm{cm^{-1}}$)*

*Complex***	$\nu_3(SeCN)$	$\nu_1(SeCN)$	$\nu_3(SCN)$	$\nu_1(SCN)$
$[\mathrm{Mn(NCSe)_6}]^{4-}$	(M) 2097 sh, 2082 s, br	640 vw		
	2070 s, br	617 w		
	(S) 2064 s, br			
$[\mathrm{Fe(NCSe)_4}]^{2-}$	(M) 2067 s, br, 2055 sh	673 sh, 666 w		
	(S) 2064 s, br			
$[\mathrm{Fe(NCSe)_6}]^{3-}$	(M) 2067 s, br; 2055 sh	673 sh, 666 w		
	(S) 2064 s, br			
$[\mathrm{Ni(NCX)_6}]^{4-}$	(M) 2118 sh, 2102 s, br	625 w	2123 sh, 2101 s	766 w
	(S) 2100 s, br; 2070 m, br		2072 s	
$[\mathrm{Zn(NCX)_4}]^{2-}$	(M) 2087 s, br	1 m	2101 sh, 2076 s	822 sh, 815 vw
				802 sh
	(S) 2087 s, br		2079 s	
$[\mathrm{Y(NCSe)_6}]^{3-}$	(M) 2067 s, br; 2030 sh	634 m		
	(S) 2068 s, br			
$[\mathrm{Rh(XCN)_6}]^{3-}$	(M) 2104 s, sp; 2071 m, br	515 w	2110 sh, 2098 s	705 w
			2084 s	695 sb
	(S) 2107 s, sp; 2071 m, br		2106 s	
$[\mathrm{Pd(XCN)_4}]^{2-}$	(M) 2107 s, sp	519 w	2122 s, 2116 sh	708 sh
	2060 w		2098 sh, 2092 sh	703 w
			2088 s, 2047 w	694 sh
	(S) 2113 s, sp		2108 s	
$[\mathrm{Pt(XCN)_4}]^{2-}$	(M) 2105 s, sp; 2060 w	516 w	2127 s, 2098 s	705 sh, 700 w
				692 sh
	(S) 2117 s, sp		2114 s	

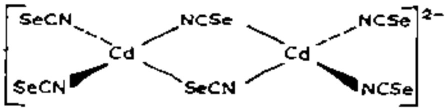
* Data for thiocyanate complexes taken from ref. 5.

** Cations present: selenocyanates, $(n\text{-}\mathrm{C_4H_9})_4\mathrm{N^+}$; thiocyanates, $\mathrm{K^+}$. (M) indicates Nujol mull spectrum; (S) indicates solution spectrum-acetone for selenocyanates, acetophenone for thiocyanates.

brown iron(III) complexes deserve special mention, for they would appear to be one and the same compound if only their infrared spectra are considered. However, the results of elemental analyses and conductivity measurements in nitrobenzene solution (all of the complexes prepared were characterized in this manner) support the indicated formulas. The oxidation state of the iron apparently has no effect on the selenocyanate bonding mode, contrary to Jørgensen's predictions[20].

The fact that yttrium(III) readily forms a complex with selenocyanate raises the intriguing possibility that the lanthanide tripositive ions, all similar in size to yttrium(III), might do likewise. We are currently investigating this possibility. The change from class *a* to class *b* behavior occurs at rhodium(III) for both the selenocyanate and thiocyanate complexes. The only known thiocyanate complex with a transition metal ion preceding rhodium in the second transition series is $[Mo(NCS)_6]^{3-}$, prepared by Lewis, *et al.*[5]

The cadmium(II) selenocyanate complex prepared was purposely not included in Table VI because of its unique constitution. The results of repetitive elemental analyses and conductivity measurements on different samples support its formulation as $[(n\text{-}C_4H_9)_4N]_2[Cd_2(CNSe)_6]$. Its solid state infrared spectrum (C–N stretch, 2125 sh, 2109 s, br; C–Se stretch, 589 sh, 582 m) and solution infrared spectrum (C–N stretch, 2120 s, sp, 2076 s, br) are compatible with the bridged structure



There is thus a very smooth change from class *a* to class *b* behavior in the selenocyanate complexes of group II B.

