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LINKAGE ISOMERISM IN METAL COMPLEXES

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INTRODUCTION

The phenomenon of inorganic linkage isomerism (the existence of two complexes differing only in the mode of attachment of an ambidentate ligand to the metal atom) serves as a graphic illustration, in terms of the number of known examples, of the progress of synthetic coordination chemistry. Although the first linkage isomeric pair of metal complexes was isolated more than 100 years ago[1] (the isoxantho and xantho complexes of cobalt(III)), their true nature was not ascertained until almost 40 years later[2]. Indeed, Werner exhibited considerable farsightedness and optimism when he included salt (linkage) isomerism in his seven-fold complex classification[3], for only two more examples[3], both also involving the nitrite ion, had been prepared. However, as shown in Table 1 and the following text, at least 29 additional isomeric pairs involving seven ambidentate ligands (NO_2^-, SCN^-, $S_2O_3^{2-}$, CN^-, $SeCN^-$, SO_3^{2-}, and 3-formylacetylacetonate) have been reported since 1960. Their syntheses, the physical methods used in the elucidation of their structures, and the factors which determine their formation and stability will be reviewed in this paper.

M-ONO AND M-NO$_2$ ISOMERS

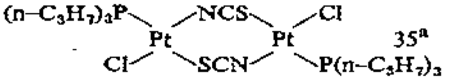
The first synthesis of linkage isomers by design, rather than by accident, resulted from the elucidation of the mechanism of the reaction leading to the formation of $[Co(NH_3)_5ONO]^{2+}$ from $[Co(NH_3)_5H_2O]^{3+}$. Both kinetic studies[5] and oxygen-18 tracer experiments[38] have shown that the reaction takes place in a buffered HNO_2/NO_2^- solution without Co–O bond cleavage. The proposed mechanism is shown in reactions (1) through (3).

$$[Co(NH_3)_5OH_2]^{3+} + OH^- \xrightleftharpoons{\text{fast}} [Co(NH_3)_5OH]^{2+} + H_2O \tag{1}$$

$$2HNO_2 \xrightarrow{\text{fast}} N_2O_3 + H_2O \tag{2}$$

TABLE 1

KNOWN LINKAGE ISOMERS OF METAL COMPLEXES

Stable isomer	*Ref.*	*Stable isomer*	*Ref.*
M–ONO and M–NO$_2$		*M–SCN and M–NCS*	
$[Co(NH_3)_5NO_2]^{2+}$	1, 2[a]	$[Cr(H_2O)_5NCS]^{2+}$	19, 20[b]
$[Co(NH_3)_2(py)_2(NO_2)_2]^+$	3[a]	$[Pd(Et_4dien)NCS]^+$	21, 22[a]
$[Co(en)_2(NO_2)_2]^+$	3, 4, 5[a]	$[Pd(4,7\text{-diphenylphen})(SCN)_2]$	23[a]
$[Rh(NH_3)_5NO_2]^{2+}$	6, 7[a]	$[Cu(tripyam)(NCS)_2]$	24[a]
$[Ir(NH_3)_5NO_2]^{2+}$	6, 7[a]	$[(C_5H_5)Fe(CO)_2NCS]$	25[a]
$[Pt(NH_3)_5NO_2]^{3+}$	7[a]	$[(C_5H_5)Mo(CO)_3NCS]$	25[a]
$[Co(CN)_5NO_2]^{3-}$	8[b]	$[Pd(P(OCH_3)_3)_2(NCS)_2]$	26[e]
$[Ni(Me_2en)_2(ONO)_2]$	9[b]	*M–SSO$_3$ and M–OS$_2$O$_2$*	
$[Ni(EtenEt)_2(ONO)_2]$	9[b]	$[Co(NH_3)_5OS_2O_2]^+$	27[c]
M–SCN and M–NCS		*M–NC and M–CN*	
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	10, 11[a]	$[Co(CN)_5CN]^{3-}$	8, 28[b]
$[Pd(bipy)(NCS)_2]$	10, 11[a]	$[Cr(H_2O)_5CN]^{2+}$	29[b]
$[Cd(CNS)_4]^{2-}$	12, 13[c]	*cis*-α-$[Co(trien)(CN)_2]^+$	29a[a]
$[Mn(CO)_5SCN]$	14[b]	*M–SeCN and M–NCSe*	
$[Pd(As(n\text{-}C_4H_9)_3)_2(SCN)_2]$	15[d]	$[Pd(Et_4dien)SeCN]^+$	30, 31[a]
$[Rh(NH_3)_5NCS]^{2+}$	16, 17[a]	*M–OSO$_2$ and M–SO$_3$*	
$[Ir(NH_3)_5NCS]^{2+}$	17, 18[a]	$[Co(NH_3)_5SO_3]^+$	32[a]
Individual complexes containing both bonding modes			
$[Co(en)_2(NO_2)(ONO)]^+$	4,5	$[Cu(tripyam)(SCN)(NCS)]$	24
$[Ni(NO_2)_4(ONO)_2]^{4-}$	33	$[Pd\{(C_6H_5)_2As(o\text{-}C_6H_4)P(C_6H_5)_2\}\text{-}$	
$[Pd(Me_2bipy)(SCN)(NCS)]$	23	$(SCN)(NCS)]$	34
Linkage isomers involving bridging ligands			
	35[a]	$K[Fe^{II}(CN)_6Cr^{III}]$	36[a]
Linkage isomers involving chelating ligand			
			37[a]

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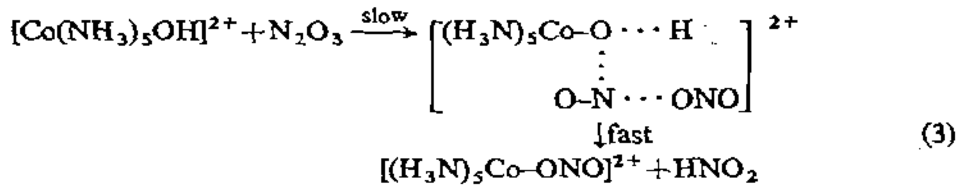
[a] Both isomers isolated. [b] Unstable isomer detected in solution, but not isolated. [c] S- and N-bonded forms are in equilibrium in solution, but solid (as $K_2[Cd(SCN)_4]\cdot 2H_2O$) contains two bridging and two S-bonded thiocyanates [Z. V. ZVONKOVA, *Zhur. Fiz. Khim.*, 26 (1952) 1798]. [d] Partial isomerization to N-bonded isomer in molten state. [e] Mixture of isomers initially isolated in solid state.

Abbreviations: py = pyridine, en = ethylenediamine, Me$_2$en = *N,N*-dimethylethylenediamine, EtenEt = *N,N'*-diethylethylenediamine, bipy = 2,2'-bipyridine, Et$_4$dien = *N,N,N',N'*-tetraethyldiethylenetriamine, 4,7-diphenylphen = 4,7-diphenyl-1,10-phenanthroline, tripyam = tri-(2-pyridyl)amine (bidentate), Me$_2$bipy = 4,4'-dimethylbipyridine, acac = acetylacetonate, trien = triethylenetetramine.



$$[Co(NH_3)_5OH]^{2+} + N_2O_3 \xrightarrow{slow} \left[\begin{array}{l}(H_3N)_5Co{-}O\cdots H \\ \qquad\qquad\quad\ \vdots \\ \qquad\qquad O{-}N\cdots ONO\end{array}\right]^{2+} \xrightarrow{fast} [(H_3N)_5Co{-}ONO]^{2+} + HNO_2 \qquad (3)$$

The O-bonded (nitrito) complex, once formed, rearranges by an intramolecular process to the stable N-bonded (nitro) form.

