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The linkage isomerism of thiocyanate bonded to cobalt(III)

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ABSTRACT

The structural differences between Co(III)–SCN and Co(III)–NCS bonding molecules are briefly reviewed as are attempts by Werner and his associates at the turn of the century to prepare (unsuccessfully) Co–SCN complexes. Work in the author's laboratory over a period of about 20 years is then reviewed. The thermal isomerisation of crystalline *trans*-[CO(NH$_3$)$_4$(^{15}NH$_3$)SCN](N^{14}CS)$_2$ to give 40% *trans*-CoNCS^{2+}, and 30% of each of *cis*-CoS^{14}CN^{2+} and *cis*-CoN^{14}CS^{2+} is discussed in terms of "frontside" intramolecular rearrangement to give the *trans* product, and "backside" attack of one specific lattice S^{14}CN$^-$ to give both the *cis* ^{14}C-labelled products. In aqueous solution the thermal rearrangement of [Co(NH$_3$)$_5$SCN]$^{2+}$ to give CoNCS^{2+} also results in some 9% CoOH$_2^{3+}$, and when carried out in the presence of S^{14}CN$^-$ results in small amounts of CoS^{14}CN^{2+} and CoN^{14}CS^{2+} also being produced. The formation of these products is discussed in terms of reactive ion-pairs, with the Co^{3+}·SCN$^-$·S^{14}CN$^-_{aq}$ transition state incorporating small amounts of S^{14}CN$^-$ and N^{14}CS$^-$ in addition to OH$_2$ and NCS$^-$. The Hg^{2+}, Ag$^+$ and OH$^-$ catalysed reactions are also reviewed. Larger amounts of CoOH$_2^{3+}$ are produced in these reactions, but solvated anions (NO$_3^-$, ClO$_4^-$, CF$_3$SO$_3^-$, N$_3^-$) are also incorporated in addition to isomerised CoNCS^{2+}. A transition state (or intermediate) containing pre-associated entering groups is required. There seems to be little discrimination between entering groups with stereochemical positioning and/or orientation of electron lone pairs being the most important factors in gaining entry. Very little activation for entry seems necessary, and the five-coordinate intermediate has no useful lifetime. Competition for entry only occurs between groups occupying adjacent stereochemical locations in the pre-associated reactant. A new mechanistic classification is suggested for substitution at a metal centre. This emphasises the timing of the breaking and making of ligand–metal bonds, and recognises the necessity for pre-association and organization of entering groups.

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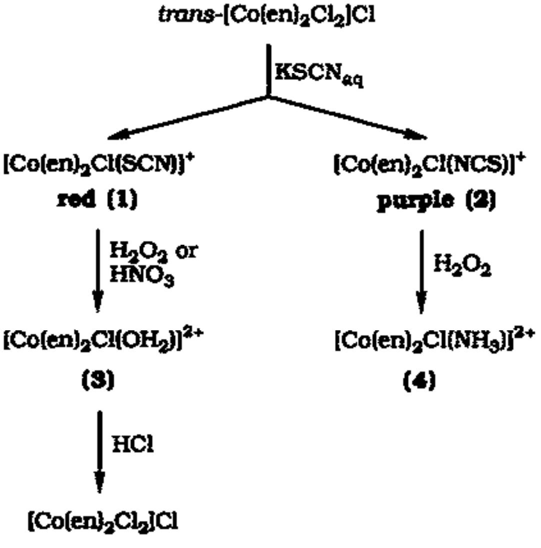
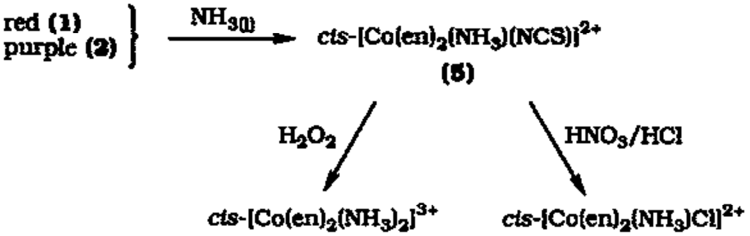
1. INTRODUCTION

The amphiphilic nature of thiocyanate coordination was first recognised by Alfred Werner in a paper published together with Braunlich in 1899 [1]. They isolated both a red and a purple complex from the reaction of green *trans*-$[Co(en)_2Cl_2]Cl$ with aqueous KSCN, Scheme 1, and designated them as thiocyanate (**1**) and isothiocyanate (**2**) isomers respectively. This was done on the basis that whereas (**2**) could be successfully oxidised (on S) to give the ammine complex (**4**), (**1**) could not, and completely lost thiocyanate to give the aqua complex (**3**). However, later Werner changed his mind [2] and relabelled them as *cis* (**1**) and *trans* (**2**) isothiocyanate isomers $[Co(en)_2Cl(NCS)]^+$, since reaction with liquid NH_3 resulted in the same *cis*-$[Co(en)_2NH_3(NCS)]^{2+}$ complex (**5**), Scheme 2, which had the property of either losing, or retaining, the N atom depending on the oxidising conditions. He recognised that *trans*→*cis* interconversion on replacing coordinated Cl^- with NH_3 was more likely than S→N isomerism under the low temperature conditions of the reaction in liquid ammonia. Werner carried out a number of other experiments on (**1**) and (**2**) [3, 4] which confirmed his suspicions, and it was clear to him that a CoSCN complex had not yet been made.



Scheme 1.

The first authentic CoSCN complex, $[Co(NH_3)_5SCN]Cl_2 \cdot H_2O$ was prepared by Inge Olsen in 1968 as part of her Ph.D. research [5]. Treatment of $[Co(NH_3)_5ONO_2]^{2+}$ with NaOH in a saturated NaSCN (10 M) solution and quenching with acid after $\sim 10\, t_{1/2}$ for base hydrolysis resulted in a mixture of $CoOH_2{}^{3+}$, $CoNCS^{2+}$ and $CoSCN^{2+}$ products, eqn. (1), and the two 2+ ions were separated from the aqua complex by column chromatography on Dowex 50W × 2



Scheme 2.

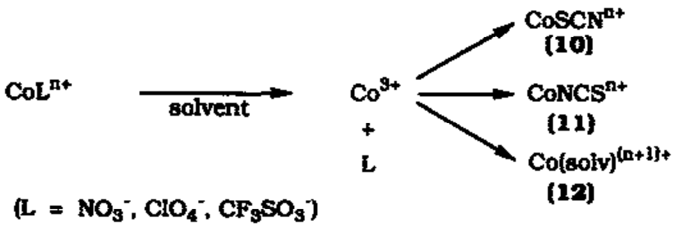
ion-exchange resin. The thiocyanato complex (**6**) was then separated from the isothiocyanato isomer (**7**) by fractional crystallisation. It was also found possible to separate the two 2+ ions by chromatography using a long ion-exchange column (**6** eluted first). Subsequently, for precise analytical work, HPLC has been found to be very useful [6].

$$\mathrm{Co(NH_3)_5ONO_2]^{2+}} \xrightarrow[\mathrm{NaSCN_{aq}}]{\mathrm{OH^-}} \begin{array}{c} \mathrm{[Co(NH_3)_5OH]^{2+}} \\ + \\ \mathrm{[Co(NH_3)_5SCN]^{2+}} \\ \textbf{red-purple (6)} \\ + \\ \mathrm{[Co(NH_3)_5NCS]^{2+}} \\ \textbf{orange (7)} \end{array} \tag{1}$$

Since that first preparation several new complexes containing CoSCN coordination have been made, and now the alternative CoNCS and CoSCN bonding modes are well known, as are bridging systems CoNCSCo and CoNCSM (M = Cr(III), or another metal) [7]. CoNCS bonding is normally the thermodynamically favoured form, demonstrating the "hardness" of Co(III) (note, protonation occurs as HNCS), but occasionally S coordination occurs. Thus both $[Co(CN)_5NCS]^{3-}$ and $[Co(CN)_5SCN]^{3-}$ are known in the solid state (as their n-Bu_4N^+ [8] and K^+ [9] salts respectively), and an equilibrium mixture is found with several dimethylglyoximato complexes in solution, eqn. (2) [10–12]. Both systems exhibit the "softer" properties of Co(III) coordination.

$$\underset{\textbf{(8)}}{\mathrm{[Co(DH)_2(L)SCN]}} \rightleftharpoons \underset{\textbf{(9)}}{\mathrm{[Co(DH)_2(L)NCS]}} \tag{2}$$

However all saturated amine systems prefer CoNCS coordination, and CoSCN complexes are only produced via a "capture" process whereby a facile leaving group (i.e. NO_3^-, ClO_4^-, $CF_3SO_3^-$) vacates a coordination site, which can then be "captured" by the S (and N) end of SCN^-, as well as by the solvent, eqn. (3).



(3)

The CoSCN complex (**10**) is reasonably stable in aqueous solution under neutral conditions, and at ambient temperature, and separation from the CoNCS complex (**11**) is usually possible by fractional crystallisation, or by chromatographic methods. The two isomers can be easily distinguished spectrally, with (**10**) having extensive charge transfer absorptions in the near UV (<320 nm), see Fig. 1.

Structurally the two coordination modes differ appreciably; Table 1 summarises these. The isothiocyanate structure (**11**), eqn. (4), is essentially linear with a Co–N bond length very similar to that found in Co(III)-amines; i.e. it is reasonably short.

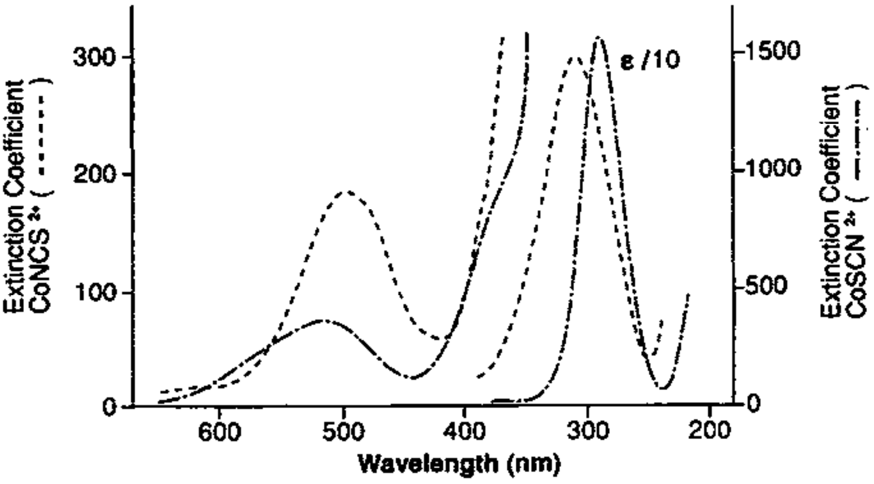
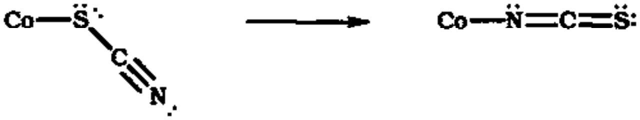


Fig. 1. Absorption spectra of [Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$ (-------) and [Co(NH$_3$)$_5$SCN]Cl$_2$1.5H$_2$O (-.-.-.-.-) in 1 M NaClO$_4$.

TABLE 1

Bond lengths and angles for Co(III) isothiocyanate (CoNCS) and thiocyanate (CoSCN) complexes

System	Bond length (pm)	Angle (°) at N or S
CoNCS	192–195	179 (2)
CoSCN	227–231	105 (2)



(10) **(11)** (4)

The thiocyanate structure (**10**) on the other hand is decidedly "bent" at the S atom (as would be expected from simple valence-bond theory), and the Co–S bond is quite long, being similar to that found for coordinate Cl^- (i.e. ~230 pm). Thus S coordination resembles true "anionic" bonding, whereas N coordination resembles an inert amine system. In a geometrical sense the more weakly held, bent, thiocyanate structure (**10**) can be considered part-way towards the stronger, linear, isothiocyanato structure (**11**).

2. REACTIONS OF CoSCN COMPLEXES

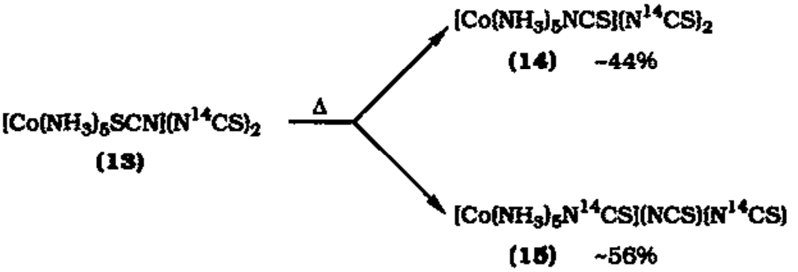
In this article I wish to summarise our own studies on the CoSCN→CoNCS interconversion, since these provide, I believe, an intimate understanding of substitution mechanism at a Co(III) centre. This comes about by using the CoSCN→CoNCS rearrangement as a mechanistic probe, since it is not exclusive under most experimental conditions, and neighbouring groups (either in the solid state, or in solution) compete for rearrangement from within the encounter sphere (outer sphere) about the octahedral ion. This allows these other processes to be monitored against the backdrop of the rearrangement. Also, at the end of this article I suggest a more exact naming system for inorganic substitution processes, since I believe the present "interchange" description now needs more precise definition.

