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SOLVOLYSES OF THIOCYANATES BY TRIFLUOROETHANOIC ACID

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Abstract—The solvolyses by trifluoroethanoic ("trifluoroacetic" TFA) acid of several known and new thiocyanates have been studied using proton magnetic resonance. For the organic linkage isomers of RNCS (R = alkyl groups) isothiocyanates react (via N-alkyl monothiocarbamato trifluoroethanoates) to form alkylamines RNH_2, whereas the thiocyanates RSCN yield thiols, RSH and ammonia. The coordinated thiocyanates include isomers (some new) of dithiocyanatobisdiaminoethanerhodium(III) salts, characterized spectroscopically and through their reactions (additions of mercury(II) ions, reductions of iodate(V), isomerizations). Both linkage isomeric forms of coordinated thiocyanate with TFA formed ammonia (showing a sharp triplet at $\delta = 6.6$ ppm).

The thiocyanate group can bond to metal ions to form mononuclear complexes either through its nitrogen atom or through its sulphur atom. We synthesized[1] a series of complexes; *cis*- and *trans*-$[Rh(en)_2(\mathit{N}C\mathit{S})_2]X$ (we have italicized the atom actually attached to the metal ion), where X is an anion which may be SCN^-.

Many methods comment upon the linkage isomers of thiocyanates. The application of NMR spectroscopy as a tool to elucidate the bonding mode of the thiocyanate ligand has gained widespread popularity. These experiments have utilized direct measurement for ^{13}C,[2] ^{14}N[3] and ^{15}N[4] of the ligand and the indirect measurement for ^1H,[5,6] ^1H with lanthanide induced shift,[7] $^1H\{^{195}Pt\}$ INDOR,[8] ^{31}P[9–13] and ^{195}Pt.[4] Following our success[14] (using a medium which slowed exchange) in analysing $^{14}N:^{15}N$ ratios in ^{15}N-labelled ammine complexes $[Co(NH_3)_5X]Y_2$ by proton magnetic resonance, we sought a similar simple distinction (using proton resonance) between M—*N*CS and M—*S*CN moieties, where M represents a metal ion in a kinetically inert oxidation state.

We anticipated that the products of reaction (1)

$$R\text{—}NCS + HOOC\cdot CF_3 \rightleftharpoons R\text{—}NCSH^+ + \bar{O}OC\cdot CF_3 \quad (1)$$

should show no coupling to the ^{14}N of the proton of the coordinated isothiocyanic acid, whereas, in the products of reaction (2), such coupling

$$R\text{—}SCN + HOOC\cdot CF_3 \rightleftharpoons RSCNH^+ + \bar{O}OC\cdot CF_3 \quad (2)$$

in coordinated thiocyanic acid (kinetics permitting) should give a triplet ^1H signal. Solid complexes containing coordinated nitrous acid have been isolated,[15] such as $[Co(en)_2(ONOH)X]^{n+}$, and similarly, there is excellent evidence[16,17] for the persistence in solution during lengthy periods of coordinated thiocyanic acid, in protonated adducts of $[M(NH_3)_5(SCN)]^{2+}$ (M = Co, Rh), or $[Co(en)_2(SCN)_2]^+$. (The solid acid adducts of $[M(NCS)_6]^{3-}$ salts, e.g. $(NH_4)_3[(Mo(NCS)_6]CH_3CO_2H$[18] and $[Cr(NCS)_6]^{3-}$[19] are of a different type.)

We report here our findings on the compounds with R = alkyl and various kinetically inert inorganic moieties, like $[M(NH_3)_5]^{3+}$ (M = Co, Rh).

RESULTS AND DISCUSSION

Thiocyanate ions in TFA

Sodium and potassium thiocyanates dissolve readily in neat trifluoroacetic acid (TFA hereafter).

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The solution turns yellow and occasionally bubbles as the salt starts to dissolve. The ^{1}H NMR of the resulting solution shows a sharp triplet centred at $\delta = 6.67$ ppm [Fig. 1(a)]. The ^{1}H NMR spectrum of ammonium thiocyanate after dissolution in TFA also shows only this triplet, the signal[14] of the proton in quaternary ammonium ions. The identical ^{1}H NMR spectrum of NH_4Cl in TFA proves this finding [Fig. 1(b)]. Ogg and Ray reported[20] that anhydrous liquid ammonia furnished a triplet signal with $J_{^{14}NH} = 46$ Hz compared to $J_{^{14}NH} = 53$ Hz for NH_4^+ ions in TFA found in the present work.