The retention of the Co–O bond during the substitution reaction suggested that other nitrito complexes might be formed and isolated from reactions, under mild conditions, with various $[M(NH_3)_5OH_2]^{n+}$ substrates. Accordingly, Basolo and Hammaker[6,7] succeeded in preparing nitritopentammine complexes of chromium(III), rhodium(III), iridium(III), and platinum(IV). With the exception of the chromium(III) complex, all isomerize, both in solution and in the solid state, to the nitro form. Only the nitro form could be isolated for platinum(II), due to its greater lability.

The bonding mode of the nitrite ion has been shown to be quite sensitive to changes in the steric requirements of other ligands in the coordination sphere of *trans*-$[NiL_4(NO_2)_2]$ complexes. As shown in Table 2, increasing steric hindrance leads to the formation of $Ni{-}O\diagdown_{N}\!{\nearrow}O$ linkages, which require less space than $Ni{-}N\!\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ linkages. The increasing steric hindrance may be introduced by increasing alkyl substitution in the bidentate ligands or, in the case of the pyridine complex, by the fact that the pyridine rings may be inclined with respect to the $Ni{-}N_4$ plane as is known[42] to be the case in *trans*-$[Ni(py)_4Cl_2]$. Two of the complexes, $[Ni(Me_2en)_2(ONO)_2]$ and $[Ni(EtenEt)_2(ONO)_2]$, exist in a nitrito-nitro equilibrium in chloroform[9], but only the nitrito isomers could be isolated in the solid state. The infrared spectrum of $[Ni(2\text{-(aminomethyl)pyridine})_2(NO_2)_2]$ supports[41] the presence of both nitro and nitrito linkages, but the electronic spectrum (both solution and

TABLE 2

STERIC EFFECTS ON THE BONDING MODE OF THE NITRITE ION IN *trans*-$[NiL_4(NO_2)_2]$ COMPLEXES

L *M–NO₂ bonds*	*Ref.*	L *M–ONO bonds*	*Ref.*
ammonia	39, 40	pyridine	40
2,2′-bipyridine/2	41		
ethylenediamine/2	9	*N,N*-dialkylethylenediamine/2	40
N-alkylethylenediamine/2	9	*N,N′*-diethylethylenediamine/2	40
2-aminomethylpiperidine/2	41	2-methylaminomethylpiperidine/2	41
		2-aminomethyl-6-methylpiperidine/2	41
2-aminomethylpyridine/2	41	2-methylaminomethylpyridine/2	41
		2-aminomethyl-6-methylpyridine/2	41

alkyl = methyl, ethyl

TABLE 3

INFRARED SPECTRA OF VARIOUS TYPES OF NITRITE COMPOUNDS (CM^{-1})

Compound	*Asymmetric N–O stretch,* ν_{as}	*Symmetric N–O stretch,* ν_s	*NO_2 deformation,* δ	*NO_2 wagging,* ρ_w	*Ref.*
Free ion (as in $NaNO_2$)	1328	1261	828	absent	44
N-bonded	increase	increase	little change	present	
trans-$[Pd(py)_2(NO_2)_2]^a$	1407	1331	821	598	45
O-bonded	increase	decrease	little change	absent	
trans-$[Ni(py)_4(NO_2)_2]^b$	1393	1114	825	–	40
O,O-bonded chelate	decrease	decrease	increase	absent	
$[Ni(\alpha\text{-picoline})_2(NO_2)_2]^b$	1272	1199	866, 862	–	46
N,O-bonded bridging group	increase	decrease	little change	absent	
$[Ni(Et_2en)(NO_2)_2]^{b,c}$	1429	1220	846, 838	–	40

[a] Potassium bromide disk. [b] Nujol and hexachlorobutadiene mulls. [c] Et_2en = *N,N*-diethylethylenediamine.

solid state) only gives evidence for the nitrito group. The electronic spectrum of a methanolic solution of $[Ni\,(2\text{-(aminomethyl)piperidine})_2(NO_2)_2]$ indicates[41] that isomerization to the nitrito complex may take place in solution.

Both visible and infrared spectra have been used extensively in determining the bonding mode of the nitrite ion in its complexes. The $-NO_2$ and $-ONO$ groups occupy quite different positions in the spectrochemical series[43]. The larger Δ value of $-NO_2$ places it between CN^- and *o*-phenanthroline, whereas the Δ value of $-ONO$ is comparable to that of $-NCS$. The shifts, relative to the free ion values, of the vibrational frequencies of the NO_2 group resulting from its various bonding modes are shown, with examples, in Table 3.

M-SCN AND M-NCS ISOMERS

The first synthesis of linkage isomers of the thiocyanate ion and the electronic and steric factors which determine its bonding mode have already been reviewed in this journal[47]. The discussion which follows will therefore be primarily limited to results published in the interim.

The π-bonding hypothesis of Turco and Pecile[48] has received further support from the thiocyanate bonding modes observed for the complexes shown in Table 4. In each triad, small decreases in the π-acidity of the other ligands results in a switch from N- to S-bonding for the thiocyanates. It is reasonable to assume that similar considerations should be operative in other low-spin d^8 systems, and the $[RhL_2(CO)NCS]$, $[RhL_3(NCS)]$ (L = phosphine, arsine, stibine, or phosphite), and $[Rh(CO)_2(NCS)_2]^-$ complexes recently reported by Jennings and Wojcicki[49] appear to verify this possibility. In each of these complexes, the N-bonded thiocyanate is *trans*- to a strong π-acceptor type ligand.

TABLE 4

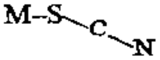
π-BONDING EFFECTS OF OTHER LIGANDS ON THE THIOCYANATE BONDING MODE

Complex	*Ref.*
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	10, 11
$[Pd\{(C_6H_5)_2As(o\text{-}C_6H_4)P(C_6H_5)_2\}(SCN)(NCS)]$	34
$[Pd(As(n\text{-}C_4H_9)_3)_2(SCN)_2]$	15
$[Pd(bipy)(NCS)_2]$	10, 11
$[Pd(4,4'\text{-dimethylbipy})(SCN)(NCS)]$	23
$[Pd(py)_2(SCN)_2]$	15
$[Pd(5\text{-nitrophen})(NCS)_2]$	15
$[Pd(4,7\text{-diphenylphen})(SCN)_2]$	23
$[Pd(phen)(SCN)_2]$	11