2.1. Solid state isomerisation of trans-$[Co(NH_3)_4(^{15}NH_3)SCN](N^{14}CS)_2$

In the first publication of a thiocyanate complex it was reported [5] that heating $[Co(NH_3)_5SCN]Cl_2{\cdot}H_2O$ under the infrared lamp, or in the absence of light at 80°C, caused the purple–violet crystals to change to an orange colour. Ion exchange chromatography confirmed that isomerisation to $[Co(NH_3)_5NCS]Cl_2$ had occurred. The reaction went to completion, and no Cl^- ion was incorporated from the lattice. Also no $[Co(NH_3)_5OH_2]^{3+}$ was formed, eqn. (5). These aspects have more recently been verified using the sensitive HPLC technique, and a similar reaction has been shown to occur with crystalline $[Co(NH_3)_5SCN]Br_2$ which does not contain lattice H_2O [13]. It is not known whether the reverse CoNCS→CoSCN change can be photochemically promoted (as can the nitro to nitrito isomerisation, $CoNO_2 \rightarrow CoONO$) but X-rays slowly facilitate the CoSCN→CoNCS change at liquid nitrogen temperatures, so that the reaction appears to be more than thermally motivated.

$$\underset{(6)}{[Co(NH_3)_5SCN]Cl_2.H_2O} \xrightarrow[\text{(or } h\nu)]{\Delta} \underset{(7)}{[Co(NH_3)_5NCS]Cl_2} + H_2O \qquad (5)$$

Following this early study Snow and Boomsma determined the crystal structure of $[Co(NH_3)_5SCN]Cl_2{\cdot}H_2O$ [14] and showed that the solid state product crystal had a structure similar to $[Co(NH_3)_5NCS]Cl_2$ crystallised from aqueous solution; viz. it was disordered with the five NH_3 ligands and NCS^- being indistinguishable within the lattice. They suggested two possible mechanisms to account for this disorder: (i) a "head to tail" intramolecular rearrangement about each Co centre followed by random reorientation of each $Co(NH_3)_5NCS^{2+}$ unit (considerable translational and rotational movement would be necessary for this to occur); or (ii) initial dissociation to give $Co(NH_3)_5^{3+} + SCN^-$ followed by random re-introduction of NCS^- from the same, or from a nearby, dissociation. The second mechanism was preferred since less movement within the crystal would be required. But ionic Cl^- could not be included, and each $Co(NH_3)_5^{3+}$ unit would need to exist for some time since the process is not autocatalytic. However in a subsequent paper [15] a somewhat different result was found on heating the ionic thiocyanate salt, $[Co(NH_3)_5SCN](N^{14}CS)_2$. In this case some mixing of coordinated and ionic thiocyanate occurred with at least half the product containing lattice $N^{14}CS^-$, eqn. (6). This suggested a dissociative process for at least a substantial part of the reaction.



(6)

We have looked again at the reaction of the thiocyanate salt, using crystalline (as opposed to freeze-dried) [15] reactant, and a *trans* $^{15}NH_3$ label to follow stereochemical change, as well as ionic $N^{14}CS^-$ to follow incorporation of thiocyanate from the lattice [13]. The stereochemical results of heating (60°C) crystals of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN](N^{14}CS)_2$ are given in Fig. 2 as a function of percentage reaction (note: the reactant contained a 12% *cis*-$[Co(NH_3)_4(^{15}NH_3)SCN](N^{14}CS)_2$ impurity). While the $CoNCS^{2+}$ product shows a slight increase in *trans*→*cis* rearrangement as the reaction progresses, there is a very significant *trans*→*cis* change in the remaining $CoSCN^{2+}$. These changes are accompanied by the incorporation of ionic $N^{14}CS^-$ and $S^{14}CN^-$, and the stereochemical change in the final $CoNCS^{2+}$ product (i.e. at 100% reaction) agrees well with the amount of ionic $N^{14}CS^-$ incorporated from the lattice (~60%). Such a result does not support a complete, or even

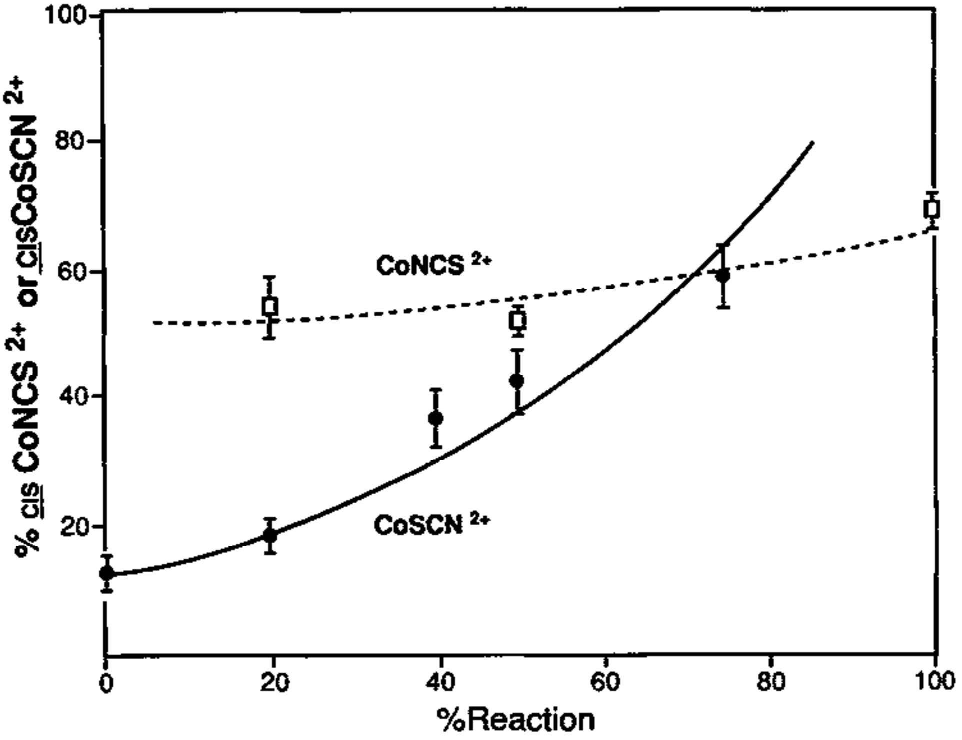
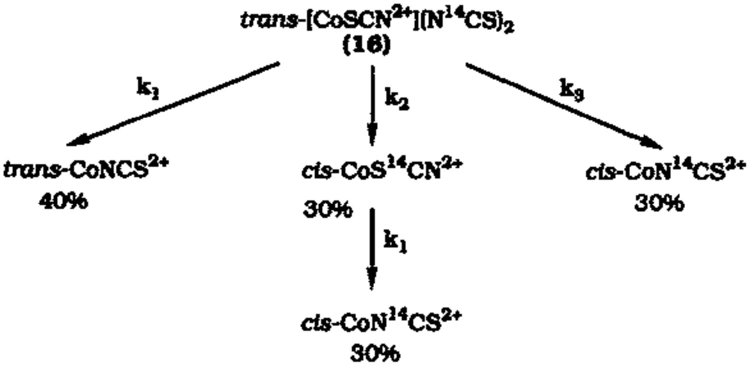


Fig. 2. Observed and calculated % *cis*-$[Co(NH_3)_5SCN]^{2+}$ (● and ———) and % *cis*-$[Co(NH_3)_5NCS]^{2+}$ (□ and --------) vs. % conversion to $CoNCS^{2+}$ on heating crystals of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN](NCS)_2$ (containing an initial 12% *cis* impurity) at 60°C. Experimental uncertainties (obtained from ^{1}H-NMR results) are given as error bars on the experimental points.

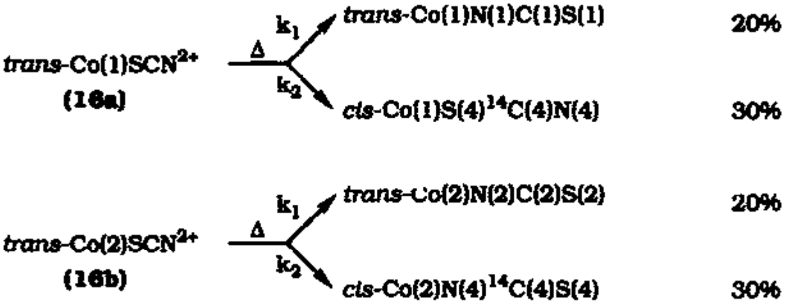
a partial, scrambling process, but is best accommodated by a combination of the three pathways given in Scheme 3, with the immediate products comprising 40% $CoNCS^{2+}$ without stereochemical change or incorporation of $N^{14}CS^-$ from the lattice, and equal amounts of *cis*-$CoS^{14}CN^{2+}$ and *cis*-$CoN^{14}CS^{2+}$ containing ionic thiocyanate and involving stereochemical change. The intermediate *cis*-$CoS^{14}CN^{2+}$ product is of course chemically indistinguishable from the *trans*-$CoSCN^{2+}$ reactant, and continues on to form *cis*-$CoN^{14}CS^{2+}$ as the reaction progresses.

A crystal structure of the $CoSCN^{2+}$ reactant gives a good explanation of these results. $[Co(NH_3)_5SCN](NCS)_2$ crystallises in the monoclinic space group $P2_1/n$, with two separate Co(III) cations in the asymmetric unit. There are, therefore, four dissimilar ionic thiocyanates. One of these stands out as an excellent candidate for subsequent coordination to each of the Co(III) centres. Figures 3A and 3B show the arrangement of ionic thiocyanates in the lattice, with those "backface" (i.e. remote from the coordinated SCN) being shaded since they are the important ones. S(4)C(4)N(4) on the backface to both units is unique. S(4) is the closest sulfur atom to Co(1) (433.4 pm), and N(4) is the closest donor atom of any kind to Co(2)



Scheme 3.

(376.7 pm). Table 2 gives distances of all lattice donor atoms within 5 Å of the two Co centres. But probably more importantly S(4) and N(4) subtend angles of 94.8° and 167.7° respectively towards the two centres which means that the S and N lone pairs point almost exactly at the metal. Also, these atoms are located almost exactly down three-fold axes comprising three coordinated ammine ligands (see Figs. 4A and 4B). With a $(t_{2g})^6(e_g)^0$ configuration such axes represent positive holes toward the metal cations and hence ideal locations for electron pairs. It appears therefore that the $S(4)C(4)N(4)^-$ anion is beautifully poised on low energy paths to both Co(III) cations. The isomerisation yields can then be apportioned as given in Scheme 4.



Scheme 4.

From this it appears that the energetics of S and N coordination using lattice $N^{14}CS^-$ are similar (they did not need to be), each representing 30% coordination, and that this remote "backside" entry occurs in competition with head-to-tail "frontside" N-entry of previously S-bound thiocyanate, 40%. Such three-way competitive entry is also found in solution (see Section 2.2).

A re-analysis of the crystal structure of $[Co(NH_3)_5SCN]Cl_2{\cdot}H_2O$ [14] suggested to us that the failure of lattice Cl^- ions to enter the coordination sphere on heating this material (see beginning of this section) resulted not from more distant

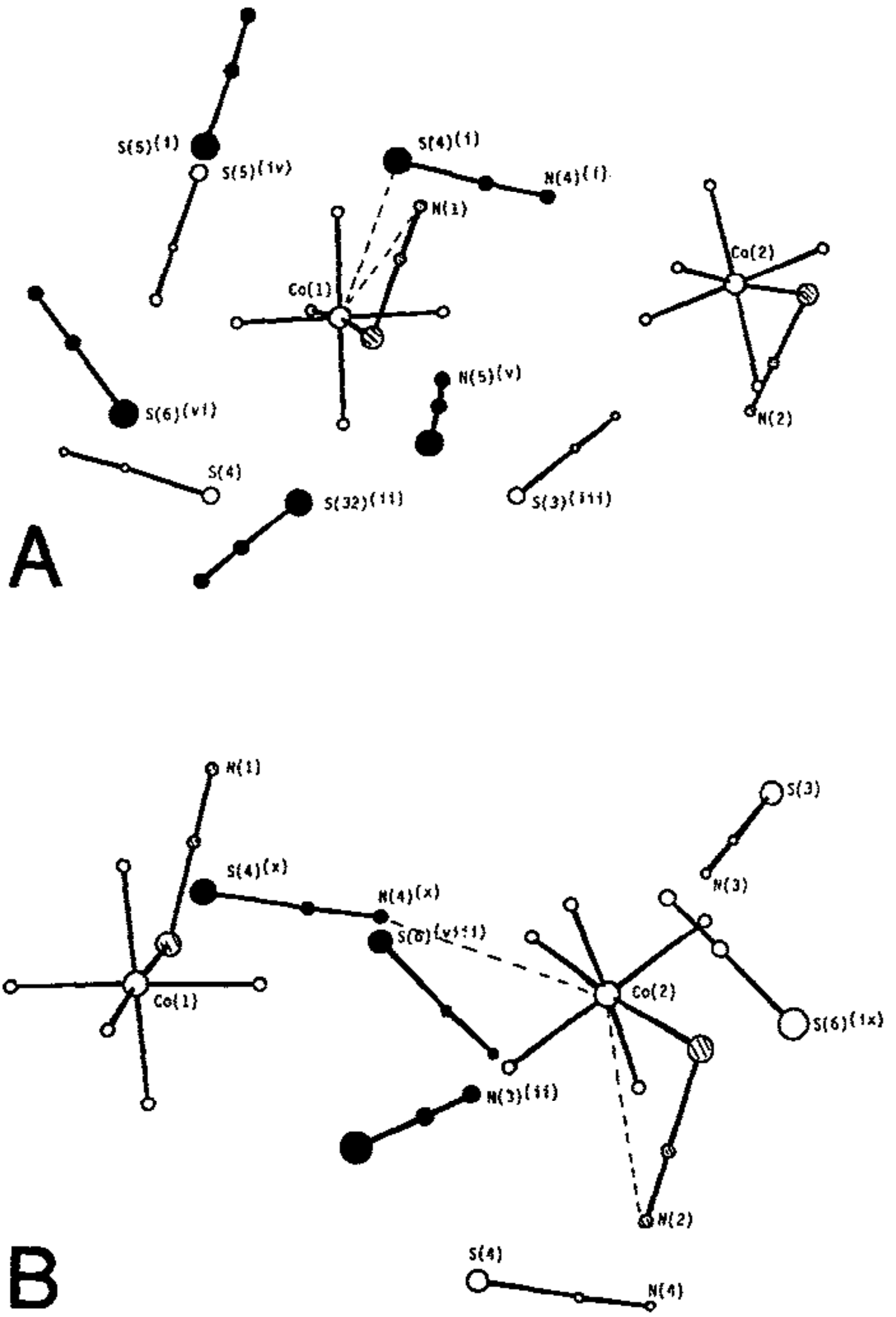


Fig. 3. Perspectives of ionic SCN^- and NCS^+ anions within 5 Å of the two Co atoms in crystalline $[\mathrm{Co(NH_3)_5SCN}](\mathrm{NCS})_2$. A: surrounding Co(1); B: surrounding Co(2). Lattice anions "backface" to the departing SCN ligand are given as ●, "frontface" anions as ○, and the coordinated SCN as ◍.