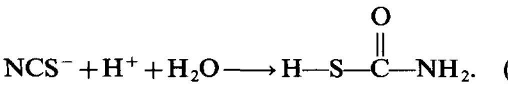
The ^{1}H NMR spectrum of a proton attached to a nitrogen atom is always very broad and sometimes unobservable, for two reasons, intermolecular proton exchanges and quadrupolar relaxation. As in anhydrous ammonia,[20] the quadrupolar mechanism is dominant[21] in the acidic solution of NH_4^+ ions. The linewidth of NH_4^+ in TFA decreases with increasing temperature and *vice versa* [Fig. 1(c)], as expected for any quadrupolar mechanism. The behaviour is opposite to that expected for chemical exchange.[22]

The study of such reactions between thiocyanate ions and mineral acid was a matter of interest some years ago. The initial step is protonation, which, theoretically, can occur at the sulphur atom to produce thiocyanic acid H—*S*—C≡N, or at the nitrogen atom to produce isothiocyanic acid H—*N*═C═S, which predominates over its isomer in the vapour state,[23] or in solution.[24,25,*] ^{1}H NMR spectra of isothiocyanic acid in CCl_4 have been reported[26] (δ 4.95 ppm): cf. isocyanic acid H*N*CO (3.35, $J_{^{14}NH} = 64$ Hz) and hydrazoic acid HN_3 (4.10). Isothiocyanic acid H*N*CS is unstable[27] in *mineral* acid. The overall hydrolysis may be presented as in eq. (3); ammonium ions are a final product.

$$H^+ + HNCS + 2H_2O \longrightarrow H_2S + CO_2 + NH_4^+. \quad (3)$$

Thiocyanate salts in conc. H_2SO_4 (98%) (in the present work) show a sharp triplet centred at δ 5.45 ppm in comparison to the proton signals of NH_4^+ in TFA at δ 6.67 ppm.

A number of intermediates are involved in the hydrolysis. One is carbonyl sulphide OCS, which is reasonably stable in acid but slowly hydrolyses[27] to CO_2 and H_2S. Another (postulated by Klason[28]) is thiocarbamic acid $HSCONH_2$ [eq. (4)]:



$$NCS^- + H^+ + H_2O \longrightarrow H{-}S{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2. \quad (4)$$

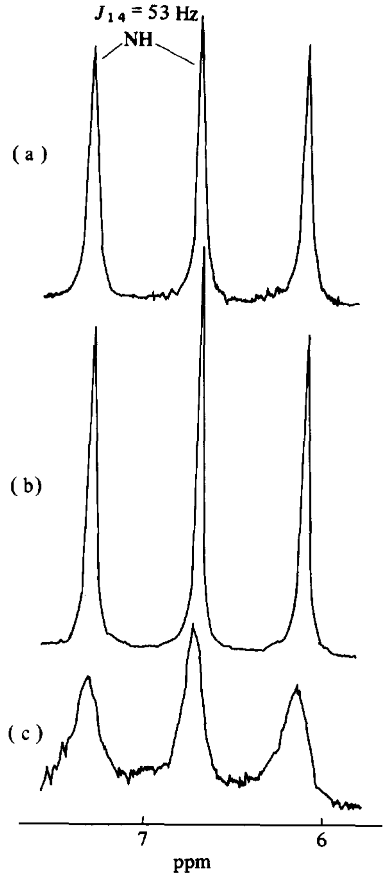
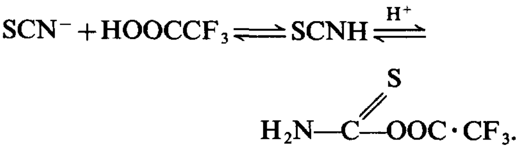


Fig. 1. Proton resonance spectra in TFA of (a) KSCN at 35°C; (b) NH_4Cl at 35°C; (c) KSCN at −5°C.

The free acid is unknown, but the ammonium salt decomposes[29] in acidic solution to produce CO_2 and H_2S via OCS. Stedman and his students have made detailed kinetic and spectroscopic studies[30,31] of the reaction of thiocyanate ions in various concentrations of H_2SO_4.

Drawing the analogy to such hydrolysis of thiocyanate ions in mineral acid solution, its solvolysis in TFA [pK_a (25°C) 0.25] is initiated by protonation to form isothiocyanic acid. The intermediate is probably monothiocarbamatotrifluoroacetate formed as in eq. (5)



$$SCN^- + HOOCCF_3 \rightleftharpoons SCNH \overset{H^+}{\rightleftharpoons} H_2N{-}\overset{\overset{\displaystyle S}{/\!/}}{C}{-}OOC\cdot CF_3. \quad (5)$$

However, reaction of SCN^- in TFA followed by ^{1}H NMR spectroscopy, failed to detect the proton signal of this thiocarbamato compound; only the triplet signal of NH_4^+ was obtained. This rapid solvolysis of thiocyanic acid has been briefly mentioned.[26] The isothiocyanic acid formed, polymerized and eventually produced the yellow iso-

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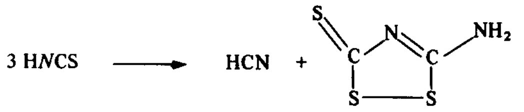
[*] The salt $[Ph_4As]H(NCS)_2$ was isolated by M. F. A. Dove from solutions of sulphur dioxide (see M. F. A. Dove, *Chem. Comm.* 1965, 23).

perthiocyanic acid, as in eq. (6).