Turco *et. al.*[15] and Cotton *et al.*[17] have found that –NCSe is very close to but slightly stronger than –NCS in the spectrochemical series. A comparison of the visible spectra of the palladium(II) and platinum(II) complexes (Table VII) indicates that –SeCN lies lower in the spectrochemical series than –SCN. The position of the lowest energy band in the spectrum of the palladium(II) complex (18.9 *kK*, or 530 mμ) places –SeCN below –Br (504 mμ) in the series.

TABLE VII

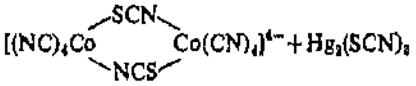
VISIBLE SPECTRA OF THIOCYANATE AND SELENOCYANATE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) (*kK*)
(28.6–13.3 *kK*)

	$X = Se$	$X = S$
$[Pd(XCN)_4]^{2-}$	23.2 sh, 18.9 sh	24.5 sh, 20.0 sh
$[Pt(XCN)_4]^{2-}$	22.2 sh	27.0 sh, 23.8 sh

The similarity in behavior ceases when other ligands are introduced into the

TABLE VIII

A COMPARISON OF OXIDATION–REDUCTION REACTIONS OF ANALOGOUS THIOCYANATE AND SELENOCYANATE COMPLEXES[21]

	*Oxidant**	*Postulated intermediate or activated complex*	*Products*
(1)**	$[Co(NH_3)_5NCS]^{2+}$	$[(H_3N)_5Co^{III}\text{–}NCS\text{–}Co^{II}(CN)_5]^-$	$[Co(CN)_5SCN]^{3-} + [Co(OH_2)_6]^{2+} + NH_3$
(2)	$[Co(NH_3)_5NCSe]^{2+}$	$[(H_3N)_5Co^{III}\text{–}NCSe\text{–}Co^{II}(CN)_5]^-$	$[Co(CN)_5OH_2]^{2-} + [Co(OH_2)_6]^{2+} + NH_3 + NCSe^-$
(3)	$[Hg(SCN)_4]^{2-}$	$[(NCS)_3Hg^{II}\text{–}SCN\text{–}Co^{II}(CN)_5]^{5-}$	 $[(NC)_4Co\overset{SCN}{\underset{NCS}{\rightleftharpoons}}Co(CN)_4]^{4-} + Hg_2(SCN)_2$
(4)	$[Hg(SeCN)_4]^{2-}$	$[(NCSe)_3Hg^{II}\text{–}SeCN\text{–}Co^{II}(CN)_5]^{5-}$	$[Co(CN)_5NCSe]^{3-} + Hg_2(SeCN)_2(?)$

* The reductant used in each reaction was $[Co(CN)_5]^{3-}$.

** The existence of the postulated intermediate or activated complex in this reaction is supported by the results of a kinetic study by Halpern and co-workers [J. P. CANDLIN, J. HALPERN AND S. NAKAMURA, *J. Am. Chem. Soc.*, 85 (1963) 2517; J. HALPERN AND S. NAKAMURA, *Proceedings of the Eighth International Conference on Coordination Chemistry*, Springer-Verlag, Vienna and New York, 1964, p. 271. The product of the reaction has been isolated by Burmeister [J. L. BURMEISTER, *Inorg. Chem.*, 3 (1964) 919].

coordination sphere[21], either by means of activated bridge electron transfer reactions (Table VIII) or substitution reactions (Table IX), the "normal" class *a*-isoselenocyanato class *b*-selenocyanato bonding pattern being followed in all of the selenocyanate-containing complexes. The C–N and C–Se stretching frequencies of the new complexes are shown in Table X.