TABLE 2

Non-bonded distances (<5 Å) of ionic SCN^-, NCS^- and coordinated SCN^- from Co(1,2) in $[Co(NH_3)_5SCN](NCS)_2$ crystal

	Interaction	Translation	Distance (Å)	Orientation (perpendicular distance from CoN_4 mean plane (Å))
Co(1)	Ionic			
	Co(1)–N(5)	(v)	4.103(5)	Backface (2.700(6))
	Co(1)–S(4)	(i)	4.334(2)	Backface (2.856(1))
	Co(1)–S(4)	(0)	4.476(2)	Frontface (1.482(1))
	Co(1)–S(6)	(vi)	4.528(2)	Backface (3.023(2))
	Co(1)–S(5)	(iv)	4.563(1)	Frontface (1.521(2))
	Co(1)–S(5)	(i)	4.593(2)	Backface (3.002(2))
	Co(1)–S(3)	(iii)	4.616(1)	Frontface (1.582(1))
	Co(1)–S(3)	(ii)	4.630(2)	Backface (2.848(1))
	Coordinated			
	Co(1)–N(2)	(i)	4.126(7)	Frontface (0.695(1)); intermolecular
	Co(1)–N(1)	(0)	4.138(6)	Frontface (3.377(5)); intramolecular
Co(2)	Ionic			
	Co(2)–N(4)	(x)	3.767(5)	Backface (2.038(6))
	Co(2)–N(3)	(ii)	3.807(6)	Backface (2.521(6))
	Co(2)–N(6)	(ix)	4.148(7)	Frontface (1.876(7))
	Co(2)–N(6)	(viii)	4.227(7)	Backface (2.755(7))
	Co(2)–S(3)	(0)	4.456(2)	Frontface (1.493(1))
	Co(2)–N(3)	(0)	4.813(2)	Frontface (2.997(6))
	Co(2)–S(4)	(0)	4.849(2)	Frontface (0.474(1))
	Co(2)–N(4)	(0)	4.952(5)	Frontface (1.691(6))
	Coordinated			
	Co(2)–N(1)	(vii)	3.819(5)	Backface (2.226(5)); intermolecular
	Co(2)–N(2)	(0)	4.089(5)	Frontface (3.269(5)); intramolecular

Coordinate translations:
(0) x, y, z
(i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$
(ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}+1$
(iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$
(iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$
(v) $-x+1, -y, -z+1$
(vi) $x, y-1, z$
(vii) $x, y, z+1$
(vii) $-x, -y+1, -z+1$
(ix) $x+\frac{1}{2}, -y+\frac{1}{2}+1, z+\frac{1}{2}$
(x) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$

Cl^- ions, or from poorer positioning with respect to the three fold axes of the octahedron, but from a more extensive network of H-bonds to ammine ligands. Thus the electron pairs of the Cl^- ions are less available to the single (in this case) Co(III) centre, and the head-to-tail intramolecular pathway is favoured. Such non-incorpora-

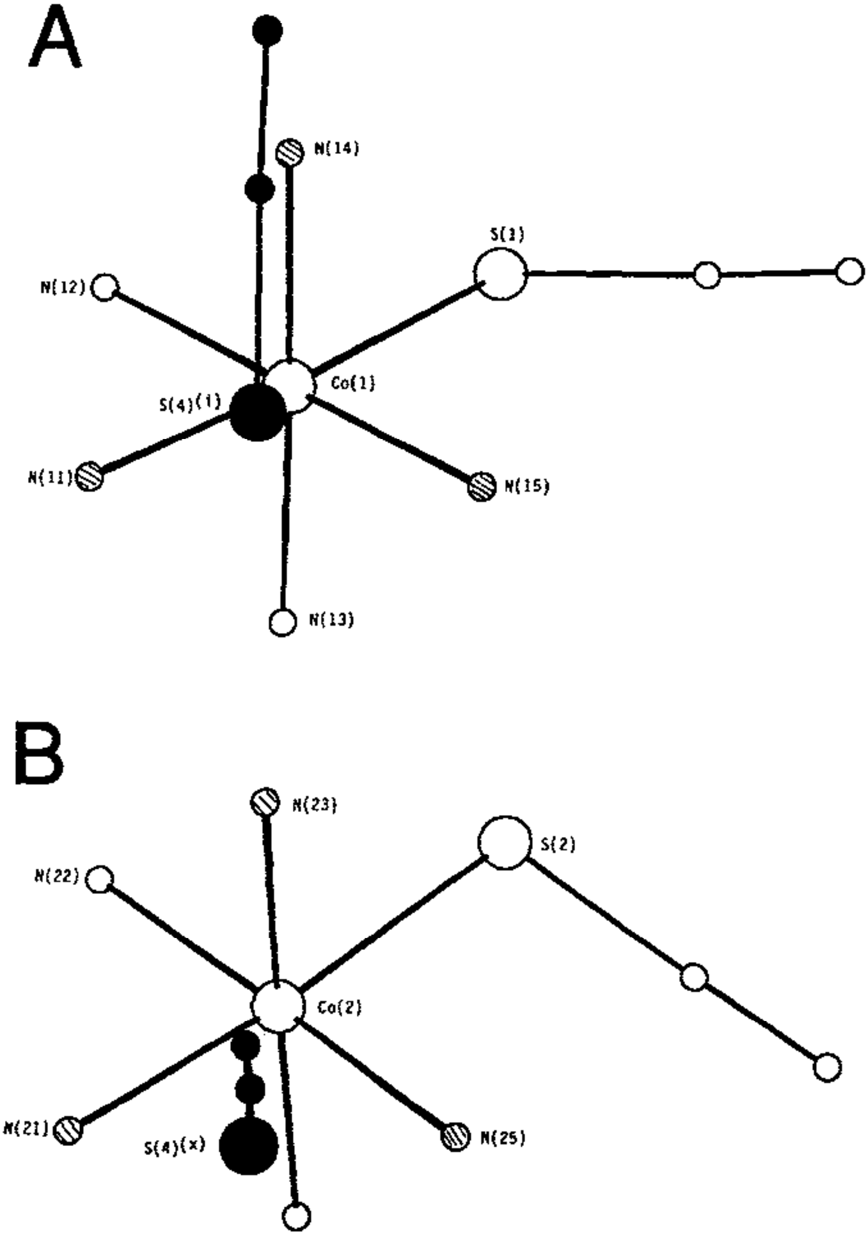


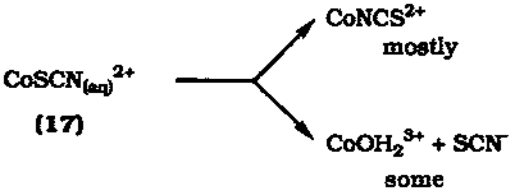
Fig. 4. Perspective views down the 3-fold axis of ammine ligands (▨) for A: "backface" entry of $S(4)CN^-$ to Co(*1*); and B: "backface" entry of $N(4)CS^-$ to Co(2).

tion of lattice Cl^- is accompanied by retention of crystal packing and non-fracturing, whereas the $[Co(NH_3)_5SCN](NCS)_2$ crystal fractured in the final stages of heating.

2.2. Spontaneous isomerisation in aqueous solution

In the same article reporting the $[Co(NH_3)_5SCN]^{2+}$ preparation [5] it was mentioned that an acidic aqueous solution slowly turned orange ($t_{1/2} = 9$ days in 0.01 M $HClO_4$, $I = 1.0$ $NaClO_4$, 25°C). More recent rate data give $k_{obs} = 1.3 \times 10^{-6}\ s^{-1}$ at $I = 0$–0.15 M in the pH range 0–5.5 [16]. Higher temperature and pressure data are also available [17], giving $\Delta H^{\ddagger} = 103\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = -14 \pm 3\ J\ K^{-1}\ mol^{-1}$ and $\Delta V^{\ddagger} = -5.3 \pm 0.8\ cm^3\ mol^{-1}$.

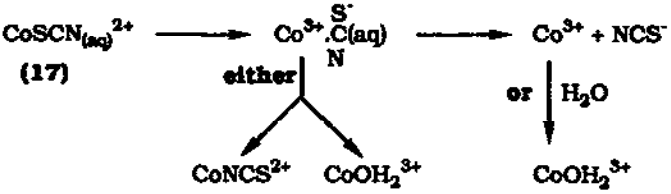
Originally the reaction was reported to be quantitative [5] with only a trace (<2%) of $[Co(NH_3)_5OH_2]^{3+}$ being detected by ion-exchange chromatography (by eye on the column) after seven days at 40°C. Subsequently it was confirmed that formation of $CoNCS^{2+}$ is "essentially quantitative" (after 1.0 h at 95°C, pH 3) [18], but later in this subsequent article "some competitive hydrolysis" or "instability in the $CoNCS^{2+}$ product" was alluded to. We have now carried out a very careful study [16] at low ionic strengths ($I = 0$–0.15 M), both in the absence and presence of ionic NCS^-, and find that small but significant amounts of $CoOH_2^{3+}$ are indeed formed at 25°C. At $I \simeq 0$ this amounts to 9.1%, and a similar amount is formed in 1.0 M $NaClO_4$ at pH 3. Likewise, with *t*-$[Co(tren)(NH_3)SCN]^{2+}$ some 5.2% *t*-$CoOH_2{}^{3+}$ is formed, so that the non-quantitative nature of the spontaneous isomerisation reaction is not restricted to the pentaammine complex, eqn. (7). The amount of $CoOH_2^{3+}$ formed is likely to be temperature dependent, but this aspect has not been examined.



(7)

The production of $CoNCS^{2+}$ is truly intramolecular since it occurs in the absence of added NCS^-, and its rate of formation and amount are first-order in complex concentration (i.e. not second-order). The formation of $CoOH_2^{3+}$ could either occur together with isomerisation, or SCN^- could be partly lost to the bulk solvent (or to a solvent-separated ion-pair) with $CoOH_2^{3+}$ being formed subsequently from that part involving the "liberated" Co^{3+} intermediate, Scheme 5. We favour the former interpretation, with $CoOH_2^{3+}$ being directly formed from the immediate $Co^{3+} \cdot SCN^-$ ion-pair since, as we shall now see, competitive entry of other anions from solution also occurs.

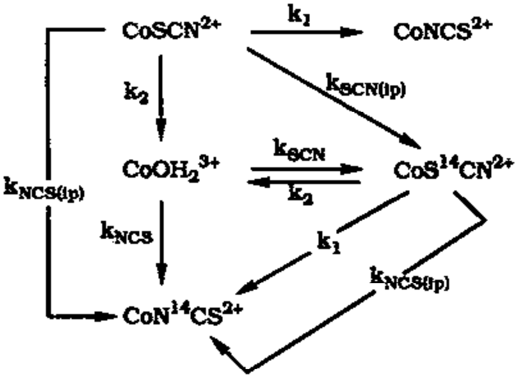
Labelled $N^{14}CS^-$ introduced to the bulk solution as $KN^{14}CS$ (0.15 M), directly



Scheme 5.

enters the coordination sphere to form $CoN^{14}CS^{2+}$ and $CoS^{14}CN^{2+}$. It has been possible, using very careful experiments, to distinguish this process from that occurring subsequently via anation of the 9.1% $CoOH_2^{3+}$ formed by hydrolysis. These results are given in Fig. 5, with the dashed curves representing $CoN^{14}CS^{2+}$ and $CoS^{14}CN^{2+}$ formed by subsequent anation of $CoOH_2^{3+}$ [16], and the full curves representing the calculated amounts based on the rate constants $k_{NCS(ip)}$, $k_{SCN(ip)}$ listed in Table 3. These latter pathways represent the direct routes referred to above, and the whole analysis is based on the reaction model given in Scheme 6.