(6)

Organic isothiocyanates in TFA

The isothiocyanates R*N*CS (R = CH_3, C_2H_5, $C_6H_5CH_2$) were studied by ^{1}H NMR using TFA as the solvent. In a typical example, methyl isothiocyanate, H_3CNCS, the simplest, was dissolved in TFA. The solution immediately turned yellow. The course of the reaction was followed against time by means of ^{1}H NMR spectroscopy. Some of the spectra and δ values are given in Figs 2(a)–(g) and Table 1.

At the beginning, a doublet centred at δ 3.09 ppm emerged slowly, in addition to the singlet at δ 3.24 ppm from the parent methyl isothiocyanate. We interpret this doublet ($J_{HH} \sim 5$ Hz) as the signal of the methyl group split by a proton attached to the nitrogen atom of the N-methylmonothiocarbamatotrifluoroacetate, $CH_3NH—CS—OOCCF_3$, the suggested intermediate. This decomposes to

Table 1. ^{1}H NMR results for the reaction of CH_3NCS with TFA at 35°C (and see Fig. 2)

Time (min)	Multiplicity	δ (ppm),	J (Hz)
0[a]	Singlet	3.24	—
2	Singlet	3.24	—
	Doublet	3.09	$J_{HH} \sim 5$
47	Singlet	3.24	
	Doublet	3.09	$J_{HH} \sim 5$
	Quartet	2.60[b]	$J_{HH} \sim 5$
292	Broad triplet	6.75	$J_{^{14}NH} \sim 53$
	Broad triplet	6.75	$J_{^{14}NH} \sim 53$
	Quartet	2.93[b]	$J_{HH} \sim 5$

[a] Measured in CCl_4.

[b] Measured at the centre of the quartet.

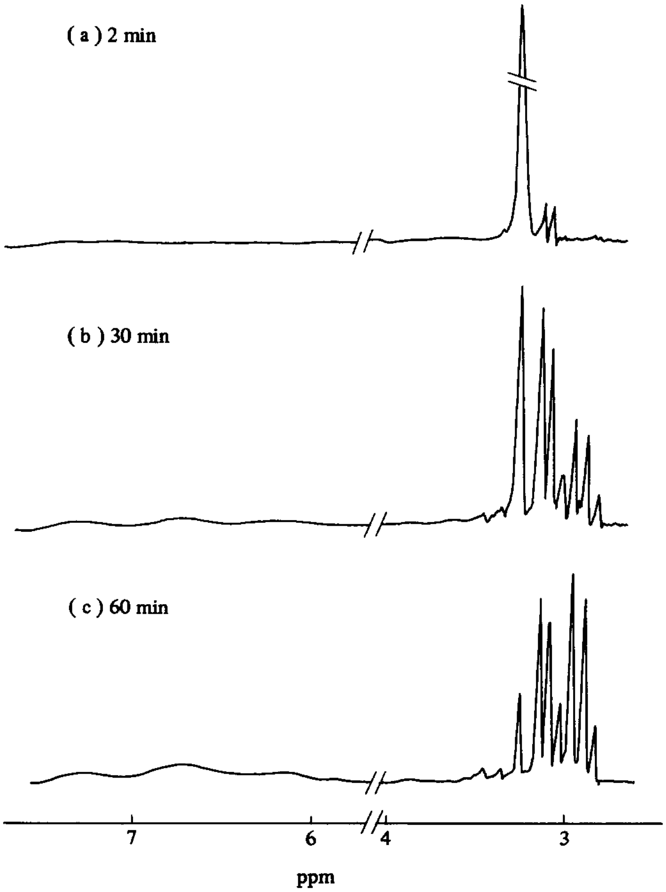


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Fig. 2. Proton magnetic resonance of methyl isothiocyanate $H_3C \cdot NCS$ dissolved in TFA after increasing times (min) of reaction: (a) 2; (b) 30; (c) 60; (d) 90; (e) 150; (f) 210; (g) 1440 (1 day)—"infinity"; (h) for comparison, $H_3C \cdot NH_2$ (in ethanol) dissolved in TFA, was used.