5-nitrophen = 5-nitro-1,10-phenanthroline, phen = 1,10-phenanthroline

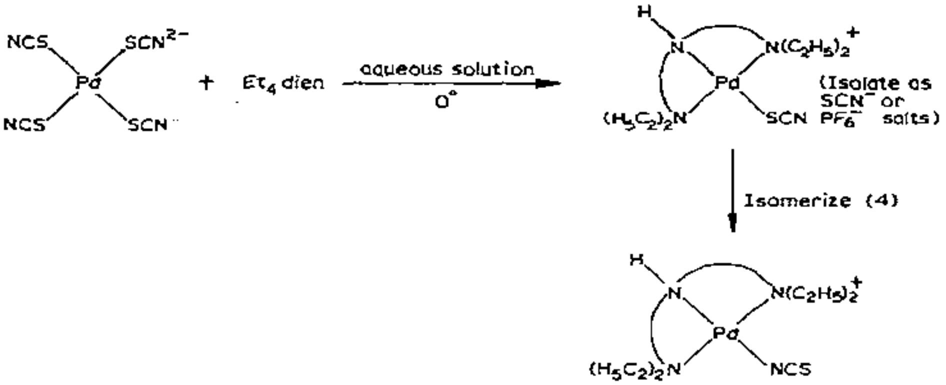
Two of the complexes shown in Table 4 merit special comment. The $[Pd(As(n\text{-}C_4H_9)_3)_2(SCN)_2]$ complex undergoes partial isomerization to the N-bonded form when melted, but only the S-bonded isomer crystallizes out of the melt on cooling[15]. The $[Pd(4,7\text{-diphenylphen})(SCN)_2]$ complex is unique in that its N-bonded isomer has been isolated at a *lower* temperature[23]. The reverse temperature dependence is exhibited by all of the other thiocyanate linkage isomers shown in Table 1, save for the $[Mn(CO)_5SCN]$ complex, the bonding mode of which is solvent dependent[14], and will be discussed later.

Seen in the light of the results obtained with square planar systems, the behavior of octahedral carbonylthiocyanate systems reported by Wojcicki and Farona stands out in even brighter contrast. Thus, whereas the stable isomer of $[Mn(CO)_5SCN]$ is S-bonded[14], the substitution of *weaker* π-bonding ligands for two of the CO groups, as in *cis*-$[Mn(CO)_3(py)_2NCS]$[50], generally yields N-bonded complexes, the two exceptions being explained on the basis of steric interactions. Similarly, an increase in negative charge on the metal, as in $[Cr(CO)_5NCS]^-$[51], results in a switch to N-bonding, despite the fact that the soft[52] or class b[53] character of the metal has increased. Obviously, the results in the square planar and octahedral systems are in need of reconciliation.

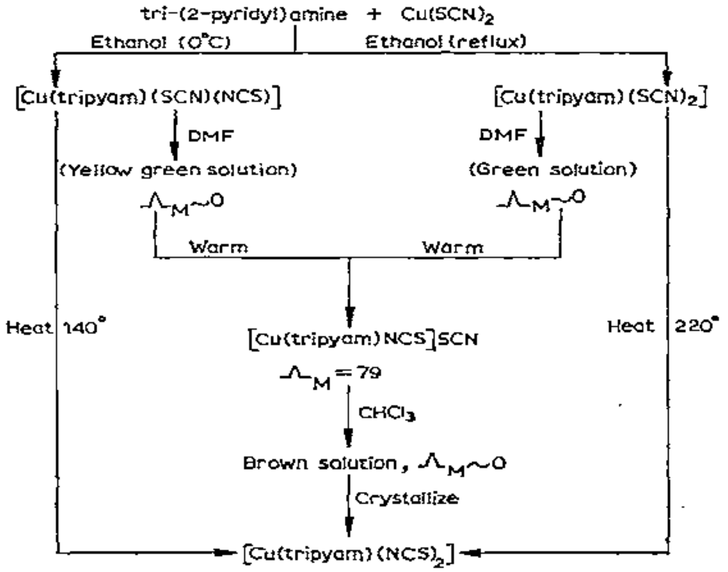
The differing steric requirements[21] of the  and M–NCS linkages were recently utilized in the synthesis of another set of linkage isomers of the thiocyanate ion[22], as shown in reaction (4).

The SCN^- salt was found to undergo complete isomerization in the solid state at room temperature in three days, whereas, under the same conditions, the PF_6^- salt does not isomerize. In aqueous solution, the isomerization is complete in *ca.* 1 hr.

The only known example of the isolation of all three possible thiocyanate



linkage isomers of a complex containing two thiocyanate groups has been reported by Kulasingam and McWhinnie[24], and is shown in reaction sequence (5).



(5)

Both S- and N-bonded linkage isomers of cyclopentadienyliron thiocyanatodicarbonyl have been prepared[25] by the reaction of $[C_5H_5Fe(CO)_2]_2$ with oxygen in the presence of thiocyanate ion in acid solution. The reaction of $[C_5H_5Mo(CO)_3H]$ with thiocyanogen also yields the two linkage isomers of cyclopentadienylmolybdenum thiocyanatotricarbonyl; however, the same reaction with $[C_5H_5W(CO)_3H]$ yields only the S-bonded complex, which does not undergo isomerization. Conversely, the thiocyanate in $[C_5H_5Cr(NO)_2NCS]$ is N-bonded. The $[C_5H_5Fe(CO)_2SCN]$ and $[C_5H_5Mo(CO)_3SCN]$ complexes were found to undergo S- → N-bonded linkage isomerizations in Nujol dispersions and in chloroform or acetonitrile solutions, respectively, at *ca.* 35°.

The most recently reported[26] example of thiocyanate linkage isomerism is somewhat novel in that the ligand was prepared *in situ*, as shown in reaction (6).

$$\begin{array}{l} [Pd(SCN)_4]^{2-} + 2PF_3 + 6CH_3OH \xrightarrow[CH_3OH]{-78°} [Pd(P(OCH_3)_3)_2(SCN)_2] + 6HF \\ \hspace{17em} \text{DMF} \ \downarrow \ \text{room temperature} \\ \hspace{16em} [Pd(P(OCH_3)_3)_2(NCS)_2] \end{array} \quad (6)$$

A complete S- → N-bonded isomerization takes place in the time required to dissolve the initial product in DMF.

Nitrogen – 14 nmr, visible, and infrared spectra have been utilized in the elucidation of the bonding mode of the coordinated thiocyanate ion. The ^{14}N resonance is shifted downfield with respect to that of the free thiocyanate ion when the group is S-bonded, and upfield when the group is N-bonded[13]. This has been interpreted[13] in terms of the effect of coordination on the $n \rightarrow \pi^*$ transition on nitrogen. Coordination through the sulfur atom is believed to lower the π^* energy level by d-orbital mixing, resulting in a small downfield shift, whereas N-bonding lowers the energy of the non-bonding orbital, resulting in an upfield shift. Evidence of this type has been used[13] to support the presence of both Cd–NCS and Cd–SCN linkages in solutions of $[Cd(SCN)_4]^{2-}$. This was first reported by Tramer[12,54] on the basis of infrared and Raman spectral studies. The –NCS and –SCN groups occupy different positions in the spectrochemical series, the former exhibiting the larger Δ value[43]. The ligand field strength of the thiocyanate group is further enhanced when it functions as a bridge between two metal atoms[55]. The shifts, relative to the free ion values, of the infrared parameters of the thiocyanate group resulting from coordination are shown, with examples, in Table 5.