The amounts of direct incorporation are not large, comparisons with the



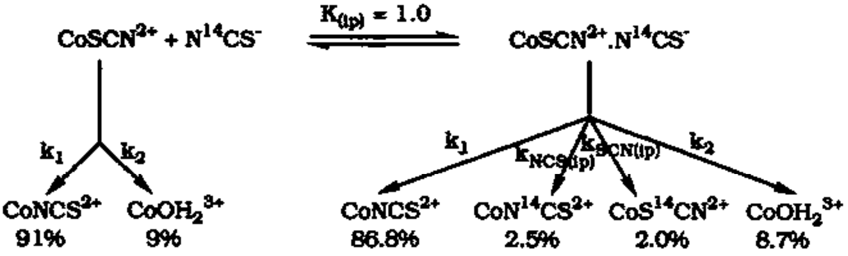
Scheme 6.

TABLE 3

Observed rate constants (s^{-1}) for the isomerisation (k_1), aquation (k_2), and direct anation ($k_{SCN(ip)}$, $k_{NCS(ip)}$) of $[Co(NH_3)_5SCN]^{2+}$, and of anation of $[Co(NH_3)_5OH_2]^{3+}$ (k_{SCN}, k_{NCS}) in 0.15 M KSCN at 25°C

Rate constant	k (s^{-1})	k/0.15 (M^{-1} s^{-1})
k_1	1.14×10^{-6}	
k_2	1.2×10^{-7}	
$k_{SCN(ip)}$	3.4×10^{-9}	2.3×10^{-8}
$k_{NCS(ip)}$	4.1×10^{-9}	2.7×10^{-8}
k_{SCN}	6.8×10^{-8}	4.5×10^{-7}
k_{NCS}	2.22×10^{-7}	1.48×10^{-6}

intramolecular pathway (k_1) being $k_{\mathrm{NCS(ip)}}/k_1=0.36\%$, $k_{\mathrm{SCN(ip)}}/k_1=0.30\%$ in the 0.15 M KSCN condition. But the competition ratio for NCS^- and SCN^- entry is about unity, $k_{\mathrm{NCS(ip)}}/k_{\mathrm{SCN(ip)}}=1.2$. As we shall see below this ratio is similar to that found for other CoX^{2+} complexes which completely lose their X^- groups to the solvent (but it must be remembered that for these other complexes immediate return of X^- from the dissociated ion pair $CoX^{2+} \rightarrow Co^{3+} \cdot X^- \rightarrow CoX^{2+}$ cannot be seen). If direct entry of $N^{14}CS^-/S^{14}CN^-$ occurs through ion pairing with the $CoSCN^{2+}$ reactant, and if an ion-pair constant (K_{ip}) of unity is assumed (the exact value is not critical), then the amounts of direct entry from this ion pair can be calculated. These are given in Scheme 7.



Scheme 7.

Such a calculation assumes equal reactivities of the ion-pair and free ion, and that the k_1/k_2 ratio is unaffected by ion-pairing. Putting these results another way, in 1.0 M $KN^{14}CS$ some 1.25% $CoN^{14}CS^{2+}$ and 1.0% $CoS^{14}CN^{2+}$ would be formed based on the results in 0.15 M $KN^{14}CS$. Such amounts are substantial, and are not too different from those found for other CoX^{2+} ions hydrolysed in 1.0 M KNCS. Jackson et al. report [19] that for CoX^{2+} ($X=CF_3SO_3^-, ClO_4^-, CH_3SO_3^-$) 2.0–2.6% $CoNCS^{2+}$ and 1.8–2.6% $CoSCN^{2+}$ are formed under such conditions. This suggests that entry of ionic NCS^-/SCN^- is not greatly affected by the nature of the leaving group, nor by its eventual fate. Almost as much ionic $N^{14}CS^-/S^{14}CN^-$ directly enters $CoSCN^{2+}$ where the leaving group re-enters as $CoNCS^{2+}$ to a major extent, as it does with other CoX^{2+} ions where the final product is largely $CoOH_2^{3+}$. The small differences might be attributed to the fact that direct re-entry of X^- from $Co^{3+} \cdot X^-$ or $Co^{3+} \cdot X^- \cdot NCS^-$ results in additional reactant, whereas direct re-entry from $Co^{3+} \cdot SCN^-$ and from $Co^{3+} \cdot SCN^- \cdot N^{14}CS$ to give $CoNCS^{2+}$ does not. Another important point coming out of this study is that the two thiocyanates in the ion-pair $CoSCN^{2+} \cdot N^{14}CS^-$ do not become equivalent at any stage since the $CoNCS^{2+}$ (86.8%), $CoN^{14}CS^{2+}$ (2.5%) amounts would then be equal. Thus if complete severance of the Co–SCN bond occurs before ligand entry (or re-entry) then the two thiocyanates remain differentiated, possibly because they adopt different stereochemical positions. The life-time of the dissociated $Co^{3+} \cdot SCN^- \cdot N^{14}CS^-$ species must therefore be very short, too short to allow for reorganisation, or rotation, of its constituents. If a specific ion pair were involved, with the two adjacent

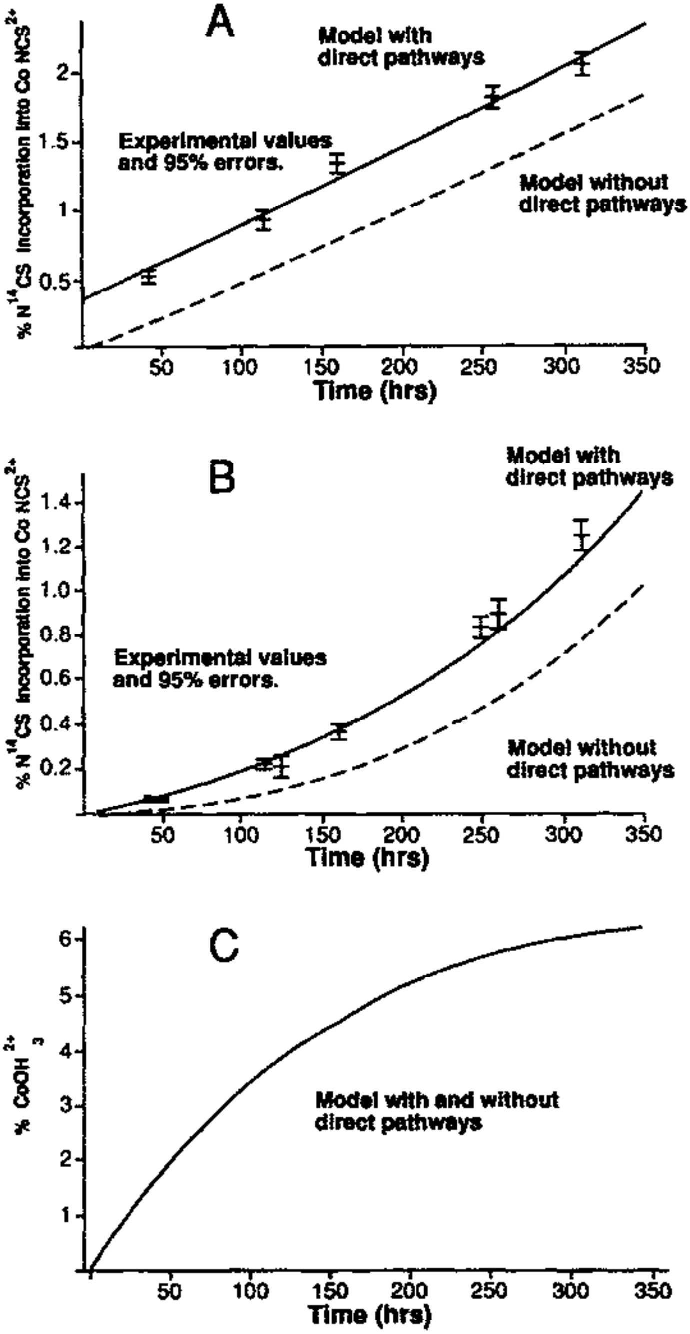


Fig. 5. A: % incorporation of N^{14}CS$^-$ into [Co(NH$_3$)$_5$NCS]$^{2+}$; B: % incorporation of S^{14}CN$^-$ into the reactant [Co(NH$_3$)$_5$SCN]$^{2+}$; C: % [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ produced; as a function of time for the spontaneous isomerisation of [Co(NH$_3$)$_5$SCN]$^{2+}$ in aqueous solution at pH 5.59 in the presence of 0.15 M ^{14}C-labelled KSCN. Observed data are given as points (together with error bars) in graphs A and B, but are not given in graph C. Calculated curves without and with the additional pathways represented by $k_{NCS(ip)}$ and $k_{SCN(ip)}$ (Table 3 and Scheme 6) are shown.

thiocyanates becoming equivalent once the bond was broken, then this would require $K_{ip(specific)}$ to be about 0.025 M^{-1}. We feel that this value is too small, even though ion pairing adjacent to the leaving group is likely to be less important than on the more positively charged "backface" of the cation (see the crystal structures mentioned in Section 2.1). We suggest that re-entry of released SCN^- is preferred over $S^{14}CN^-$ because the former is vibrationally excited with H-bonding to the solvent and ammine ligands not yet fully consummated. This suggests a very short life-time for a $Co^{3+} \cdot SCN^- \cdot N^{14}CS^-$ intermediate. We will return to this aspect below.

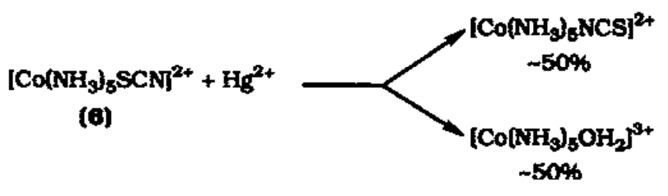
2.3. Hg^{2+} and Ag^+ assisted isomerisations

Werner and Mueller first reported investigations in this area [20]. They found that addition of $AgNO_3$ to an aqueous solution of $[Co(NH_3)_5NCS]^{2+}$ gave an immediate orange to yellow colour change and suggested that a rather stable $CoNCSAg^{3+}$ coordination system had formed. This species did not give an immediate precipitate with HCl, a claim that could not be subsequently verified. Later, Werner [21] isolated $[Co(NH_3)_5NCSAg](NO_3)_3$ as well as $[Co(NH_3)_4(NO_2)(NCSAg)](NO_3)Cl$, $[Co(en)_2(OH_2)(NCSAg)](ClO_4)_2(NO_3) \cdot H_2O$ and $[Co(en)_2Cl(NCSAg)](NO_3)_2$ (note the bonding to S rather than to Cl) containing one-to-one Co(III): Ag(I) stoichiometries. But more interestingly some di-silver complexes were also reported; $[Co(en)_2(OH_2)(NCSAg_2)](NO_3)_4 \cdot H_2O$, $[Co(en)_2(NH_3)(NCSAg_2)](NO_3)_4 \cdot H_2O$ and $[Co(en)_2Cl(NCSAg_2)](NO_3)_3$ formulated as containing both Ag^+ ions bonded to the terminal S atom. These di-silver complexes have not been re-investigated, although recently we have found a term in the rate law for the reaction of *t*-$[Co(tren)(NH_3)SCN]^{2+}$ with silver ions which is second order in $[Ag^+]$, and have interpreted this as resulting from a reactive $Co{-}S(Ag)CNAg^{4+}$ species [22]. Early mole ratio studies by Waggener et al. [23] make no mention of di-silver complexes, but suggest a 2:1, Co:Ag stoichiometry. The Co–NCS bond appears to be quite stable towards aquation in the presence of Ag^+ (or Hg^{2+}) ions, whereas analogous CrNCS systems are known to undergo rather rapid hydrolysis under similar conditions.

Waggener et al. [23] appear to be the first to have reported a stable addition complex between $[Co(NH_3)_5NCS](NO_3)_2$ and $Hg(NO_3)_2$, but apart from its golden yellow colour, and a Hg:Co ratio of close to 1.0, no further details were available. Falk and Linck [24] report reasonably large equilibrium constants for both 1:1 $CoNCSHg^{4+}$ and 2:1 $CoNCS(Hg)_2^{6+}$ systems ($K_1 = 9.8 \times 10^4$ M^{-1}, $K_2 = 1.4 \times 10^4$ M^{-1}) with the latter presumably involving two Hg^{2+} ions bonded to the terminal S atom in an analogous fashion to the Ag(I) complexes reported by Werner. The chemistry of Hg^{2+} involvement with Co(III) halides appears not to have begun with Werner but with Bronsted and Livingston [25]. They investigated the catalytic effect of Hg^{2+} on the hydrolysis of $[Co(NH_3)_5Br]^{2+}$ but did not observe any associated $CoBrHg^{4+}$ species. However Bifano and Linck [26] reported the existence of a stable $[Co(en)_2Cl_2Hg]^{3+}$ intermediate in their kinetic studies on several Co(III) halide systems. The Olson and Simonson paper of 1949 raised the question of specific anion interactions in the rate laws for these reactions [27], and Posey and Taube [28] discussed the question of concerted (S_N2) vs. stepwise dissociative (S_N1) mechanisms in the Hg^{2+} and Ag^+ catalysed removal of coordinated halide.