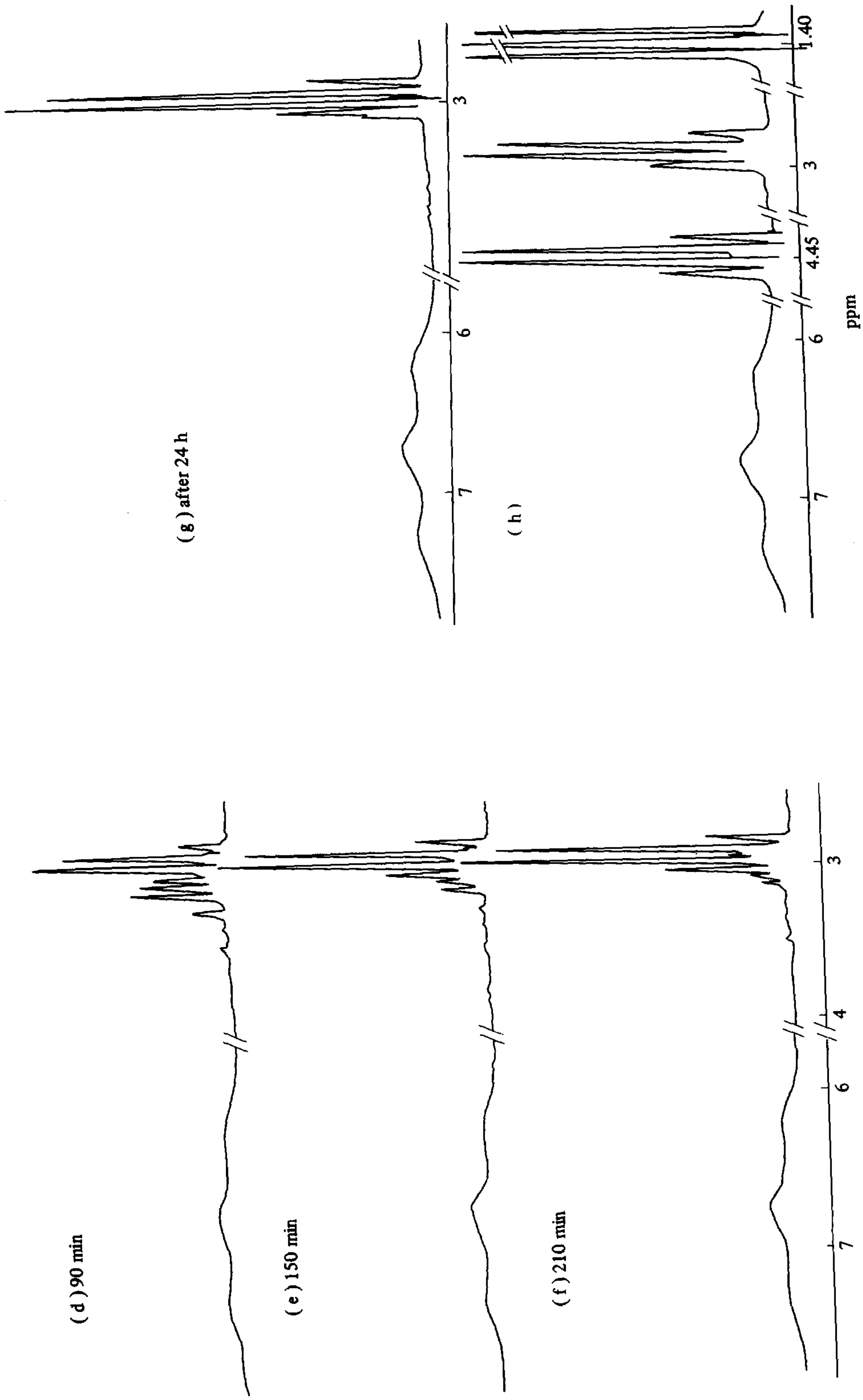

Fig. 2 (*continued*).

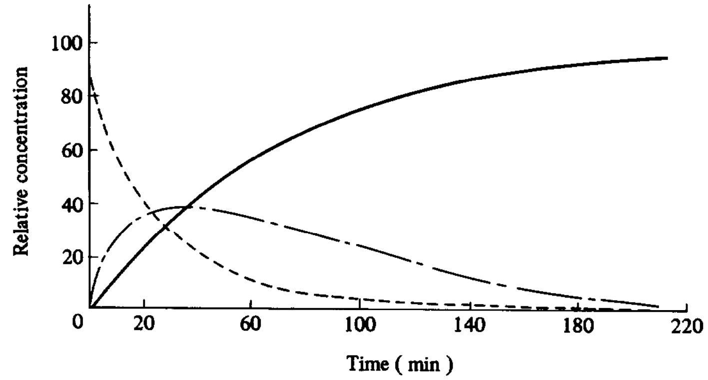

Fig. 3. Relative concentrations of various species in the reaction of $H_3C \cdot NCS$ with TFA: (———) $(H_3C \cdot NH_3)^+(F_3C \cdot COO)^-$; (— · — · —) $H_3CNHC(S)OCOCF_3$; (– – – –) $H_3C \cdot NCS$.