TABLE 5

INFRARED SPECTRA OF VARIOUS TYPES OF THIOCYANATE COMPOUNDS

			C–N stretch		
Compound	*C–S stretch,*[a] $\nu_1(SCN)$, *cm*$^{-1}$	*SCN bend,*[a] $\nu_2(SCN)$, *cm*$^{-1}$	$\nu_3(SCN)$, *cm*$^{-1}$	*Integrated absorption intensity*[b,c], $M^{-1}cm^{-2}$	*Ref.*
Free ion, as in KSCN	749	486, 471	2060[b]	4.4×10^4	56, 57
N-bonded	increase, 780–860	single band, 440–490	increase, $\gtrsim 2100$	$\sim 10 \times 10^4$	
$Q_2[Co(NCS)_4]$[d]	844	481	2077[b]	12×10^4	57, 58
S-bonded	decrease, 690–720	main band, 400–440	increase, $\lesssim 2100$	$\sim 1 \times 10^4$	
$K_2[Pd(SCN)_4]$	703	474, 468 442, 432	2110[b]	1.9×10^4	57, 58
N,S-bonded bridge	relatively small increase	?	$\lesssim 2140$	?	
$Co(NCS)_4Hg$	795	?	2145[a]	?	59

[a] Nujol mulls. [b] Butanone solutions. [c] Calculated per mole of coordinated thiocyanate group.
[d] $Q = (C_2H_5)_4N^+$.

FORMATION AND DETECTION OF LINKAGE ISOMERS *via* INNER SPHERE REDOX REACTIONS

As shown in Table 6, the use of ambidentate ligands as bridging groups in redox reactions proceeding *via* the inner sphere mechanism has proved to be a fertile source of linkage isomers, although all of the unstable isomers formed in this manner isomerize too rapidly to permit their isolation. Indeed, the detection of the unstable isomers serves as a good indication that the inner sphere mechanism is operative. It is also apparent that the non-bridging ligands originally in the coordination sphere of the reductant play a very important role in determining the nature of the metal-ambidentate ligand bond in the final product. For example, whereas the pentaammines $[Co(NH_3)_5NCS]^{2+}$[62] and $[Co(NH_3)_5NCSe]^{2+}$[61] both contain N-bonded pseudohalides, the pentacyanides $[Co(CN)_5SCN]^{3-}$[60] and $[Co(CN)_5NCSe]^{3-}$[61] are, respectively, S- and N-bonded.

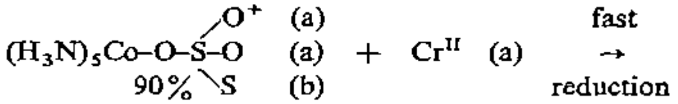
In an interesting reversal of emphasis, the discovery of two different reaction rates for the chromium(II) reduction of thiosulfatopentaamminecobalt(III) has been cited[27] as evidence for both O- (90%) and S-bonded isomers in the complex as it is usually prepared[63]. The specific rate found for the fast component (pathway (a) in reaction (7)) is comparable to those observed for the chromium(II)

TABLE 6

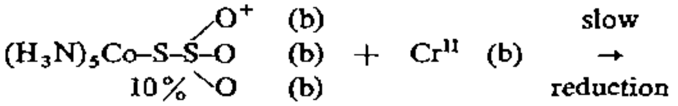
INNER SPHERE REDOX REACTIONS INVOLVING AMBIDENTATE BRIDGING GROUPS

Oxidant	*Reductant*	*Activated complex*[a]	*Product containing bridging group*[b]		*Ref.*
$[Co(NH_3)_5ONO]^{2+}$	$[Co(CN)_5]^{3-}$	$[Co^{III}{-}O{-}\underset{\underset{O}{\Vert}}{N}{-}Co^{II}]^{-}$	$[Co(CN)_5NO_2]^{3-}$	(S)	8
$[Co(NH_3)_5NO_2]^{2+}$	$[Co(CN)_5]^{3-}$	$[Co^{III}{-}\underset{\underset{O}{\Vert}}{N}{-}O{-}Co^{II}]^{-}$	$[Co(CN)_5ONO]^{3-}$	(I)	8
$[Co(NH_3)_5NCS]^{2+}$	$[Co(CN)_5]^{3-}$	$[Co^{III}{-}NCS{-}Co^{II}]^{-}$	$[Co(CN)_5SCN]^{3-}$	(S)	60
$[Fe(H_2O)_5NCS]^{2+}$	$[Cr(H_2O)_6]^{2+}$	$[Fe^{III}{-}NCS{-}Cr^{II}]^{4+}$	$[Cr(H_2O)_5SCN]^{2+}$	(I)	19
$[Hg(SeCN)_4]^{2-}$	$[Co(CN)_5]^{3-}$	$[Hg^{II}{-}SeCN{-}Co^{II}]^{5-}$	$[Co(CN)_5NCSe]^{3-}$	(S)	61
$[Co(NH_3)_5CN]^{2+}$	$[Co(CN)_5]^{3-}$	$[Co^{III}{-}CN{-}Co^{II}]^{-}$	$[Co(CN)_5NC]^{3-}$	(I)	8,28
$[Co(NH_3)_5CN]^{2+}$	$[Cr(H_2O)_6]^{2+}$	$[Co^{III}{-}CN{-}Cr^{II}]^{4+}$	$[Cr(H_2O)_5NC]^{2+}$	(I)	29

[a] Non-bridging ligands not shown. [b] (S) = stable with respect to isomerization; (I) = isomerizes.



$$\begin{array}{rlcccc} & \diagup O^{+} & (a) & & & \text{fast} \\ (H_3N)_5Co{-}O{-}S{-}O & & (a) & + & Cr^{II}\ (a) & \rightarrow \\ 90\% & \diagdown S & (b) & & & \text{reduction} \end{array} \qquad (7)$$



$$\begin{array}{rlcccc} & \diagup O^{+} & (b) & & & \text{slow} \\ (H_3N)_5Co{-}S{-}S{-}O & & (b) & + & Cr^{II}\ (b) & \rightarrow \\ 10\% & \diagdown O & (b) & & & \text{reduction} \end{array} \qquad (8)$$

reduction of the corresponding sulfato[64,65] and sulfito[27] complexes, while that found for the slow isomer (pathway (b) in reaction (8)) is as slow as that for the 4-carboxythiodibenzene-4'-carboxylatopentaamminecobalt(III) ion[65], a complex which also contains a divalent sulfur in the electron transfer pathway.

The presence and relative amounts of the isomers were also confirmed by infrared data[27]. As shown in Table 7, shoulders associated with the main ν(S–S) and ν_s(S–O) peaks were found which are displaced from the main peaks in directions toward the corresponding absorptions in the spectra of S-alkyl thiosulfates. The splitting of ν_e(S–O) is attributed to the non-equivalence of the S–O bonds in the O-bonded isomer.