TABLE IX

A COMPARISON OF SUBSTITUTION REACTIONS OF ANALOGOUS THIOCYANATE AND SELENOCYANATE COMPLEXES[a,21]

Substrate[b]	*Entering ligand*	*Product*[c]	
		(X = S)[d]	*(X = Se)*
$[M(XCN)_4]^{2-}$	2,2′-bipyridine	$[M(bipy)(NCS)_2]$	No reaction
$[M(XCN)_4]^{2-}$	$P(C_6H_5)_3$	$[M(P(C_6H_5)_3)_2(NCS)_2]$	$[M(P(C_6H_5)_3)_4]^{2+}$
$[M(XCN)_4]^{2-}$	$As(C_6H_5)_3$	$[M(As(C_6H_5)_3)_2(NCS)_2]$	No reaction
$[M(bipy)(OH_2)_2]^{2+}$	NCX^-	$[M(bipy)(NCS)_2]$	$[M(bipy)(SeCN)_2]$

[a] Identical conditions employed in the reaction of a given ligand with analogous substrates.

[b] M = Pd(II), Pt(II).

[c] The thiocyanate and selenocyanate-containing complexes shown were found to be stable with respect to isomerization.

[d] Reference 2.

TABLE X

C–N AND C–Se STRETCHING FREQUENCIES OF SELENOCYANATE COMPLEXES OF COBALT(III), PALLADIUM(II), AND PLATINUM(II) (cm^{-1})[21]

Compound	ν_3*(C–N)*	ν_1*(C–Se)*
$K_3[Co(CN)_5NCSe]$	2127 s (–CN)	664 w
	2124 s (–CN)	
	2095 w (–CN)	
	2072 s (–NCSe)	
$[Co(NH_3)_4(CN)NCSe]Cl$	2140 m (–CN)	607 w
	2105 s (–NCSe)	
$[Co(NH_3)_5NCSe](NO_3)_2$*	2116 s	624 m
$[Pd(bipy)(SeCN)_2]$**	2116 s	523 w
	2112 s	518 w
$[Pt(bipy)(SeCN)_2]$**	2135 s	532 w
	2125 s	527 w
 $K_4[(NC)_4Co(NCS)(SCN)Co(CN)_4] \cdot 5H_2O$	2180 s (Co–NCS–Co)	
	2120 s (–CN)	

* Cotton *et al.*[17], have pointed out that analogous M–NCS and M–NCSe complexes exhibit C–N stretching frequencies within 10 cm^{-1} of each other. The C–N stretching frequency of $[Co(NH_3)_5NCS](NO_3)_2$ has been determined[4] to be 2120 cm^{-1}.

** Splitting of C–N and C–Se stretching modes due to the *cis*-configurations of the complexes.

Cyano and Isocyano Complexes

It is generally believed that the cyanide ion, when acting as a monodentate ligand, coordinates only through the carbon atom. With the synthesis[22,23], in 1964, of $[Co(NH_3)_5CN]^{2+}$, an oxidant became available which, when reduced by $[Co(CN)_5]^{3-}$ *via* an inner sphere activated bridge mechanism, could lead to the formation of an N-bonded cyanide complex:

$$\begin{tikzcd}
{[Co(NH_3)_5{}^{14}CN]^{2+} + [Co(CN)_5]^{3-}} \arrow[r] & {[(H_3N)_5Co^{III}-CN-Co^{II}(CN)_5]^-} \arrow[d] \\
{[Co(H_2O)_6]^{2+} + 5NH_3} & {[Co(NH_3)_5]^{2+} + [Co(CN)_5N^{14}C]^{3-}} \arrow[l, "H_2O"'] \arrow[d] \\
 & {[Co(CN)_5{}^{14}CN]^{3-}}
\end{tikzcd}$$