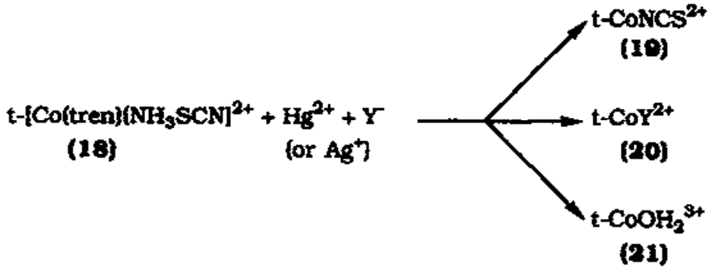
Our work in this area began with a comparison of the products of the induced reactions of *t*-$[Co(tren)(NH_3)Cl]^{2+}$ with Hg^{2+} and *t*-$[Co(tren)(NH_3)N_3]^{2+}$ with NO^+ in the presence of $NO_3{}^-$ ions [29]. Previous work had suggested the existence of a common five-coordinate intermediate for this type of reaction [30]. We found however that while considerable quantities of *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ were formed the $CoNO_3^{2+}/CoOH_2^{3+}3+$ ratio differed for the two reactions, and this suggested either a different five-coordinate intermediate or that the life-time of the five-coordinate intermediate was not sufficient for the different surroundings to equilibrate. We then embarked [31] on a careful study of the Hg^{2+} induced reaction of *t*-$[Co(tren)(NH_3)(NH_3)X]^{2+}$ (X = Cl, Br) in the presence of NO_3^- (as well as ClO_4^- and $CF_3SO_3^-$ ions)[31], and confirmed the earlier observations of Olson and Simonson [27] that the rates of reaction did not depend on the ionic strength, but rather on the specific anion present, and its concentration. This was so even at low ionic strengths where Debye–Huckel type expressions might be expected to hold. Changing the cation, or its charge (La^{3+}, Ba^{2+}, Mg^{2+}, Na^+, K^+), was relatively unimportant. Anion (Y^-) association to form a reactive species such as *t*-$[Co(tren)(NH_3)XHgY]^{3+}$ was suggested (rate limiting kinetics were approached), and direct insertion of Y^- to form *t*-$[Co(tren)(NH_3)Y]^{2+}$ ($Y = NO_3, ClO_4, CF_3SO_3$) was taken to occur from within this species, in addition to aquation to form *t*-$[Co(tren)(NH_3)OH_2]^{3+}$.

We also knew that Hg^{2+} would catalyse the isomerisation of thiocyanate in the pseudo-halide complex *t*-$[Co(tren)(NH_3)SCN]^{2+}$ since a previous study by Adegite et al. [32] had shown this to occur for the pentaammine–thiocyanato complex, eqn. (8). A $[Co(NH_3)_5S(Hg)CN]^{4+}$ intermediate had been proposed [32] with Hg^{2+} bonded to the coordinated S atom. We undertook [22] a detailed kinetic



$$[Co(NH_3)_5SCN]^{2+} + Hg^{2+} \rightarrow [Co(NH_3)_5NCS]^{2+}\ (\sim 50\%) + [Co(NH_3)_5OH_2]^{3+}\ (\sim 50\%) \qquad (8)$$

and product study of the reaction given by eqn. (9), using both single and double anion mixtures ($Y^- = NO_3^-, ClO_4^-, CF_3SO_3^-$). Kinetic data at constant $Y_1^- + Y_2^- =$ 1.00 M but varying $[Hg^{2+}] = 0.04$–0.40 M are shown in Fig. 6. This shows an approach to limiting kinetics, as well as a clear dependence on the nature of Y^-, with NO_3^- being the most effective anion. Varying $[Y^-]$ at low but constant $[Hg^{2+}]$ (0.04 M) however, shows a linear dependence on $[Y^-]$, Fig. 7. Therefore the association of Y^- with Hg^{2+} is small (K_{Hg}) but the binding of HgY^+ to Co is substantial



(9)

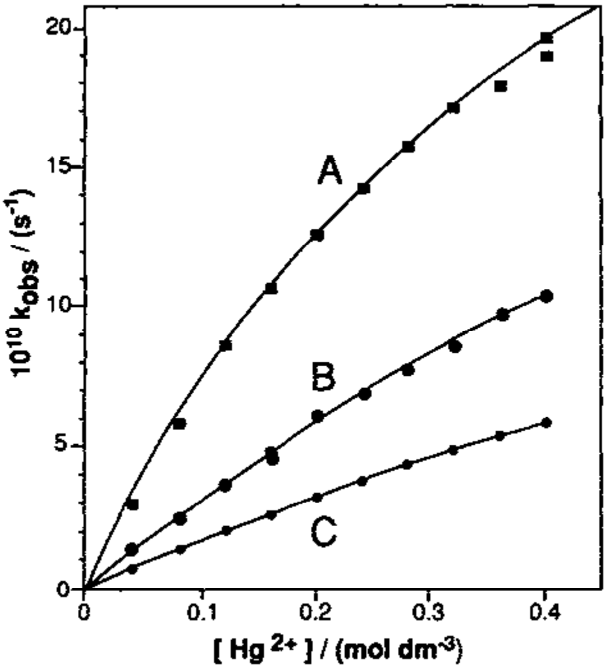


Fig. 6. Variation in k_{obs} (25°C) with $[Hg^{2+}]$ (0.04–0.40 M) at constant $[Y^-]$ (1.0 M) and $[H^+]$ (0.2 M), for the Hg^{2+}-catalysed isomerisation/hydrolysis of t-$[Co(tren)(NH_3)SCN]^{2+}$. Curve A (■) $Y=NO_3^-$; Curve B (●) $Y=ClO_4^-$; Curve C (●) $Y=CF_3SO_3^-$.

(K_{Co}). With the similar $CoBr^{2+}$ complex curvature was observed under both sets of experimental conditions [31], and this may be interpreted as a larger binding constant of HgY^+ to $CoBr^{2+}$ than to $CoSCN^{2+}$. Both systems show a common non-zero intercept (k^{o}_{obs}) for each Y^- at $[Y^-]=0$, and this was interpreted as the anion independent reaction of Hg^{2+} with $CoSCN^{2+}$ (or $CoBr^{2+}$). This term is clearly of minor importance under most electrolyte conditions. Scheme 8 gives the overall scheme on which the kinetic and product parameters were based, and Table 4 gives limiting rate constants for the decomposition of the important $CoX(HgY)^{3+}$ intermediates. The main conclusions arising from these two studies [22,31] were:

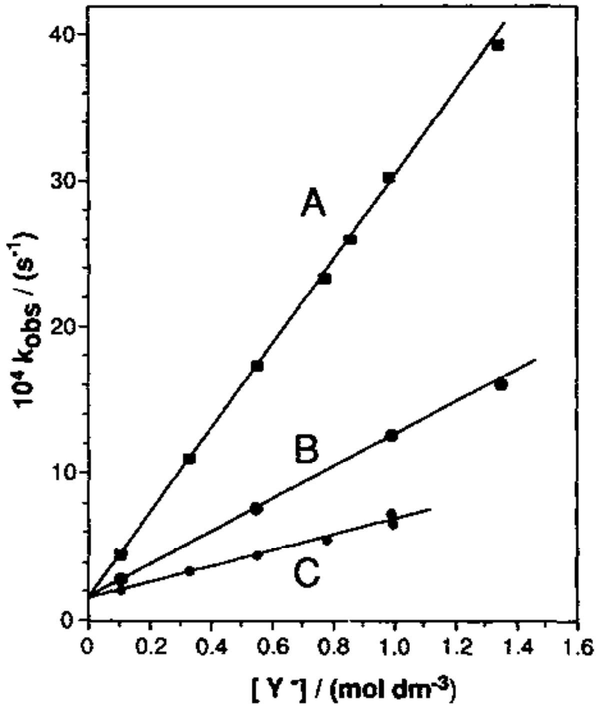
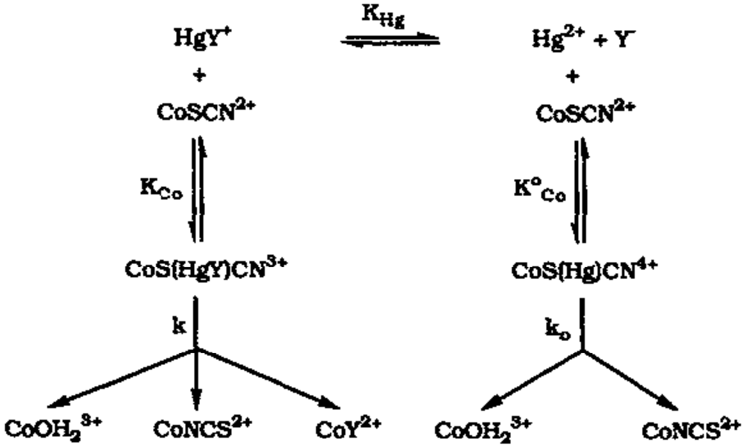


Fig. 7. Variation in k_{obs} (25°C) with [Y^-] (0.1–1.36 M) at constant [Hg^{2+}] (0.04 M) and [H^+] (0.02 M), for the Hg^{2+}-catalysed isomerisation/hydrolysis of *t*-[$Co(tren)(NH_3)SCN$]$^{2+}$. Line A (■) $Y^- = NO_3^-$; line B (●) $Y = ClO_4^-$; line C (●) $Y = CF_3SO_3^-$.



Scheme 8.

TABLE 4

Rate and association constants for the Hg^{2+} catalysed reactions of t-$[Co(tren)(NH_3)X]^{2+}$ (X=SCN, Br) in aqueous solution (25°C)

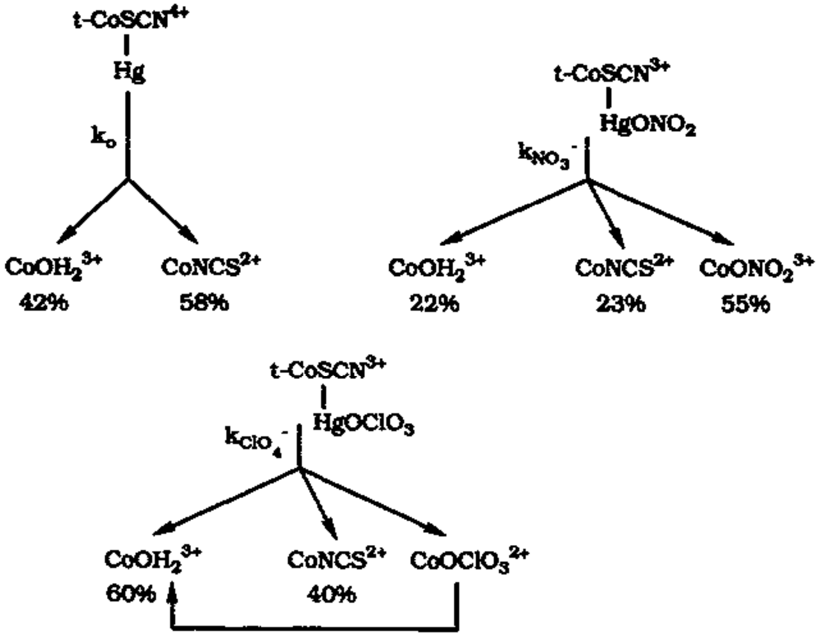
	t-$CoSCN^{2+}$ System	t-$CoBr^{2+}$ System
k (s^{-1})	0.04 (NO_3^-) 0.035 (ClO_4^-) 0.026 ($CF_3SO_3^-$)	34 (NO_3^-) 28 (ClO_4^-) 30 ($CF_3SO_3^-$)
$K_{Co}K_{Hg}$ (M^{-2})	2.2 (NO_3^-) 0.9 (ClO_4^-) 0.6 ($CF_3SO_3^-$)	13 (NO_3^-) 5 (ClO_4^-) 2.5 ($CF^3SO_3^-$)
$k_0K_{Co}^0$ ($M^{-1}\ s^{-1}$)	0.0042	0.75

(i) The observed rates (k_{obs}), and rate differences for different Y^- anions (Δk_{obs}), result from differences in the binding of Hg^{2+} to Y^- (K_{Hg}) and of HgY^+ to CoX^{2+} (K_{Co}). The combined $K_{Co}K_{Hg}$ values (Table 4) show this, and since K_{Hg} is rather small ($K_{Hg2+}/M^{-1}=0.53$ (NO_3^-), 0.20 (ClO_4^-), 0.10 ($CF_3SO_3^-$)) the association constant for the binding of HgY^{2+} to CoX^{2+} is reasonably large ($K_{Co}>1$).

(ii) Rate constants k for the decomposition of $CoX(HgY)^{3+}$ vary little with different Y, implying that the presence of Y^- either plays no significant role, or the same role, in the activation process for breaking the Co–X bond. The Co–Br bond is about 10^3 times easier to break than the Co–SCN bond. If no significant role is played by Y^- then k_o takes the value 0.04 s^{-1}, making $K_{Co}^o=0.1\ M^{-1}$ for the $CoSCN^{2+}$ system.

(iii) The presence of the internal competitor SCN^- allows a fairly detailed picture to be drawn as to how the CoY^{2+} and $CoOH_2^{3+}$ products are formed. The 58% $CoNCS^{2+}$ produced in the absence of electrolyte, 42% in 1.0 M ClO_4^- and 24% in 1.0 M NO_3^- (Scheme 9 gives limiting values), shows that the presence of Y^- significantly affects the formation of $CoNCS^{2+}$. This means that each of the products CoY^{2+}, $CoNCS^{2+}$ and $CoOH_2^{3+}$ are either formed from the same Co^{3+} intermediate, or are formed from different intermediates which are in equilibrium. To our way of thinking this essentially rules out the formation of $CoNCS^{2+}$ at an early stage (with $CoONO_2^{2+}$ and $CoOH_2^{3+}$ being formed subsequently following diffusion of SCN^- into the adjoining solvent) since this would predict an essentially constant amount of $CoNCS^{2+}$. It is likely that all three entering groups are in direct competition for the same Co^{3+} intermediate.