TABLE 7

INFRARED SPECTRA OF VARIOUS TYPES OF THIOSULFATE COMPOUNDS (CM^{-1})

Ion	*ν(S–S)*	*ν_s(S–O)*	*ν_e(S–O)*	*Ref.*
$S_2O_3^{2-}$	451	997	1125	27, 67
$CH_3SSO_3^-$	410–412	1026–1032	1203–1215	68
$[Co(NH_3)_5S_2O_3]^+$				
O-bonded component	424	997	1167, 1137	27
S-bonded component	415 sh	1010 sh		27

M–NC AND M–CN ISOMERS

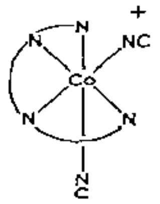
Unlike the unstable isocyano (N-bonded) isomers[8,28,29] shown in Table 6, two isocyano complexes have recently been reported[29a] which do not undergo isomerization to the C-bonded forms, and represent the first mononuclear N-bonded cyanide complexes ever isolated. The reaction schemes used in their syntheses, and that of the linkage isomer of one of them, are shown in reactions (9) through (11).

$$\textit{trans}\text{–}[\mathrm{Co(trien)\,(CH_3CO_2)_2}]^+ + \mathrm{CN}^- \xrightarrow[\mathrm{H_2O}]{40°} \xrightarrow[\text{(2) cool at 0°}]{\text{(1) 50\% NaClO}_4} \textit{cis}\text{–}\beta\text{–}[\mathrm{Co(trien)\,(NC)_2}]\mathrm{ClO_4} \quad \text{deep yellow} \tag{9}$$

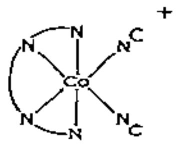
$$\textit{cis}\text{–}[\mathrm{Co(trien)\,(CHCl_2CO_2)_2}]^+ + \mathrm{CN}^- \xrightarrow[\mathrm{H_2O}]{40°} \xrightarrow[\text{(2) cool at 0°}]{\text{(1) 50\% NaClO}_4} \textit{cis}\text{–}\alpha\text{–}[\mathrm{Co(trien)\,(NC)_2}]\mathrm{ClO_4} \quad \text{deep yellow} \tag{10}$$

$$[\mathrm{Co(trien)CO_3}]^+ + \mathrm{CN}^- \xrightarrow[\mathrm{H_2O}]{60°} \xrightarrow[\text{(2) cool at 0°}]{\text{(1) 50\% NaClO}_4} \textit{cis}\text{–}\alpha\text{–}[\mathrm{Co(trien)\,(CN)_2}]\mathrm{ClO_4} \quad \text{light yellow} \tag{11}$$

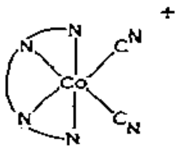
The following structures were assigned to the products:



cis-β-isocyano



cis-α-isocyano



cis-α-cyano

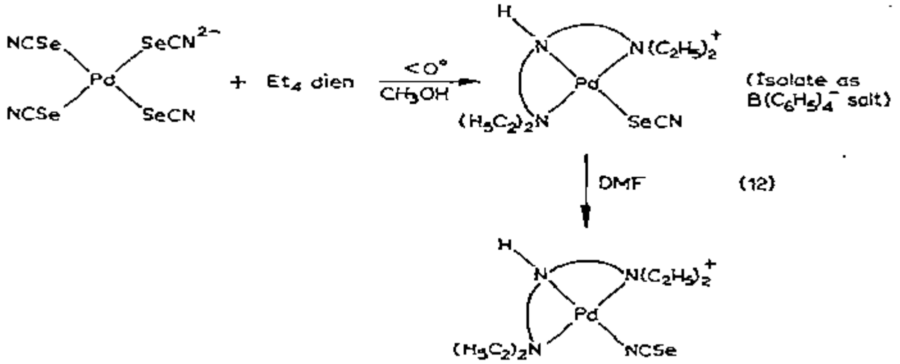
Bonding through the nitrogen atoms of the cyanide groups is supported by red shifts in the d–d transitions of the isocyano complexes (the ligand field strength of N-coordinated cyanide has been shown[36] to be less than that of ammonia) relative to those of the cyano complex. The differentiation between the *cis-β*-and *cis-α*-isocyanides was supported on the basis of the similarity of their visible spectra and differences in their infrared spectra. While differing in intensity, the visible absorption maxima of both forms are found at virtually identical wavenumbers, and the magnitude of the splitting of their low frequency bands is as large as that found for *cis*-$[\mathrm{Co(trien)(CN)_2}]\mathrm{ClO_4}$, implying that both have a *cis*-configuration. The authors contend that the split C–N stretching band in the infrared spectrum of the isomer synthesized from *trans*-$[\mathrm{Co(trien)(CH_3CO_2)_2}]^+$ indicates that it should be formulated as the *cis-β*-complex, since no such splitting appears in the spectrum of the isomer synthesized from *cis*-$[\mathrm{Co(trien)(CHCl_2CO_2)_2}]^+$. This argument is open to question, since, in point of fact, both the *cis-α*- and *β*-forms should exhibit infrared active in-phase and out-of-phase C–N stretching vibrations.

No rationale for the formation and stability (all of the complexes were recrystallized from hot water) of the isocyanides was offered or is evident. The authors do point out that, contrary to the behavior exhibited hy most cobalt(III) complexes, cobalt(III) complexes of the triethylenetetramine series react rapidly with cyanide ion, even at room temperature and in organic solvents such as ethanol, implying the existence of a different reaction route and/or a different mode of coordination of the cyanide ion.

M-SeCN AND M-NCSe ISOMERS

Chemical analogy has always been a powerful synthetic tool, and the considerations which resulted in the syntheses of thiocyanate linkage isomers might well be expected to be generally applicable to its higher homologue, the selenocyanate ion. Such has not proved to be the case, however, and the latter continues to exhibit maverick behavior. Whereas the selenocyanate ion follows, as expected, a $\mathrm{M_{(class\ a)}}$-NCSe, $\mathrm{M_{(class\ b)}}$-SeCN bonding pattern in complexes wherein no other ligands are present[47,59,69–75], its bonding mode has proved to be insensitive to the introduction of π-acceptor ligands into the coordination sphere. Thus, the ligands triethylphosphine[48], tri-n-propylphosphine[76], tri-n-butylphosphine[11], triphenylphosphine[11], triphenylarsine[10,11], 2,2'-bipyridine[10,11], 2,2'2"-tripyridine[11], 5-nitro-1,10-phenanthroline[15], and trimethylphosphite[26] initiate M-NCS bonding in palladium(II) and/or platinum(II) complexes, but the corresponding palladium(II)-selenocyanate complexes which have been prepared[26] all contain Se-bonded selenocyanates.

The only example of selenocyanate linkage isomers thus far reported[30,31] resulted from the assumption that the steric requirements of the coordinated selenocyanate group should be similar to those of the thiocyanate group, and the synthetic procedure employed, shown in reaction (12), parallels that used to prepare the corresponding thiocyanate linkage isomers[22] (reaction (4)). However, unlike the N-bonded thiocyanate complex, the N-bonded selenocyanate, once isolated in the solid state, slowly *reisomerizes* to the Se-bonded form[77]. This behavior is reminiscent of that exhibited by [Mn(CO)$_5$SCN][14], which, although stable in the solid state, isomerizes to the N-bonded form in acetonitrile solution.



(12)

The results of rate studies[77] show that the rate of isomerization of the Se-bonded isomer in solution decreases as the dielectric constant of the solvent is decreased, suggesting, as in the case of the isomerization of the S-bonded thiocyanate[22], that a dissociative, intermolecular process is operative.