products. One has a quartet (1 : 3 : 3 : 1) centred at δ 2.90 ppm and a broad triplet centred at δ 6.75 ppm. This set is the ^1H NMR spectrum of the methylammonium ion, confirmed by comparison with the signal of the authentic methylamine (in alcohol) dissolved in TFA [see Figs 2(g,h)]. Under our experimental conditions (the concentration of H_3CNCS in TFA is 0.739 M at 35°C), the reaction goes to completion. The relative concentrations (reminiscent of a consecutive reaction) of various species during the course of the reaction were calculated from the proton integration and are plotted in Fig. 3.

The reaction of ethyl isothiocyanate CH_3CH_2NCS was also followed by ^1H NMR spectroscopy: examples of the spectra are shown in Figs 4(a)–(e). The intermediate (with a slightly more complicated splitting pattern) is believed to be

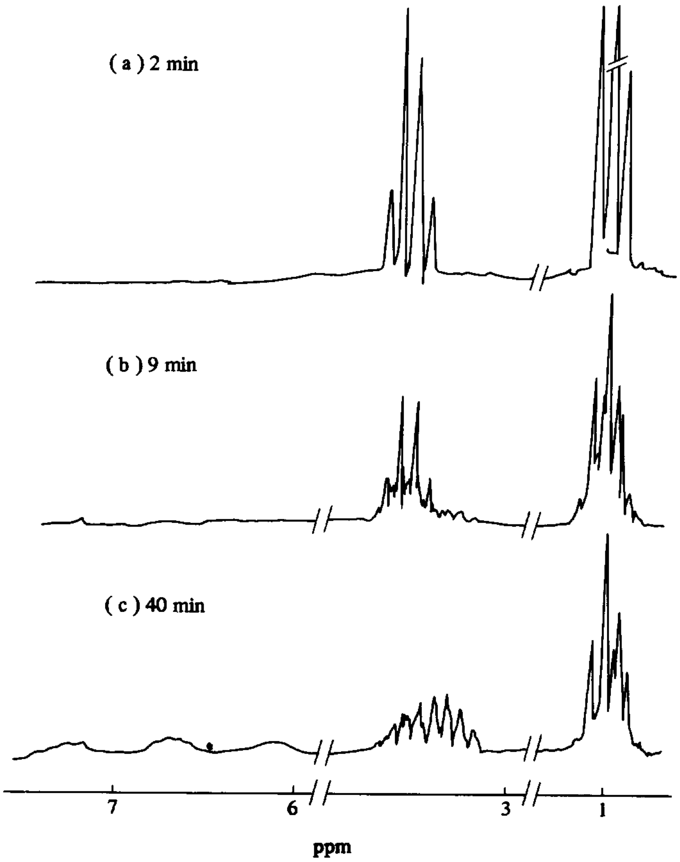

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Fig. 4. Proton resonance spectra of ethyl isothiocyanate, C_2H_5NCS, in TFA, after varying times of reaction (min): (a) 2; (b) 9; (c) 40; (d) 80; (e) 1440 (1 day)—"infinity"; (f) for comparison, aqueous ethylamine in TFA was used.