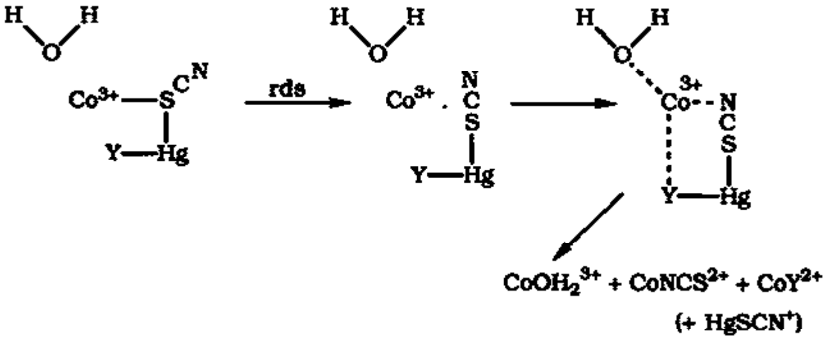
(iv) The intermediacy in the amount of $CoNCS^{2+}$ formed in a ClO_4^- medium (42% in 1 M ClO_4^-) compared to that in its absence (58%) and that in the presence of 1 M NO_3^- (24%) means that ClO_4^- competes for the intramolecular rotation process to a lesser extent than NO_3^-. Furthermore, the larger amount of $CoOH_2{}^{3+}$ formed in a ClO_4^- medium (58%) compared to that in its absence (42%), or to that in 1 M NO_3^- (23%) suggests either that ClO_4^- in some way encourages OH_2 entry (whereas NO_3^- inhibits it), or that ClO_4^- also enters to give $CoOClO_3^{2+}$ which



Scheme 9.

subsequently aquates (rapidly) to give CoOH$_2^{3+}$. The latter possibility is almost certainly true since substantial amounts of CoOSO$_2$CF$_3^{2+}$ and CoOClO$_3^{2+}$ were actually observed [31] in the more rapid reaction of CoBr^{2+} with Hg^{2+} under the same conditions.

(v) The fact all the CoONO$_2$$^{2+}$ product can be accounted for by the k_{NO3} pathway means that the activated complex for breaking the Co–SCN^{2+} bond, and for forming CoONO$_2$$^{2+}$, have the same composition. The juxtaposition of HgONO$_2$$^{+}$ and the departing ligand suggests that the kinetically active NO$_3^-$ species is that which enters the complex, Scheme 10, (Y$^-$ = NO$_3^-$). The product distributions (Scheme 9) for the

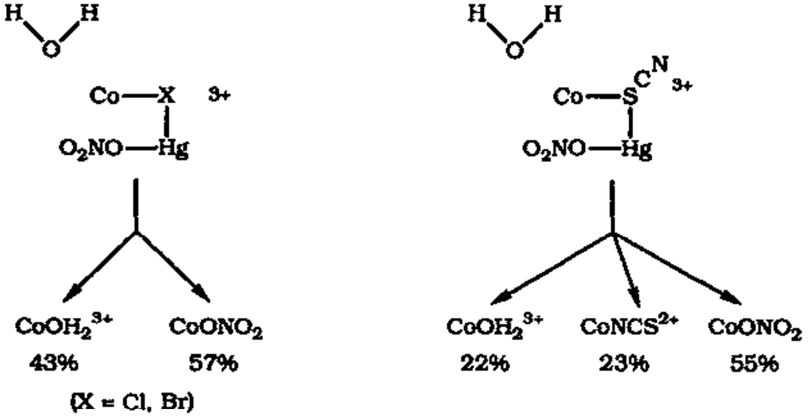


Scheme 10.

anion-independent pathway k_o, the k_{ClO_4} pathway, and the k_{NO3} pathway obtained in the presence of a single anion (NO_3^- or ClO_4^-) also satisfy the product distributions obtained when both ClO_4^- and NO_3^- ions are present together. This means that the products arise from independent processes; i.e. ClO_4^- does not affect the entry of NO_3^-, and vice versa.

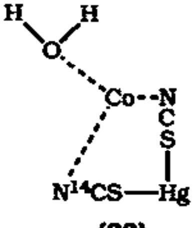
(vi) The small, but real, differences in the $CoNCS^{2+}/CoOH_2^{3+}$ ratio for the k_o and k_{NO3} paths (1.38 vs. 1.05) imply that the same intermediate is not involved in the two processes. NO_3^- competes more effectively for NCS^- entry than for OH_2 entry. Water entry derives from the adjacent solvent, whereas the rotating SCN^- ligand and entering ONO_2^- almost certainly derive from attachment to Hg^{2+}. Their juxtaposition apparently influences each other to a greater extent than it influences OH_2 entry (the same solvent isotope fractionation factors were obtained by Dolbear and Taube [33] for $CoOH_2^{3+}$ produced in the Hg^{2+}-induced and spontaneous reactions of $[Co(NH_3)_5Br]^{2+}$).

(vii) The almost identical amounts of NO_3^- entry to give $CoONO_2^{2+}$ (~55–57%) starting with the three reactants *t*-$[Co(tren)(NH_3)Cl]^{2+}$, *t*-$[Co(tren)(NH_3)Br]^{2+}$ and *t*-$[Co(tren)(NH_3)SCN]^{2+}$, Scheme 11, reinforces the idea that the products derive essentially from the stereochemical location of the entering group at the instant of Co–X bond rupture. It does not matter what the leaving group is, or its eventual fate (in the case of SCN^- significant re-entry to form $CoNCS^{2+}$ occurs). As long as the entering group is correctly positioned it will enter, even if the resulting product is not stable (e.g. $CoOClO_3^{2+}$, $CoOSO_2CF_3^{2+}$); i.e. an enforced capture process with practically no activation energy. With *t*-$CoS(HgONO_2)CN^{3+}$ the N end of the departing ligand will take up a position otherwise occupied by solvent, and so reduce solvent entry without affecting entry of ONO_2^-. Such observations parallel those mentioned in the previous section for the spontaneous reactions of CoX^{2+} and $CoSCN^{2+}$.



Scheme 11.

(viii) In an experiment using equi-molar quantities of Hg^{2+} and labelled $N^{14}CS^-$ (0.033 M) only 0.7% $N^{14}CS^-$ label turned up in the t-$CoNCS^{2+}$ product. Under such conditions $HgS^{14}CN^+$ is likely to be the major catalyst, and the low incorporation suggests that the immediately released thiocyanate is more acceptable to the incipient "Co^{3+}" centre than that strongly bonded to Hg^{2+} (**22**). Once again it can be argued that the immediately released thiocyanate will be vibrationally excited,



(22)

with H-bonding to adjacent solvent not fully developed. It will therefore be more acceptable to the electrophilic Co^{3+} acceptor than the more stable $HgS^{14}CN^+$ species. Alternatively, or additionally, the orientation of the $HgS^{14}CN^+$ species may not be as good. Similar arguments were advanced for the low incorporation of $N^{14}CS^-$ from the specific ion pair $Co^{3+}\cdot SCN^-\cdot N^{14}CS^-$ in the spontaneous reaction (see previous section).

Less information is available [22] on the Ag^+ induced reaction, but a

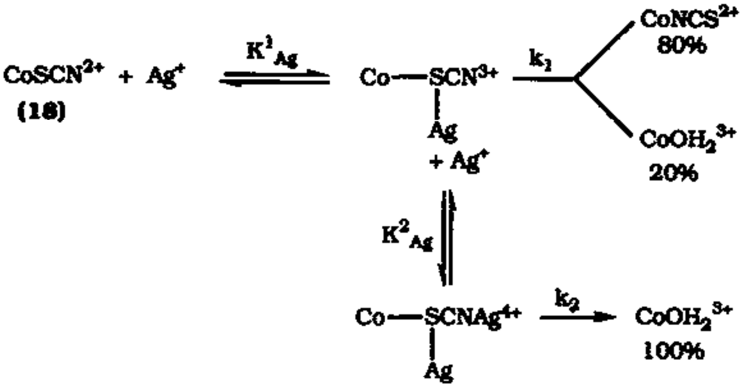
$$k_{obs} = \frac{k_{1(obs)}[Ag^+] + k_{2(obs)}[Ag^+]^2}{1 + [Ag^+]} \qquad (10)$$

rate law of the form given by eqn. (10), was found in 1 M ClO_4^- ($k_{1(obs)} = 3.4 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_{2(obs)} = 6.8 \times 10^{-4}\ M^{-2}\ s^{-1}$). The $CoNCS^{2+}/CoOH_2^{3+}$ ratio in this case showed a marked $[Ag^+]$ dependence, and this was interpreted as shown in Scheme 12 with the second-order $[Ag^+]^2$ pathway involving Ag^+ ions bonded to both S and N giving rise to only $CoOH_2^{3+}$. This differs from the Werner assignment for $[Co(NH_3)_5NCSAg_2](NO_3)_4\cdot H_2O$; (see beginning of this section). In the presence of NO_3^- both the k_1 and k_2 pathways result in some $CoONO_2^{2+}$ but more experiments are needed to fully document these results.

2.4. Hydrolysis under alkaline conditions

Isothiocyanate complexes ($CoNCS^{2+}$) are usually quite stable towards alkaline hydrolysis. Only for some very labile systems does the well known "base hydrolysis" reaction occur. Thus p-$[Co(tren)(NH_3)NCS]^{2+}$ (**23**) loses NCS^- slowly compared to other anions (Table 5) [34], whereas the t-isomer (**24**) prefers to lose p-NH_3 rather than t-NCS^-. The usual $k_{obs} = k_{OH}[OH^-]$ rate law is observed in both cases.

Thiocyanate ($CoSCN^{2+}$) complexes on the other hand are quite a different



Scheme 12.

TABLE 5

Base hydrolysis rate constants for some p-$[Co(tren)(NH_3)X]^{2+}$ complexes (25°C, 1 M $NaClO_4$)

X	k_{OH} ($M^{-1}\ s^{-1}$)
SCN^-	1.1×10^4
Cl^-	4×10^2
N_3^-	4.4×10^{-1}
NCS^-	3.4×10^{-2}

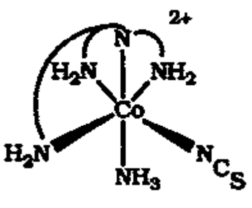
TABLE 6

Base hydrolysis rate constants for some halide, or halide-like, $[Co(NH_3)_5X]^{2+}$ systems (25°C, 1 M $NaClO_4$)

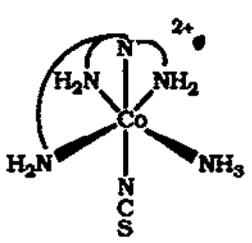
X	k_{OH} ($M^{-1}\ s^{-1}$)
F^-	0.021
SCN^-	0.16
Cl^-	0.25
Br^-	1.4
I^-	3.0
NO_3^-	5.7

story, with hydrolysis and isomerisation occurring readily (k_{OH} has a similar value to that for chloro complexes, Table 6). This is another example of the "halide-like" reactivity of $Co–SCN^{2+}$ compared to the "amine-like" inertness of $Co–NCS^{2+}$.

I will now outline our recent study of the $[Co(NH_3)_5SCN]^{2+}$ ion [35] since the results gained here also provide important details on the substitution process. An early study [5] showed that isomerisation (to give $CoNCS^{2+}$) accompanied hydrolysis (to give $CoOH^{2+}$), and that the two processes followed the same rate law

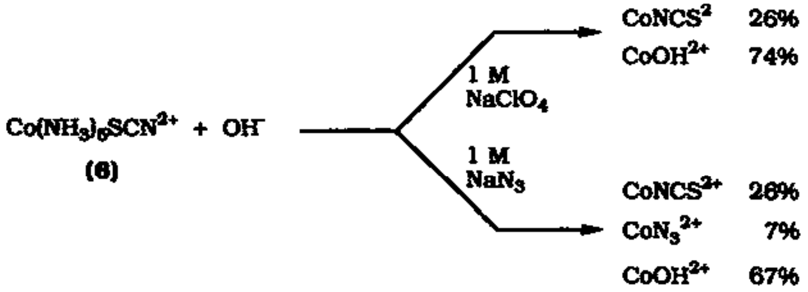


(23) p-isomer



(24) t-isomer

$k_{obs} = k_{OH}[OH^-]$ ($k_{OH} = 0.16$ M^{-1} s^{-1}). The product distributions were shown to be independent of $[OH^-]$ and $[CoSCN]^{2+}$, eqn. (11). Thus formation of $CoNCS^{2+}$ must be intramolecular.



(11)

The new study [35] used the *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]^{2+}$ ion to follow stereochemical change (^1H NMR), and very accurate RP-HPLC analyses to follow the product distributions. Experiments were carried out under various electrolyte conditions and at two temperatures. The following results were the most significant:

(i) The $CoNCS^{2+}$ product retains the *trans* stereochemistry under all conditions. This is to be contrasted with the substantial rearrangement to the *cis* geometry found with both $CoOH^{2+}$ (~55%) and the competition product CoN_3^{2+} (66–70%). This suggests that $CoNCS^{2+}$ is formed either without complete detachment of SCN^- from the metal (i.e. in a concerted process via a π-bonded transition state), or that the lifetime of the dissociated, $Co^{3+} \cdot SCN^-$ ion-pair, is too short to allow translational re-organisation of the two components. In this regard the reported [36] 0.5% rearrangement to give *cis*-$CoNCS^{2+}$ (together with 6.5% *trans*-$CoNCS^{2+}$) in the base hydrolysis of *trans*-$[Co(en)_2(NH_3)SCN]^{2+}$ should be checked since the result suggests an ion-pair of longer lifetime.