The elucidation of the selenocyanate's bonding mode has utilized both visible and infrared spectral data, with emphasis on the latter. In both cases, the trends observed are completely analogous to those exhibited by the thiocyanate ion. The ligand field strengths of N-bonded selenocyanate and thiocyanate are virtually identical[59,69], but that of Se-bonded selenocyanate is less than that of S-bonded thiocyanate, placing it below the bromide ion in the spectrochemical series[72]. The ligand field strength of the selenocyanate is increased when it functions as a bridging group[59]. The shifts, relative to the free ion values, of the infrared parameters of the selenocyanate group resulting from coordination are shown, with examples, in Table 8.

TABLE 8

INFRARED SPECTRA OF VARIOUS TYPES OF SELENOCYANATE COMPOUNDS

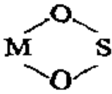
Compound	*C–Se stretch, ν_1(SeCN), cm^{-1}*	*SeCN bend, ν_2(SeCN), cm^{-1}*	*C–N stretch*		*Ref.*
			ν_3(SeCN), cm^{-1}	*Integrated absorption intensity^f, M^{-1}cm^{-2}*	
Free ion, as in KSeCN	558	424, 416	2069^d	3.1×10^4	57, 78
N-bonded	increase	single band, >400	small increase or decrease	$\sim 10 \times 10^4$	
$R_4[Mn(NCSe)_6]^a$	640, 617^b	424^b	2064^e	8.7×10^4	72
Se-bonded	decrease	main band <400	increase	$\sim 1 \times 10^4$	
$R_3[Rh(SeCN)_6]^a$	523^c	435, 400, 392^c	2107^e	0.96×10^4	72, 75
N,Se-bonded bridge	increase	?	$\lesssim 2130$	?	
$Co(NCSe)_4Hg$	639^b	?	2135^b	?	59

[a] $R = (n\text{-}C_4H_9)_4N^+$. [b] Nujol mull. [c] KBr disk. [d] Butanone solution. [e] Acetone solution. [f] Calculated per mole of coordinated selenocyanate group.

M-OSO$_2$ AND M-SO$_3$ ISOMERS

The only published information[32] concerning the synthesis of linkage isomers of the sulfite ion (specifically those of $[Co(NH_3)_5SO_3]^+$) has thus far been restricted to the statement that adding sulfur dioxide or sodium sulfite to solutions of $[Co(NH_3)_5H_2O]^{3+}$ at low temperatures and low pH yields the unstable pink O-bonded sulfito complex rather than the stable yellow-brown S-bonded isomer, the latter having been known[79] for some time. Such a procedure would be closely analogous to that employed in the synthesis of the corresponding O-bonded nitrite complex[2,5,38]. However, we have not yet been able to reproduce the synthesis of the O-bonded sulfite isomer in our laboratory[80].

Infrared spectroscopy would appear to be a useful tool for distinguishing between S- and O-bonded monodentate sulfite complexes. As pointed out by Newman and Powell[81], the C_{3v} symmetry of the free ion is essentially preserved when S-coordination takes place. Four peaks would be expected, two at higher frequencies associated with the stretching vibrations, and two at lower frequencies associated with the bending modes. The stretching vibrations should then shift to higher frequencies, as compared with the free ion. Coordination through oxygen would lower the symmetry to C_s, and three stretching vibrations would be expected, due to the removal of the degeneracy in ν_d. Likewise, three bending vibrations should be observed, due to the removal of the degeneracy in δ_d. A lowering in frequency of one of the S–O stretching vibrations should occur. As shown in Table 9, these predictions appear to be borne out in practice, although the

$Tl_2[Cu(OSO_2)_2]$ complex is the only monodentate sulfite complex reported wherein coordination is believed to take place through an oxygen atom. The authors also concluded[81] that, although the symmetry of a bidentate chelating sulfite group,  $M\overset{O}{\underset{O}{\diamond}}S{-}O$, was the same ($C_s$) as that of an O-bonded monodentate group, the band shifts of the stretching bands, relative to the free ion values, were quite different (see Table 9) and permitted a clear determination of bond type. They could not, however, distinguish between chelating sulfite groups and bridging groups of the types on the basis of their infrared data.

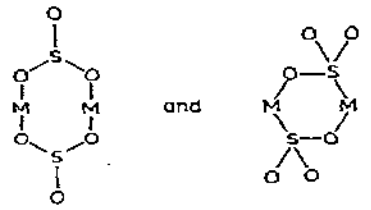


TABLE 9

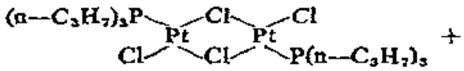
INFRARED SPECTRA OF VARIOUS TYPES OF SULFITE COMPOUNDS (CM^{-1})[81]

Compound[a]	ν_s(S–O)	δ_s(O–S–O)	ν_d(S–O)	δ_d(O–S–O)
Free ion, as in Na_2SO_3	970[b] 947[c]	498	970[b] 983[c]	633
S-bonded $[Co(NH_3)_5SO_3]Cl$	985	519	1110	633
O-bonded $Tl_2[Cu(OSO_2)_2]$	989	506	902, 862	673, 602
Bidentate $K_3[Rh(SO_3)_3]\cdot 2H_2O$	939	527	1113, 1058	690, 647

[a] Samples examined as dispersions in Nujol and hexachlorobutadiene. [b] Not resolved into separate components. [c] Raman spectrum.

LINKAGE ISOMERS INVOLVING BRIDGING AND CHELATING LIGANDS

Linkage isomerism involving bridging groups is quite rare, and the synthesis of the first such linkage isomeric pair[82], α- and β-$[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$, prompted some controversy in the literature. The isomers were prepared according to the scheme shown in reaction (13).



$$(n{-}C_3H_7)_3P\text{Pt}(\mu\text{-}Cl)_2\text{Pt}Cl_2\text{-}P(n{-}C_3H_7)_3 + 2KSCN \xrightarrow[\text{acetone}]{\text{cold}}$$

$$\alpha\text{-}[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2] \quad + \quad 2KCl \qquad (13)$$

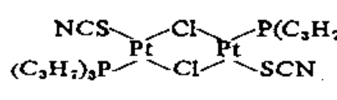
yellow, m.p. 144–152°

$$\Big\downarrow \text{boiling benzene}$$

$$\beta\text{-}[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$$

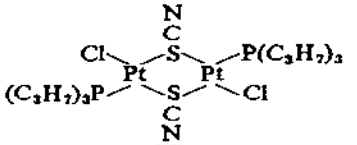
greenish-yellow, m.p. 173–174.5°

They were at first thought to be the structural isomers



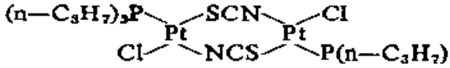
(I)

and



(II)

but later infrared studies[83] led to the conclusion that the thiocyanate groups must lie in the bridge between the two metal atoms in both isomers ($\nu(\text{C–N})_\alpha = 2162$ cm^{-1}, $\nu(\text{C–N})_\beta = 2169\ \text{cm}^{-1}$; also see Table 5). Chatt and Duncanson therefore suggested they might be geometrical isomers of structure (II), in which the CN groups attached to the sulfur atoms are in *cis* or *trans* positions with respect to the central ring. The actual structures of the isomers,



α

and

β

were later demonstrated[35,84,85] by X-ray analysis. It is interesting to note that the more stable β-isomer has the sulfur atoms *trans* to the phosphine groups, contrary to the π-bonding argument previously discussed.