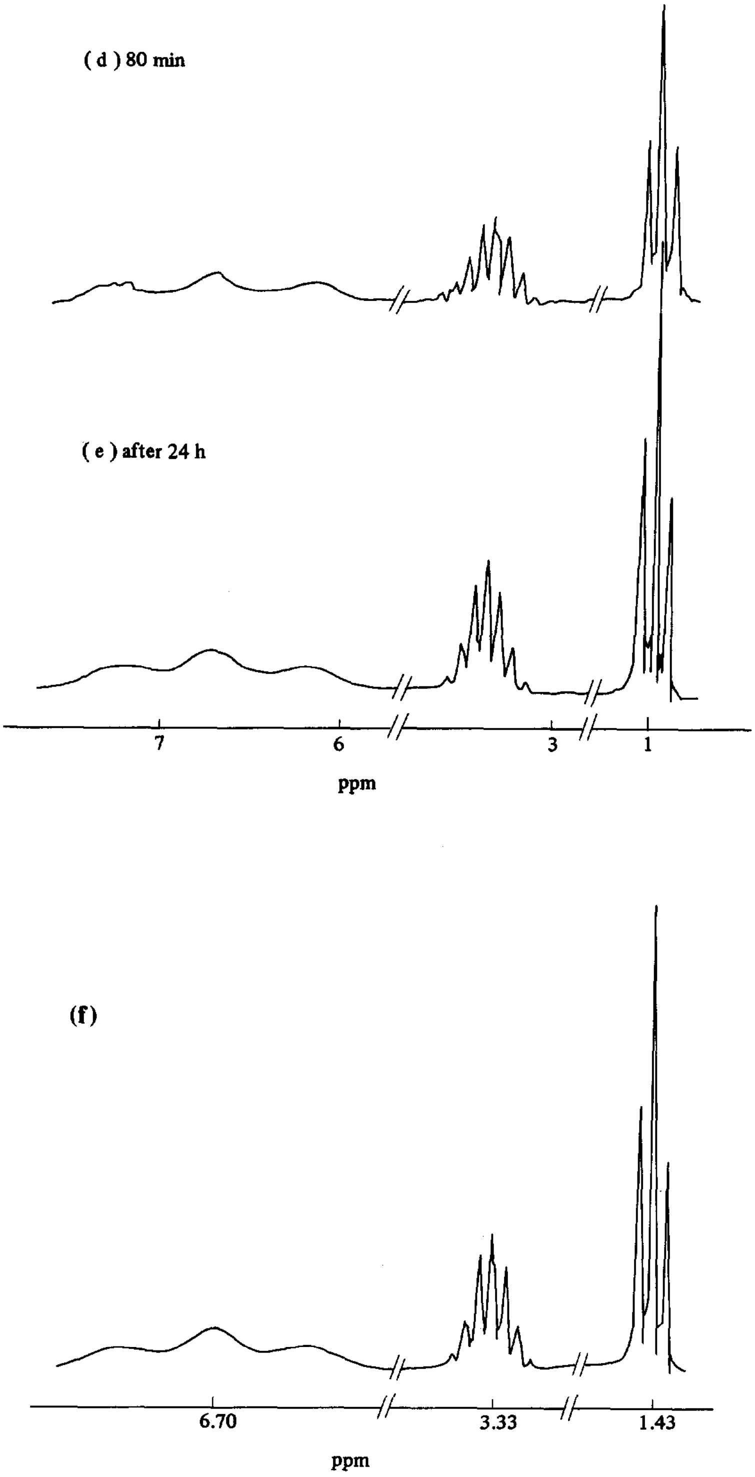
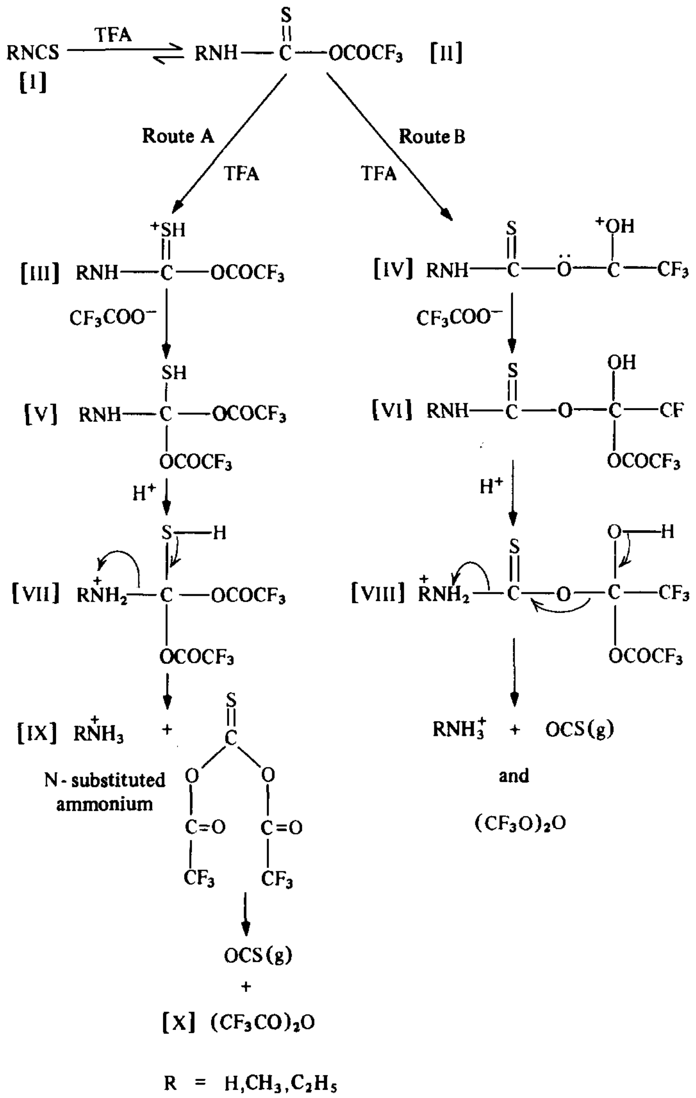


Fig. 4 (*continued*).