An alternative outer-sphere electron-transfer mechanism would also be possible:

$$\begin{tikzcd}
{[Co(NH_3)_5{}^{14}CN]^{2+} +} & {[Co(CN)_6]^{4-}} \arrow[r] \arrow[d, shift left, "CN^-"'] & {\{[Co(NH_3)_5{}^{14}CN]\ [Co(CN)_6]\}^{2-}} \arrow[d] \\
 & {[Co(CN)_5]^{3-}} \arrow[u, shift left] & {[Co(NH_3)_5{}^{14}CN]^{+} + [Co(CN)_6]^{3-}} \arrow[d, "H_2O"] \\
 & & {[Co(H_2O)_6]^{2+} + 5NH_3 + {}^{14}CN^-}
\end{tikzcd}$$

That the reaction proceeds predominately *via* the inner-sphere mechanism was shown[24] by the results of tracer experiments using ^{14}C-labelled cyanide in the oxidant and an excess ($[CN^-]/[Co(NH_3)_5{}^{14}CN]^{2+} = 10$) of unlabelled cyanide in solution. The radioactivity of both the $[Co(NH_3)_5{}^{14}CN]^{2+}$ oxidant and $[Co(CN)_5{}^{14}CN]^{3-}$ product was essentially the same, within experimental error ($\sim$21,000 cpm.). The infrared spectrum of the product was, however, identical with that of $[Co(CN)_6]^{3-}$ prepared by Schlessinger's method[25,26], indicating that rapid isomerization of the initial product containing the N-bonded cyanide had taken place.

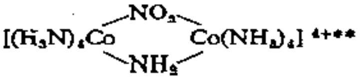
Halpern and Nakamura[27] have studied the kinetics of the reaction and found, at 0.03 *M* CN^-, with the inner-sphere path accounting for some 70% of the reaction, that the disappearance of $[Co(NH_3)_5CN]^{2+}$ ($t_{\frac{1}{2}} = 0.8$ sec at 25°) coincided with the appearance of a transient which absorbed more strongly than $[Co(CN)_6]^{3-}$ at 320 mμ (consistent with a pentacyanocobaltate(III) complex containing an N-bonded ligand) and which underwent first order decay to $[Co(CN)_6]^{3-}$ with a half-life of 1.6 sec. Espenson and Birk[28], using aqueous chromium(II) as the reductant, have obtained kinetic and spectrophotometric evidence for a somewhat longer-lived ($t_{\frac{1}{2}} = 1.28$ min at 15°) $[Cr(H_2O)_5NC]^{2+}$ intermediate. Shriver, *et al.*[29], using *Dq* values to calculate site preference energies for mixed cyanide polymers, predicted and found linkage isomerism for $K[FeCr(CN)_6]$, which, when heated, isomerizes to $K[CrFe(CN)_6]$, wherein the isomerization involves, in effect, a cyanide flip: $Cr^{III}-C\equiv N-Fe^{II} \rightarrow Cr^{III}-N\equiv C-Fe^{II}$.

Nitrito and Nitro Complexes

The nitrite ion is undoubtedly the most versatile of the common ambidentate ligands. In addition to functioning as an N- or O-bonded monodentate ligand and as an N,O-bonded bridging group, it has also been found to be capable of functioning as an O,O-bonded bidentate ligand[30] (Table XI). An explanation involving steric factors has been proposed to account for the change from N- to O-bonding in the complexes $[Ni(NO_2)_6]^{4-}$, $[Ni(py)_4(ONO)_2]$, and $Ni(diamine)_2(ONO)_2]$ (ref. 30).

TABLE XI

INFRARED SPECTRA OF VARIOUS TYPES OF NITRITE COMPOUNDS (cm^{-1})[30]

Compound	*Asymmetric N–O str.,* ν_{as}	*Symmetric N–O str.,* ν_s	*NO_2 deformation,* δ	*NO_2 wagging* ϱ_w
$NaNO_2$	1328	1261	828	—
$[Co(NH_3)_5NO_2]Cl_2$	1428	1310	825	594
$CH_3{-}NO_2$	1586	1377		
$[Ni(py)_4(ONO)_2]$	1393	1114	825	—
cis-$CH_3{-}ONO$	1625	844		
$[Ni(\alpha\text{-pic})_2(NO_2)_2]$*	1272	1199	866, 862	
 $[(H_3N)_4Co\overset{NO_2}{\underset{NH_2}{\rightleftarrows}}Co(NH_3)_4]^{4+}$**	1485	1183		

* O,O chelate.
** N,O-bridge.