Shriver, *et al.*[36], using *Dq* values to calculate site preference energies for mixed cubic cyanide polymers, predicted and found linkage isomerism for $\text{K}[\text{FeCr(CN)}_6]$. When $\text{K}[\text{FeCr(CN)}_6]$ (precipitated by mixing $\text{K}_3[\text{Cr(CN)}_6]$ and iron(II)) is heated to 100°C., the brick red precipitate (cyanide stretching frequencies at 2168 and 2114 cm.^{-1}) changes to a dark green compound which exhibits a single cyanide stretching band at 2092 cm^{-1}, which is characteristic of ferrocyanides. Apparently, the isomerization of $\text{K}[\text{FeCr(CN)}_6]$ to $\text{K}[\text{CrFe(CN)}_6]$ involves a CN flip, from $\text{Fe}^{\text{II}}\text{–N}\equiv\text{C–Cr}^{\text{III}}$ linkages to $\text{Fe}^{\text{II}}\text{–C}\equiv\text{N–Cr}^{\text{III}}$.

Even rarer than bridging linkage isomers are linkage isomers involving chelating ligands. Following an earlier suggestion[86], Collman and Sun[37], in studying the disproportionation of unsymmetrically substituted tris (acetylacetonates) of cobalt(III) and chromium(III) in solution at elevated temperatures, observed the linkage isomerization of (3-formyl-2,4-pentanediono) bis (2,4-pentanediono)cobalt(III) (A) to (2-acetyl-1,3-butanediono) bis (2,4-pentanediono)cobalt(III) (B) (see Table 1) with accompanying intermolecular ligand exchange in boiling toluene. The products of the reaction resulting from ligand exchange were $[\text{Co(acac)}_3]$, (2,4-pentanediono) bis (3-formyl-2, 4-pentanediono)cobalt(III) (C), and two unknown substances (presumably linkage isomers of the latter). The disproportionation and linkage isomerization of (A) was found to resemble a steady-state equilibrium in that boiling a solution of the pure linkage isomer (B) in toluene resulted in a mixture of the same components. Disproportionation and linkage isomerization of (C) were found to occur in a similar manner.

TABLE 10

KINETIC DATA FOR LINKAGE ISOMERIZATIONS

Unstable Isomer	*State*	*Temp., °C.*	*k x 10⁵, sec⁻¹*	*ΔH*, kcal.*	*ΔS*, e.u.*	*Ref.*
			M–ONO → M–NO$_2$			
$[Co(NH_3)_5ONO](NO_3)_2$	solid	25	0.80^a			88
	aq. soln.	25	7.7			5
$[Co(NH_3)_5ONO]Cl_2$	solid	25	0.19^a			88
	KCl disk	50	3.5^a	26	3	89
	aq. soln.	25	3.2^a	22	–5	90, 91
$[Rh(NH_3)_5ONO]Cl_2$	KBr disk	25	7.5^a	18	–16	7
	Nujol mull	32	16			7
	KBr disk	35	17			7
	KBr disk	51	55			7
	aq. soln.	25	96	18	–12	7
$[Ir(NH_3)_5ONO]Cl_2$	Nujol mull	32	0.42			7
	KBr disk	35	0.68	22	–10	7
	KBr disk	50	3.3^a			7
	aq. soln.	25	4.4	19	–14	7
	aq. soln.	50	67			7
$[Pt(NH_3)_5ONO]Cl_3$	KBr disk	50	0.84^a			7
	aq. soln.	25	5.6			7
$[Co(CN)_5ONO]^{3-}$	aq. soln.	25	($t_{1/2}$ = 7 sec)			8
			M–NO$_2$ → M–ONO			
$[Co(NH_3)_5NO_2]Cl_2$	KCl disk	50	7.4^a			89
			M–SCN → M–NCS			
$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	KBr disk	125	3.3^a			11
		150	8.6^a			11
$[Rh(NH_3)_5SCN](ClO_4)_2$	aq. soln.	78	0.27			17
$[Cr(H_2O)_5SCN]^{2+}$	aq. soln.	25	2.9			19
$[Pd(Et_4dien)SCN]PF_6$	aq. soln.	20	26	16	–20	22
	aq. soln.	35	105			22
	aq. soln.	45	256			22
			M–NC → M–CN			
$[Co(CN)_5NC]^{3-}$	aq. soln.	25	($t_{1/2}$ = 1.6 sec.)			8
$[Cr(H_2O)_5NC]^{2+}$	aq. soln.	15	920			29
			M–SeCN → M–NCSe			
$[Pd(Et_4dien)SeCN]B(C_6H_5)_4$	DMF soln.	20	9.6			77
	CH_3CN soln.	20	7.6			77

[a] Calculated by Fraser[87] from data given in references.

REACTIONS OF LINKAGE ISOMERS

Synthetic and mechanistic studies utilizing linkage isomers have been limited by the rapid rearrangement, in most cases, of the unstable isomer. The simplest reaction, that of the isomerization itself, has been studied in a number of cases, and examples of the kinetic data obtained are shown in Table 10. Kinetic data for substitution and oxidation–reduction reactions involving linkage isomeric pairs are shown in Tables 11 and 12.

A number of interesting inferences and comparisons may be drawn from the available data. The results obtained for the isomerization of the nitritopentaammines indicate that the rearrangement involves an intramolecular process.

TABLE 11

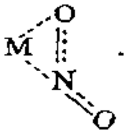
KINETIC DATA FOR SUBSTITUTION REACTIONS INVOLVING LINKAGE ISOMERS

Reaction	*Temp., °C.*	*k, sec*$^{-1}$	ΔH^*, *kcal.*	ΔS^*, *e.u.*	*Ref.*
$[Cr(H_2O)_5SCN]^{2+} + H_2O$	25	4.8×10^{-5}			19
$[Cr(H_2O)_5NCS]^{2+} + H_2O$	25	9.2×10^{-9}			94
$[Pd(Et_4dien)SCN]^{+} + Br^{-}$	35	1.1×10^{-3}	16	−20	22
	45	2.6×10^{-3}			22
$[Pd(Et_4dien)NCS]^{+} + Br^{-}$	35	5.1×10^{-4}	18	−14	22
	45	1.3×10^{-3}			22

TABLE 12

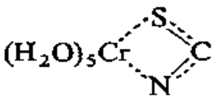
KINETIC DATA FOR REDOX REACTIONS INVOLVING LINKAGE ISOMERS

Complex	*Reductant*	*Temp., °C.*	M^{-1} k, *sec*$^{-1}$	*Ref.*
$[Co(NH_3)_5ONO]^{2+}$	Eu^{II}	25	75	92
$[Co(NH_3)_5NO_2]^{2+}$	Eu^{II}	25	100	92
$[Cr(H_2O)_5SCN]^{2+}$	Cr^{II}	25	42	19
$[Cr(H_2O)_5NCS]^{2+}$	Cr^{II}	25	1.4×10^{-4}	93
$[Co(NH_3)_5SSO_3]^{+}$	Cr^{II}	25	0.18	27
$[Co(NH_3)_5OS_2O_2]^{+}$	Cr^{II}	25	13.3	27

As pointed out by Basolo and Hammaker[7], the rates of rearrangement of the nitrito complexes in solutions containing no excess nitrite ion are too great to be compatible with a dissociation–recombination mechanism. The entropies of activation for isomerization are negative, suggesting a decrease in degrees of freedom in going from the ground to the transition states. Such would be the case if the activated complex did contain a nitro group at a mid-point in intramolecular rearrangement, *i.e.*,  . Halpern and Nakamura[8] reached a similar conclusion regarding the isomerization of $[Co(CN)_5ONO]^{3-}$, noting that the first order rate was unaffected by increasing $[Co(CN)_5]^{3-}$ concentration. This implies that the isomerization does not take place *via* ligand transfer between $[Co(CN)_5ONO]^{3-}$ and $[Co(CN)_5]^{3-}$.