(ii) The amount of $CoNCS^{2+}$ formed (26–29%) is almost constant, being little affected by the presence of electrolytes (see Table 7). This is particularly obvious in N_3^- media where the formation of increasing amounts of CoN_3^{2+} (8.6% in 1.0 M, 14.7% in 2.0 M) does not appreciably alter the amount of $CoNCS^{2+}$ formed. The small changes which do occur in the presence of electrolytes are always decreases (these effects are real), and are about the same irrespective of whether a CoY^{2+}

TABLE 7

Products for the base hydrolysis (0.05 M NaOH) of $[Co(NH_3)_5SCN]^{2+}$ in various electrolytes and at two temperatures

Electrolyte	T (°C)	% $CoNCS^{2+}$	% $CoOH_2^{3+}$	% CoN_3^{2+}
None	25	28.7	71.3	
1.0 M $NaOSO_2CF_3$	25	27.5	72.5	
1.0 M NaN_3	25	27.5	63.9	8.6
2.0 M NaN_3	25	27.8	57.5	14.7
1.0 M $NaClO_4$	25	26.2	73.8	
None	0	36.3	63.7	
1.0 M NaN_3	0	32.2	58.9	8.8
1.0 M $NaClO_4$	0	31.8	68.2	

product is actually observed (e.g. CoN_3^{2+}) or not. The inference is that a CoY^{2+} product is formed for all Y^-, irrespective of whether it is observed, or whether it is subsequently rapidly hydrolysed to give $CoOH^{2+}$ (i.e. $CoOClO_3^{2+}$, $CoOSO_2CF_3^{2+}$).

(iii) Just as much CoN_3^{2+} is produced from $CoSCN^{2+}$ as from $CoCl^{2+}$ (8.6% in 1.0 M N_3 electrolyte), and this amount fits in nicely (Fig. 8) with the general trend

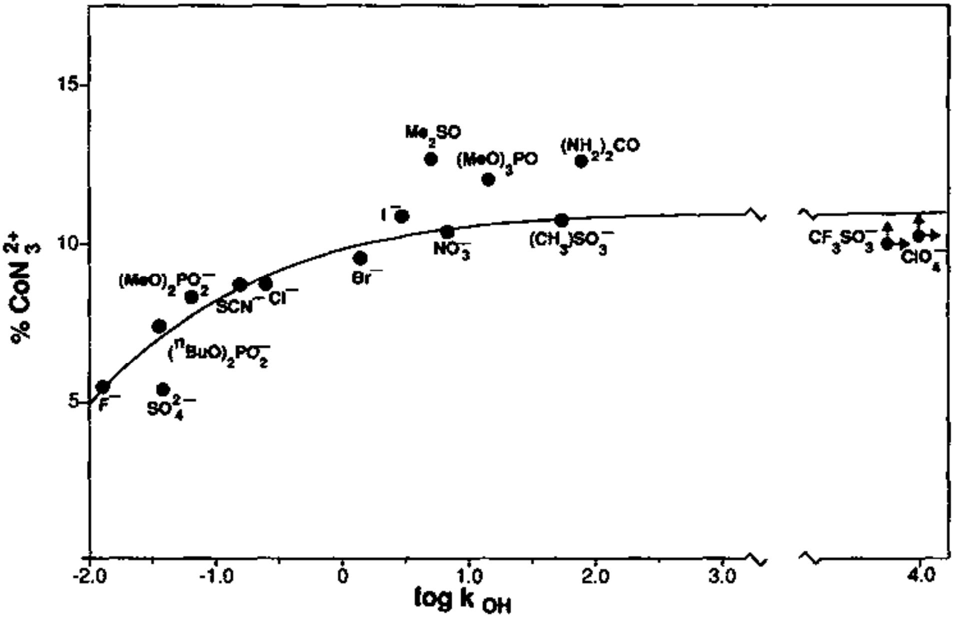
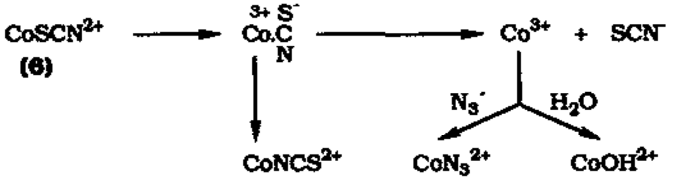


Fig. 8. $\%[Co(NH_3)_5N_3]^{2+}$ produced in the OH^--catalysed hydrolysis of several $[Co(NH_3)_5Y]^{+,2+,3+}$ complexes ($Y = F^-$, SO_4^{2+}, $(^nBuO)_2PO_2^-$, $(MeO)_2PO_2^-$, SCN^-, Cl^-, Br^-, I^-, Me_2SO, $(MeO)_3PO$, $(NH_2)_2CO$, NO_3^-, $CH_3SO_3^-$, $CF_3SO_3^-$, ClO_4^-) in 1.0 M NaN_3 at 25°C, plotted against log k_{OH} (k_{OH} represents the second-order rate constant for alkaline hydrolysis of these complexes.

found with other CoX^{2+} reactants which do not have alternative intramolecular pathways for reaction. This suggests that the $\text{CoSCN}^{2+} \rightarrow \text{CoNCS}^{2+}$ rearrangement occurs at the same time as N_3^- (and OH_2) entry and not at an earlier stage. Earlier entry, Scheme 13, would necessarily remove some 27% of the reactant from further consideration, and this would almost certainly result in a reduced N_3^- entry (6.3% calculated).



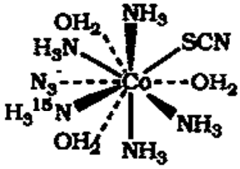
Scheme 13.

(iv) This constant amount of CoN_3^{2+} is also consistent with the observation that most of the N_3^- enters from a position remote (backside) to the leaving group (i.e. 66–70% *cis*-CoN_3^{2-}) and is therefore largely unaffected by events occurring on the "frontface" of the molecule. A similar amount of stereochemical change (*cis*-CoN_3^{2+}) is observed with other reactants, CoX^{2+} ($\text{X}=\text{NO}_3$, Cl, Br) where no intramolecular pathway is observed.

(v) NCS^- entry on the "frontface" competes with OH_2 entry on the frontface. The larger amount of *cis*-CoOH^{2+} produced from CoSCN^{2+} (56% in the absence of electrolyte) compared to the 46% from CoCl^{2+} is just that which would be expected if 29% of the frontside retentive pathway to give *trans*-CoOH^{2+} were blocked by re-entry of the rotating SCN^- ligand, $100 \times 46/(100-0.29 \times 54)=55\%$. In the presence of electrolytes rearrangement to give *cis*-CoOH^{2+} is marginally reduced (56% in the absence of electrolytes, 54% in their presence) and this is to be expected if Y^- (N_3, ClO_4, CF_3SO_3) competes with OH_2 more on the "backface "than on the "frontface".

(vi) Lower temperatures (0°C) favour CoNCS^{2+} formation at the expense of CoOH^{2+}, Table 7. This must arise through solvent entry having a higher activation energy, which is consistent with OH_2 having to be abstracted from the solvent shell of the ion-pair $[\text{Co}^{3+} \cdot \text{SCN}^-]_{\text{aq}}$. This could be interpreted as immediately released SCN^- being in a vibrationally excited state not yet having formed stable H-bonds to the surrounding solvent (at least they will be in a state of flux), whereas the entering OH_2 molecule will be coming from the equilibrium solvent environment and will have strong H-bonds to dissociate before its lone pair can become available. The energy required to do this would be expected to be greater than for the former isomerisation. The unchanged amount of N_3^- entry to form CoN_3^{2+} at the lower temperature could well result from a balancing of a larger ion-pair constant (K_{ip}) at the lower temperature and a reduced entry from $\text{N}_3^- \cdot \text{Co}^{3+} \cdot \text{SCN}^-$ for the reasons stated above. At the lower temperature the presence of electrolytes in general have a more pronounced effect on $CoNCS^{2+}$ production (36% $CoNCS^{2+}$ in the absence of electrolytes, 32% in their presence) so that the relative entering abilities of NCS^-, OH_2, and electrolyte anion Y^- are now rather more sensitive to the electrolyte component. This effect could be further explored.

The above results imply a direct coupling of OH_2 entry with N_3^- and NCS^- entry in the product forming step, but with N_3^- entry being largely uncoupled to NCS^- entry. All three processes however appear to be competitive in the sense that they occur at the same time; that is, immediately following Co–SCN bond rupture. Also little activation seems to be required for ligand entry, the major requirement being the presence of the entering group adjacent to the complex, with (possibly) electron lone pairs pointing towards the metal. Large amounts of stereochemical change are observed in the $CoOH^{2+}$ and CoY^{2+} products (but not with $CoSCN^{2+}$) requiring solvent and Y^- entry to occur from positions additional to those adjacent to the leaving group. A number of pre-associated reactants are likely to be involved, each containing entering groups in stereochemical locations closely related to positions adopted in the final product. An important member of this set is (**25**) with N_3^- distant (backside) to thiocyanate.

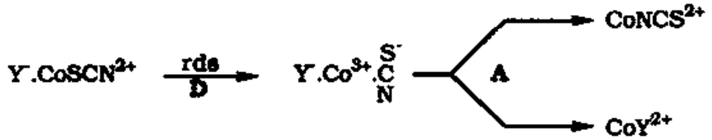


(**25**)

3. SUMMARY, AND REACTION MECHANISM

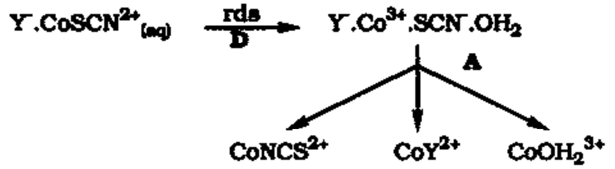
It seems clear that the substitution processes described in this article depend critically on the presence of an entering group adjacent to the cobalt(III) centre at the instant of bond rupture. This comes about through the interplay of solvent (OH_2) and anion (Y^-) entry with the intramolecular rearrangement process CoSCN→CoNCS. We will assume in the following mechanistic summary that dissociation of the initial ligand (SCN^-) occurs first (D), followed by parallel associative entry (A) of the various entering groups.

Solid State Reaction



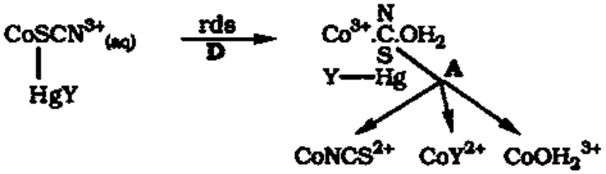
(12)

Aqueous Solution Reactions (spontaneous, OH⁻-catalysed)



(13)

Induced Reactions



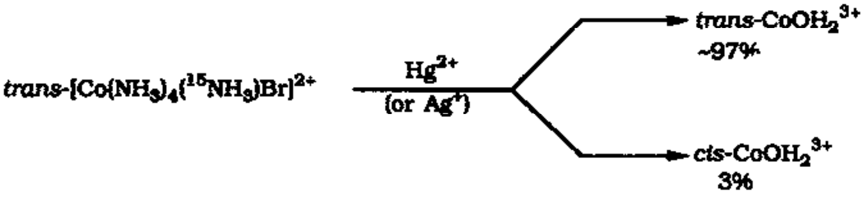
(14)

If Y^-, or H_2O, is not present (as an intimate ion pair, or pre-associated species), at the instant of Co–SCN bond rupture then it does not enter. Even solvent-separated ion pairs such as $Y^- \cdot H_2O \cdot CoSCN^{2+}$ probably result in OH_2 rather than Y^- entry. The lifetime of the transient $Y^- \cdot Co^{3+} \cdot SCN^- \cdot OH_2$ species is so short that equilibration between alternative ion-pairs is not possible, although rotation of SCN within the ion-pair does occur. In the solid state it appears that only correctly oriented lone pairs result in coordination so that location at a particular stereochemical site in the solution ion-pair may not be sufficient to cause entry.

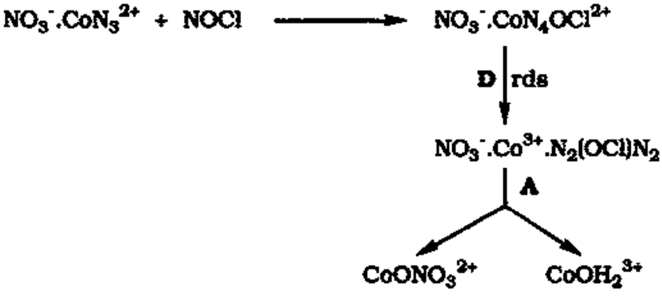
The various Y^- show little discrimination when thought of as nucleophiles. Even very poor donors such as ClO_4^- and $CF_3SO_3^-$ coordinate if they are correctly located (see Hg^{2+} catalysed reaction; see Section 2.3). However, some activation seems necessary to abstract the entering group from the solvent, with those groups more weakly H-bonded being preferred ($NO_3^- > ClO_4^- \geqslant CF_3SO_3^-$). In this regard entry of OH_2 is often appreciable, not because it is less tightly held by H-bonding but because the solvent occupies all available sites about the complex not otherwise occupied by Y^- or the N end of the rotating SCN^- ligand (or leaving group); i.e. a concentration effect. Also entry of released NCS^- has a lower activation enthalpy, possibly because it is already vibrationally excited by dissociation. Entry can therefore be viewed as a statistical temperature independent (entropy) effect. In the spontaneous reaction of $CoSCN^{2+}$ (Section 2.2), where large amounts of $CoNCS^{2+}$ are formed, almost as much $N^{14}CS^-$ enters from the ion pair (to give $CoN^{14}CS^{2+}$ and $CoS^{14}CN^{2+}$), as when a $CoOClO_3^{2+}$ substrate is used where no (obvious) intramolecular re-entry occurs. However, because the life-time of $Y^- \cdot Co^{3+} \cdot SCN^- \cdot OH_2$ is probably at least a few vibrational periods ($> 10^{-13}$ s) it can probably be classed as an intermediate rather than as a transition state, with separate elemental steps for its formation and decay.