A commonly accepted explanation[31] for the fact that the N-bonded nitrite ion occupies a much higher position in the spectrochemical series than O-bonded nitrite is that, in the former case, there is a considerable amount of back donation of electron density from the d_π metal orbitals to a vacant π-anti-bonding orbital localized mainly on the nitrogen atom. This stabilizes the d_π metal orbitals (essentially non-bonding d_{xy}, d_{xz} and d_{yz} orbitals in complexes containing no π-bonding ligands), increasing the value of Δ. This explanation, though commonly accepted, had not hitherto been subjected to a systematic physical study specifically designed to test the π-bonding hypothesis.

Since the presence of electron density in the π-anti-bonding orbital of the nitrite results in a lowering of the formal N–O bond order, both the symmetric and asymmetric N–O stretching frequencies, ν_s and ν_{as}, should decrease as the amount of back donation to the nitrite increases, and *vice-versa*. Thus, in a series of complexes such as $[ML_2(NO_2)_2]$, where the metal ion (palladium(II) or platinum (II)) is kept the same to minimize changes in the M–N σ-bond strength, the values of ν_s and ν_{as} should vary directly with the π-bonding capacity of the L ligands, much in the same manner as the C–O and N–O stretching frequencies have been found to vary in a series of mono- and disubstituted derivatives[32] of

$[Co(CO)_3NO]$. The possibility also arises, in the case of the better π-bonding ligands, of changing the preferred mode of attachment of the nitrite from the nitrogen to the oxygen atom in palladium(II) and platinum(II) complexes. Such a change would be somewhat analogous to that which has been observed[1,2] for similar thiocyanate complexes.

The frequencies of the absorption bands arising from coordinated nitrite ion in the complexes prepared are shown in Table XII. The positions of these bands were determined by comparing the spectra of the dinitro complexes with those of the analogous dichloro complexes. The potassium bromide disk technique was used in measuring the spectra.

TABLE XII

NITRITE INFRARED FREQUENCIES FOR THE $[ML_2(NO_2)_2]$ AND $[ML'(NO_2)_2]$ COMPLEXES (± 1 cm^{-1})

Ligand or Compound	*Asymmetric N–O str.*, ν_{as}		*Symmetric N–O str.*, ν_s		NO_2 *deformation*, δ		NO_2 *wagging*, ϱ_w	
$M =$	Pd^{II}	Pt^{II}	Pd^{II}	Pt^{II}	Pd^{II}	Pt^{II}	Pd^{II}	Pt^{II}
$K_2[M(NO_2)_4]$*	1376 s 1390 s 1426 s	1386 s 1410 s 1436 s	1340 s	1350 s	831 m 838 m	828 s 832 s 838 s	579 w	613 m 636 m
$P(C_6H_5)_3$	1414 s	1417 s	1324 s	1336 s	816 m	822 s	579 w	624 sh 632 m
$As(C_6H_5)_3$	1412 s	1411 s	1327 s	1334 s	816 ms	822 s	582 ms	628 sh 637 m
2,2′-bipyridine	1417 s	1403 s	1333 s 1350 m	1343 sh 1351 s	820 sh 825 m	828 s 835 s	573 w 600 w	581 m 608 m
$Sb(C_6H_5)_3$	1408 s	1399 s	1320 s	1328 s	814 m	819 s	569 m	586 w 630 m
o-phenanthroline	1410 s	1401 s	1323 s 1336 m	1330 s 1343 sh	821 sh 827 ms	827 m 834 m	572 w 610 w	581 w 611 w
pyridine	1407 s	1400 s	1331 s	1329 s 1357 ms	821 ms	824 s 831 s	598 w	578 m 612 m
NH_3	1392 s	1381 s	1329 s	1341 s	829 ms	832 s 841 s	597 w	574 m 590 m
$NaNO_2$**	1328 w, sh		1261 s		828 w		—	

* Pd–N stretching band at 460 cm^{-1}. Pt–N stretching band at 450 cm^{-1}. M–N stretching bands for mixed ligand complexes could not be assigned with certainty. Values for $K_2[Pt(NO_2)_4]$ taken from K. NAKAMOTO, J. FUJITA AND H. MURATA, *J. Am. Chem. Soc.*, 80 (1958) 4817.