These results contrast with those obtained for the isomerization of $[Pd(Et_4dien)SCN]^+$, for which an *intermolecular* process has been postulated[22]. The kinetic parameters for the isomerization (Table 10) and reaction (Table 11) of the complex are identical, both reactions being first order, suggesting that both processes take place by the same mechanism, either one of dissociation or solvent assisted ligand interchange[95]. The observation (Table 11) that the stable isomer, $[Pd(Et_4dien)NCS]^+$, reacts more slowly than the less stable form further supports the choice of an intermolecular process. Haim and Sutin[20] have also suggested the possibility of an ion-pair mechanism (reaction 14) for the isomerization of $[Cr(H_2O)_5SCN]^{2+}$, which isomerizes and aquates at comparable rates (see Tables 10 and 11).

$$\begin{tikzcd}
 & RSCN^{2+} \arrow[d, shift left] & (R = Cr(OH_2)_5) \\
R^{3+} \cdot NCS^- \arrow[d] & R^{3+} \cdot SCN^- \arrow[u, shift left] \arrow[l] \arrow[r, shift left] \arrow[d, "H_2O"] & R^{3+} + SCN^- \arrow[l, shift left] \arrow[d, "H_2O"] \\
RNCS^{2+} & ROH_2^{3+} \cdot SCN^- & ROH_2^{3+} + SCN^-
\end{tikzcd} \qquad (14)$$

The mechanisms suggested are reasonable in view of the prohibitive amount of energy required to bend the linear thiocyanate group to form the seven-coordinated transition state  analogous to that of the M–ONO → $M–NO_2$ isomerization. The solid state rates of isomerization of the nitrito complexes also differ from that of $[Pd(As(C_6H_5)_3)_2(SCN)_2]$ (see Table 10) in that they are unaffected by changing the supporting medium from Nujol to KBr. The thiocyanato complex exhibits a large decrease in rate when it is incorporated in a potassium bromide disk[11], based on qualitative observations on its rate of isomerization in the pure solid state.

The $[Co(NH_3)_5ONO]^{2+}$ complex is unique among the nitrito complexes listed in Table 10 in that an equilibrium involving the two isomers is reached in the

$$[Co(NH_3)_5ONO]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Co(NH_3)_5NO_2]^{2+} \qquad (15)$$

solid state[89], and the rate constants determined in earlier studies[88] probably represent (k_1+k_2) rather than k_1 alone. Adell[90] has also demonstrated that the irradiation of $[Co(NH_3)_5NO_2]Cl_2$ with sunlight produces $[Co(NH_3)_5ONO]Cl_2$. Of the $M–NO_2$ complexes prepared by Basolo and Hammaker[7], only the iridium(III) complex isomerized (partially) when irradiated with ultraviolet light for four days.

Of the unstable linkage isomers prepared by inner sphere redox reactions (see Tables 6 and 10), the $[Cr(H_2O)_5SCN]^{2+}$ complex prepared by Haim and Sutin[19,20] is unique in that, in addition to isomerization, it undergoes both aquation (Table 11) and a second redox reaction (Table 12).

The reaction of nitrito- and nitropentaamminecobalt(III) with europium(II)[92] (Table 12) first involves the reduction of the cobalt(III) center, followed by the reduction of the ligand itself. The kinetics are complicated by the fact that the nitrous acid liberated in the first step oxidizes the europium(II) more rapidly than does the remaining cobalt(III) complex. The use of chromium(II)[96] as the reducing agent proceeds somewhat analogously, in that both the cobalt(III) center and the ligand are reduced, but the reaction rates were too rapid to permit the determination of rate constants. The mechanism proposed for the reduction of the nitro isomer is shown in reactions (16) through (18).

$$Co^{III}NO_2 + Cr^{II} \xrightarrow{k_1} Co^{II} + ONOCr^{III} \tag{16}$$

$$Cr^{III}ONO + Cr^{II} \xrightarrow{k_2} Cr^{III} + \cdot O_2NCr^{III} \tag{17}$$

$$Cr^{III}NO_2\cdot + Cr^{II} \xrightarrow[2H^+]{k_3} (Cr^{III}NO) + H_2OCr^{III} \tag{18}$$

(NH_3 and H_2O molecules have been omitted from the formulae)

As required by the mechanism, three equivalents of reductant were found to be needed for the formation of one chromium nitrosyl. The ratio of rate constants, (k_3/k_2) for reactions (17) and (18) was determined, and was found to be different than that observed for the reduction of the nitrito complex. This would be expected, since the chromium(II) can attack the nitro complex only at an oxygen, but can attack the nitrito complex at either the oxygen or nitrogen atom, giving rise to both $[(H_2O)_5Cr^{III}ONO]^{2+}$ and $[(H_2O)_5Cr^{III}NO_2]^{2+}$. It should be pointed out that Halpern and Nakamura[8] observed only the formation of $[Co(CN)_5NO_2]^{3-}$ when $[Co(NH_3)_5ONO]^{2+}$ is reduced by $[Co(CN)_5]^{3-}$. However, Haim and Sutin[20] have observed both remote (S) and adjacent (N) attack by chromium(II) when it reacts with *trans*-$[Co(en)_2OH_2(NCS)]^{2+}$.

AN OVERVIEW

It might be logically supposed that ambidentate ligands having similar donor atoms, *e.g.*, the hard oxygen and nitrogen donors of NO_2^-, would be more susceptible to the formation of linkage isomers. As shown in Table 1, such has not proved to be the case in practice. With the exception of the nitrite ion and 3-formylacetylacetonate, all of the linkage isomers thus far observed have involved ligands with hard-soft donor atom pairs. It would appear that the larger difference in bond type is more amenable to controlled mediation by means of electronic, steric and mechanistic considerations. Thus, although the ambidentate behavior of the thiocyanate and selenocyanate ions is well established, and linkage isomers have been prepared for both, all of the coordination complexes of the cyanate ion, NCO^-, which have thus far been reported in the literature[97–103] are N-bonded. We have just succeeded[104] in preparing what we believe to be the first O-bonded cyanate, $[(C_5H_5)_2Ti(OCN)_2]$. Parenthetically, it is of interest to note that the corresponding titanium(III) complex, $[(C_5H_5)_2TiNCO]$, has been reported[103] to be N-bonded.

In seeking new examples of the phenomenon of linkage isomerism, it would therefore seem more profitable to utilize ligands such as thiourea and dimethylsulfoxide rather than urea, although ambidentate behavior has been established[105–110] for all three. Such studies are currently in progress in our laboratory.

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