The stereochemical location of the entering groups is important. In acidic solution stereochemical retention is preferred, although recent experiments [37] have shown some stereochemical change in the $CoOH_2^{3+}$ product of the Hg^{2+} and Ag^+ reactions, eqn. (15).

Likewise, water exchange in *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2]^{3+}$ under acidic conditions shows some stereochemical change (~1.4%) [37]. Anion entry in acidic solution seems to give full retention, and this exclusive entry from the "front face" may well result from the disruption of H-bonds arising from stretching the Co–X bond. This would make abstraction of Y^- and OH_2 from the immediate environment easier. With the Hg^{2+} and Ag^+ catalysed reactions entry from HgY^+ and AgY is likely, resulting in retention. But some care must be taken in accepting this picture. In the NO^+ catalysed reaction of $[Co(NH_3)_5N_3]^{2+}$ in mixed Cl^-/NO_3^- media NOCl has been shown to be the effective catalyst, but substantial quantities of $CoONO_2^{2+}$ are still formed [38]. A pre-associated ion pair incorporating NO_3^- has been suggested, eqn. (16).



(15)



(16)

Large amounts of stereochemical change occur in the solid state reaction (Section 2.1), and in base hydrolysis (Section 2.4). With base hydrolysis prior removal of an amine proton from a stereochemical location backside to the leaving group is thought to occur [39]. This would produce a distorted solvent structure at this location, therefore accounting for the substantial entry of Y^- and OH_2 at this site (with inversion). The solid state entry of $S^{14}CN^-$ and $N^{14}CS^-$ exclusively from the "backface" shows that this possibility is feasible.

Finally a brief comment on reaction mechanism, and suggestions for naming the reactions described in this article. In my opinion the recent discussions on inorganic substitution processes at a metal centre [40–44], based as they are on the Langford and Gray mechanistic classification [45], suffer from the same disadvantages as the Ingold description of organic reactions. They use a naming system based on operational definitions rather than a system which distinguishes between the various possibilities. A reaction mechanism is a sequence of microscopic elementary processes ("mechanism" is synonymous with reaction "pathway") and a particular reaction may adopt more than one mechanism if several pathways of similar free energy exist. However a mechanism does not change with the accumulation of experimental fact, nor with the method used to gather these facts. It is there for the experimentalist to discover; to distinguish between the alternatives. But first of all, all the possible sequences must be clearly spelt out, and a naming system employed which distinguishes between them. This has not yet been done for inorganic coordination chemistry.

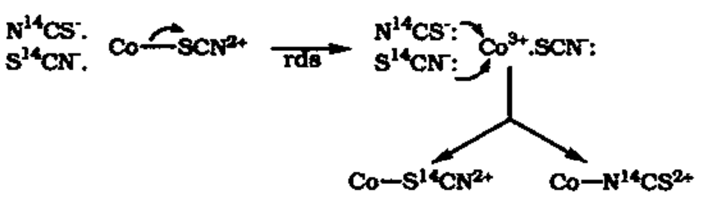
Some 14 years ago, because of these very same difficulties, the Organic Chemistry Division of IUPAC set up a Commission to look into the naming of organic reaction mechanism. They recognised that a succession of two fundamental (primitive) changes makes up all chemical reactions – bond breaking and bond making. Attempts to adapt the Ingold system to the timing of these changes for all types of organic reaction was found impractical, and so they came up with a new system [46,47]. I will adopt this system. It gives a clear description of the sequence of elementary steps, and, in my view, once mastered is easy to use.

Names are given to the various mechanisms given by eqns. (12)–(14). I have made one further addition, and one modification to the IUPAC system. The addition is to add a parenthesised subscript (i) to the primitive associative process leading to stereochemical inversion at the (octahedral) metal centre; $A_{(i)}$. The corresponding stereochemically retentive path is left without a subscript; A. The modification is to use a specific subscript S for addition or dissociation of a solvent nucleophile or

Mechanism **Name**

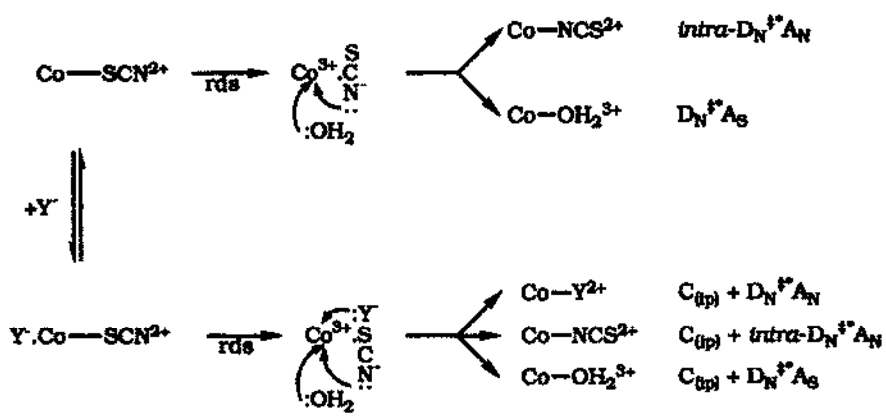
1. Solid State Reaction

intra-$D_N^{‡*}A_N$
(or *intra*-D_NA_N)

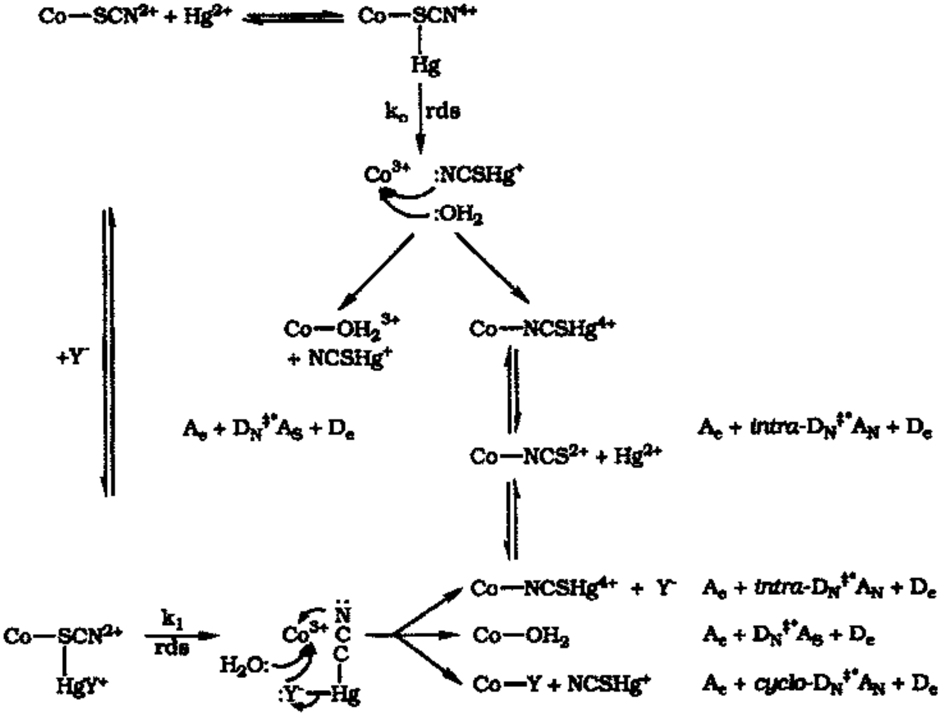


$D_N^{‡*}A_{N(i)}$
(or $D_NA_{N(i)}$)

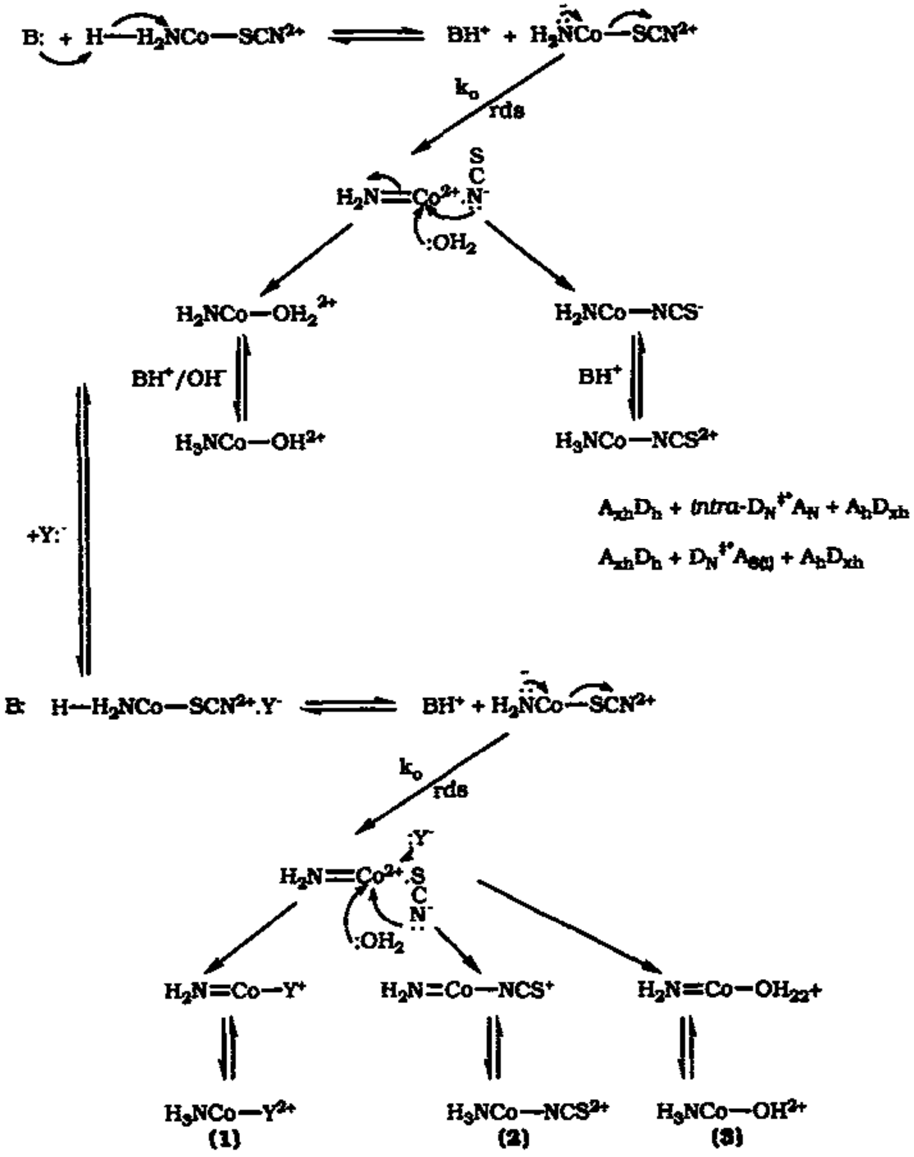
2. Spontaneous Reaction in Aqueous Solution



3. Hg^{2+} (and Ag$^+$) Catalysed Reactions



4. Base Hydrolysis



$$A_{xh}D_h + intra\text{-}D_N{}^{\ddagger *}A_N + A_hD_{xh}$$

$$A_{xh}D_h + D_N{}^{\ddagger *}A_{e(I)} + A_hD_{xh}$$

(1) **(2)** **(3)**

$$+ D_N{}^{\ddagger *}A_{N(I)} + A_hD_{xh} \qquad (1)$$

$$C_{(tp)} + A_{xh}D_h + intra\text{-}D_N{}^{\ddagger *}A_N + A_hD_{xh} \qquad (2)$$

$$+ D_N{}^{\ddagger *}A_{e(I)} + A_hD_{xh} \qquad (3)$$

nucleofuge, A_S or D_S, so that this species is distinguished from the others (which retain the A_N, D_N classification). In metal ion chemistry the solvent is often directly involved (this is a difficulty kinetically), and a specific label for it is then very useful. In nearly all cases dissociation of the nucleofuge is rate limiting ($D^{\ddagger}$), and it will be assumed that the electrofugic metal ion bonds to the nucleophile in a subsequent process, but before the nucleofuge has had time to diffuse away ($D_N{}^{\ddagger *}A_N$). In some situations (e.g. the solid state) bond making and bond breaking may be synchronous, i.e. concerted, ($D_NA_N{}^{\ddagger}$). The two mechanisms are distinguished by a transient intermediate of reduced valency. It is our belief that such an intermediate is formed in solution, but that it does not last much longer than one or two bond vibrations. Of course electronic relocation in the electrofuge (Co^{3+}) is instantaneous on this time scale (Born–Oppenheimer) so that orbital availability and inversion at the metal centre is quite possible. Experimental proof of such short-lived intermediates is however still lacking, although there has been recently some attempts at a theoretical justification [44,47].

In mechanisms **1** and **2** above the $C_{(ip)}$ term is added to signify that the products are formed from a preformed ion-paired electrophile.

In mechanism **3** the stereochemical evidence for the pathway leading to $CoOH_2^{3+}$ is that there is a small amount of inversion. This part would then become $A_e + D_N{}^{\ddagger *}A_{S(i)} + D_e$.

In mechanism **4** the term $C_{(ip)}$ is again used to indicate that subsequent processes occur within the ion pair (with Y^-), and the (i) subscript is used because a large proportion of the product involves stereochemical inversion.

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