** Values taken from R. E. WESTON AND T. F. BRODASKY, *J. Chem. Phys.*, 27 (1957) 683. Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.

In addition to the bands shown, an additional band at *ca.* 1270 cm^{-1} was observed in all of the spectra of the palladium(II)–dinitro complexes, but was absent in those of the platinum(II) complexes. This is most certainly due to the symmetric N–O stretching vibration of "ionic" nitrite, freed from the coordination sphere of the relatively labile palladium(II) by bromide ion substitution in the solid state. Strong support for this explanation is found in the fact that this band disappeared entirely in each of several test cases when the spectrum was measured with the complex held in Nujol suspension.

Inspection of Table XII reveals that, in each case, both ν_{as} and ν_s have been raised with respect to the free ion values, and a wagging band, ρ_W, has also appeared. This leaves little doubt that the nitrites are coordinated through the nitrogen atom[33].

By analogy to similar reactions involving halogeno complexes, the reactions utilized in this study would be expected to produce the *trans*-isomer in the case of the palladium(II) complexes[34,35] (with the obvious exceptions of the 2,2′-bipyridine and *o*-phenanthroline derivatives) and the *cis*-isomer in the case of the platinum(II) complexes[36]. This is substantiated by the infrared spectra of the products, in that none of the bands of the *trans*-palladium(II) complexes are split while all of the ρ_W bands and most of the ν_s and δ bands (exceptions being those of the triphenylphosphine, triphenylarsine and triphenylstibine derivatives of platinum(II)) of the *cis*-complexes of both palladium(II) and platinum(II) are split, the splitting arising from in- and out-of-phase vibrations[37,38].

To interpret the data shown in Table XII in a meaningful manner, it is necessary to first consider the effects of the M–N σ-bond formation on the N–O stretching frequencies. Since both of these frequencies experience a substantial blue shift upon N-coordination, the most important bond, as far as the nitrite is concerned, is the σ-bond, since any π-bonding would tend to lower these frequencies below the free ion values. However, a clear indication that π-bonding is also taking place in the $[M(NO_2)_4]^{2-}$ complexes is seen in the fact that, for nitromethane (Table XI) where no π-bonding is possible, both of these frequencies are considerably higher than those of the $[M(NO_2)_4]^{2-}$ complexes. Considering only σ-bonding effects, the introduction of other ligands more basic than the nitrite ion ($pK_a = 3.37$) would weaken the M–NO_2 σ-bonds of the remaining nitrites and would, therefore, lower their N–O stretching frequencies. Summarizing the σ- and π-bonding effects, the N–O stretching frequencies should *decrease* as the basicity of the L ligand *increases* and should *increase* as the π-bonding ability of the L ligand *increases*.

Since the basicity and the π-bonding ability of the L ligands do not necessarily vary in the same direction for a given group of ligands, it is necessary to divide the ligands shown in Table XII into three different types, and consider each type separately: (a) triphenylphosphine, triphenylarsine and triphenylstibine (relatively weak bases, but strongly π-bonding ligands), (b) 2,2′-bipyridine, *o*-phenanthroline and pyridine (relatively strong bases capable of π-bonding, but to a lesser extent than (a), and (c) ammonia (a relatively strong base, incapable of π-bonding).