N-ethylmonothiocarbamatotrifluoroacetate. The intermediates then decomposed to the ethylammonium ion as one of the products [see Fig. 4(e)], again confirmed by comparing with authentic ethylamine in TFA [Fig. 4(f)].

Mechanism of the reactions between organic isothiocyanate and TFA. The rate and mechanism of hydrolysis of isothiocyanic acid by mineral acids has received adequate attention.[30,31] In contrast, the kinetics and mechanism of the hydrolysis of the

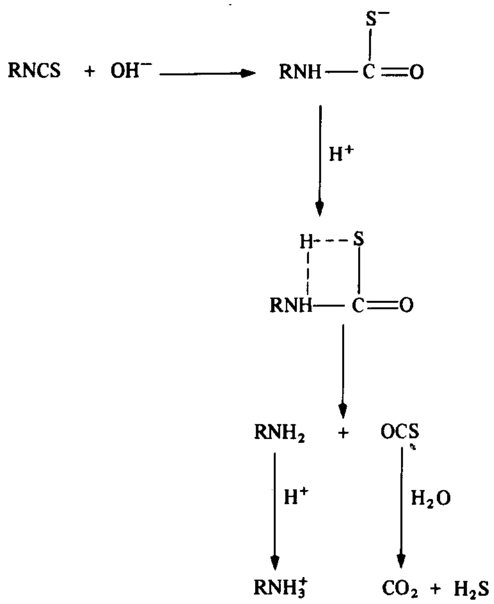


Scheme 1. Mechanisms for solvolysis of thiocyanates.

organic isothiocyanate derivatives has been little studied. However, simple organic isothiocyanates should[32] resemble isothiocyanic acid with respect to ready hydrolysis, giving an amine and carbonyl sulphide, which is in turn hydrolysed to CO_2 and H_2S. Mechanisms for solvolysis of organic isothiocyanates with TFA are shown in Scheme 1. From ^1H NMR spectra, the N-substituted monothiocarbamatotrifluoroacetate (**II**) is the common intermediate. This finding also indirectly confirms the proposed mechanism of solvolysis of isothiocyanic acid by TFA.

Subsequent decomposition (Scheme 1) of the intermediate is initiated either by further addition of TFA to C=S (route A) or to C=O (route B). The choice depends on (a) relative basicities, and (b) relative electrophilicities of the protonated form of intermediates (**III**) and (**IV**). Decomposition via either route A or B, will produce N-substituted ammonium ions (**IX**), carbonyl sulphide (OCS) and trifluoroacetic anhydride (**X**). The broad triplet signal of N-substituted ammonium ions is due to its lower symmetry compared to tetrahedral NH_4^+. The decomposition of simpler N-substituted monothiocarbamate formed from the reaction of RNCS with OH^- had been proposed[33] as in Scheme 2. So, it is possible that V of route A decomposes without further protonation on the nitrogen atom, as shown in Scheme 3.

Reaction of organic thiocyanate (RSCN) *with* TFA. Solutions of organic thiocyanates (RSCN) ($R = CH_3, C_2H_5, \phi CH_2$) do not exhibit a ^1H NMR signal other than that from the parent. Never-



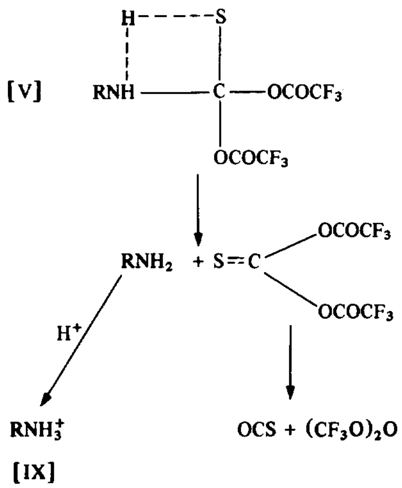
Scheme 2. Possible intermediates of base hydrolysis.

theless, the protonation shown in eq. (2) probably occurs, but the NMR signal of the proton attached to the quadrupolar nitrogen atom is too broad to be observed.