Of the ligands in group (a), only the pK_a of triphenylphosphine has been determined[39] ($pK_a(H_2O) = 2.73$, calculated from the results of titrations in nitromethane, using half-neutralization potentials). However, it is reasonable to assume that the basicity of these ligands increases in the order $Sb(C_6H_5)_3 < As(C_6H_5)_3 <$

$< P(C_6H_5)_3$. Their π-bonding ability increases in the same order[2,8]. Since both of the N–O stretching frequencies (Table XII) *increase* in this order (only ν_s of the palladium(II)–triphenylarsine complex is out of line) the π-bonding effect is believed to be the controlling factor in this group.

In group (b), the basicity of the ligands increases in the order bipy < phen < < py (pK_a's, respectively, in water at 25° of 4.37 (ref. 40), 4.96 (ref. 41) and 5.22 (ref. 42)). It should be noted that 2,2′-bipyridine and *o*-phenanthroline function only as monoprotic bases. Their π-bonding ability increases[2,8] in the reverse order py ⩽ phen < bipy. In this case, both trends predict an N–O stretching frequency order of py < phen < bipy, and, for the platinum(II) complexes, where all have the *cis*-configuration, this is observed (Table XII). The palladium(II)–2,2′-bipyridine and *o*-phenanthroline complexes also exhibit N–O stretching frequencies in line with the prediction. The palladium(II)–pyridine complex is not included in the comparison because of its *trans*-configuration.

Ammonia's high basicity ($pK_a = 9.25$) and inability to π-bond should both serve to lower the N–O stretching frequencies of its complexes below those of all the other complexes. This is realized in the case of the asymmetric stretching frequencies, but not in the case of the symmetric stretching frequencies, a discrepancy which cannot be rationalized at present.

Turning to the $K_2[M(NO_2)_4]$ complexes, the higher value of the Pd–N stretching frequency (460 cm^{-1} *versus* 450 cm^{-1} for the Pt–N stretch) is indicative[33] of a higher bond order. If this is a result of greater π-bonding, both ν_{as} and ν_s should be lower in the case of the palladium(II) complex because of greater electron density in the π-antibonding orbitals of the nitrites, the observed data being in agreement with the prediction.

A final piece of evidence which strongly supports the π-bonding hypothesis involves a comparison of the *cis*- and *trans*-dinitro isomers of platinum(II) prepared by Gatehouse[37], a comparison which was not noted by the author. If the nitrite groups are coplanar with the rest of the molecule, in plane π-bonding with the d_{xy} metal orbital would not be expected to be significant because only oxygens would be involved (taking nitrogen to be sp^2 hybridized). In the *cis*-$[Pt(L)_2(NO_2)_2]$ isomer, each nitrite would, therefore, share one filled metal d_π orbital (d_{xz} or d_{yz}) with a relatively strongly π-bonding L ligand. Consequently, less electron density is available for donation to the π-antibonding orbitals of the nitrites than is available in the case of the *trans*-isomer, where no metal d_π orbitals would be shared with the L ligands. The NO_2 stretching frequencies should, therefore, be higher in the case of the *cis*-isomer. Gatehouse[37] prepared three such isomeric pairs, employing the ligands 4-*n*-pentylpyridine, di-*n*-butylsulfide, and tri-*n*-butylphosphine. In each case, both the asymmetric and symmetric N–O stretching frequencies of the *cis*-isomer are appreciably (5–13 cm^{-1}) higher. This is also true in the case of *cis*-$[Pt(As(n\text{-}C_3H_7)_3)_2(NO_2)_2]$ *vs.* *trans*-$[Pt(As(n\text{-}C_4H_9)_3)_2(NO_2)_2]$, where the π-bonding capabilities of the two trialkylarsines would be expected to be quite similar.

The first known example of the phenomenon of linkage isomerism in coordination complexes dates back to Jørgensen's isolation[43], in 1893, of nitrito- and nitropentaamminecobalt(III). Subsequently, Basolo and Hammaker[44] succeeded in extending nitrito–nitro linkage isomerism to include the pentaammines of rhodium(III), iridium(III), and platinum(IV).

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