Organic thiocyanates are hydrolysed by *mineral* acid, to give a thiol RSH, CO_2 and NH_3 as shown in reactions (7)–(10). The initial step (7) is the protonation of the thiocyanate group.

$$R{-}S{-}C{\equiv}N \overset{H^+}{\rightleftharpoons} R{-}S{-}C{\equiv}\overset{+}{N}H \qquad (7)$$

$$R{-}S{-}C{\equiv}\overset{+}{N}H + 2H_2O \longrightarrow RS{-}C(OH)NH + H_3O^+ \qquad (8)$$



Scheme 3. Possible alternative decomposition of intermediate (V) of Scheme 1.

$$RSC(OH){=}NH \longrightarrow RSC(O)NH_2 \longrightarrow RSH + CO_2 + NH_3 \qquad (9)$$

$$NH_3 + H^+ \longrightarrow NH_4^+. \qquad (10)$$

A typical example of the reaction of ethyl thiocyanate with conc. H_2SO_4 is shown in Fig. 5. The sharp triplet is obviously due to the ammonium ion. The broad singlet at δ 7.9 ppm is most probably due to the proton attached to the nitrogen atom of the $RSC(O)NH_2$ molecule. The signals centred at δ 1.0 and 2.8 ppm are due to the ethyl group of the thiol compound.

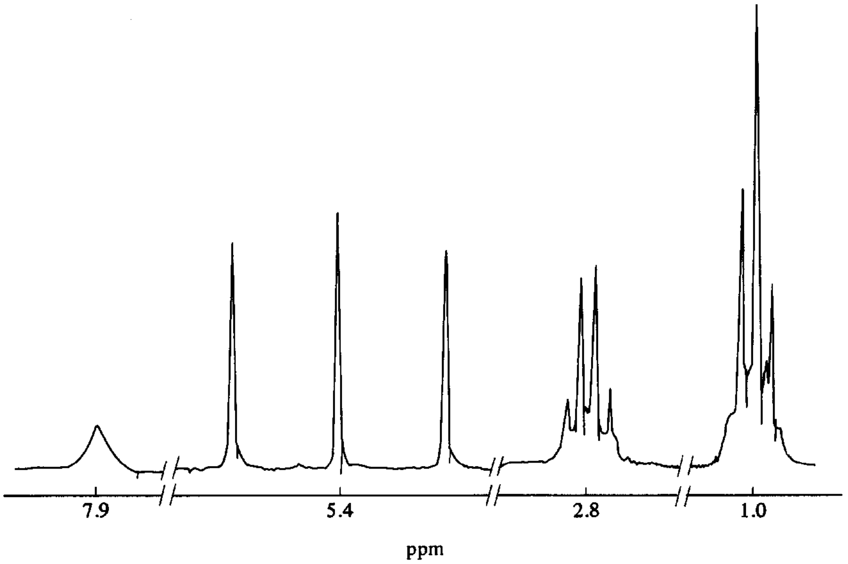


Fig. 5. Proton magnetic resonance spectrum of ethyl thiocyanate in 98% H_2SO_4.

Metal–thiocyanate complexes in TFA

To distinguish between reactivities of coordinated isothiocyanic acid and thiocyanic acid, a range of metal complexes containing linkage isomeric thiocyanates was needed. We used some well-known examples {such as[34] [Pd(bipy)(*N*CS)$_2$] and [Pd(bipy)(*S*CN)$_2$]} and have also made[1] a number of isomers of [Rh(en)$_2$(*S*C*N*)$_2$]$^+$. We comment briefly on these compounds. Analytical results are given in Table 2 and some spectroscopic properties in Table 3 (supporting assignment of linkage isomers[39,40]) and Table 4 (confirming assignment of geometric isomerism, from the—chiefly hydrogenic—modes of the chelating ligands, at frequencies greater than 1000 cm^{-1}). A feature, which we re-

Table 2. Conductometric and analytical results for isomeric thiocyanato complexes of rhodium(III), [Rh(en)$_2$(*N*C*S*)$_2$]X

Compound	Λ_{H_2O}[a]	C Calc.	C Found	H Calc.	H Found	N Calc.	N Found	Ionic NCS$^-$ Calc.	Ionic NCS$^-$ Found[b]
cis-[Rh(en)$_2$(*N*CS)$_2$]Cl · H$_2$O	129	18.3	18.4	4.6	4.3	21.4	21.9	—	—
cis-[Rh(en)$_2$(*N*CS)$_2$](NCS) · H$_2$O		20.2	20.6	4.3	4.2	23.6	23.2	14.0	13.9
cis-[Rh(en)$_2$(*N*CS)(*S*CN)](NCS) · H$_2$O	126	20.2	19.4	4.3	4.5	23.6	23.2	14.0	13.4
trans-[Rh(en)$_2$(*N*CS)$_2$](NCS) · H$_2$O		20.2	20.7	4.3	4.3	23.6	23.1		
trans-[Rh(en)$_2$(*N*CS)(*S*CN)](NCS) · H$_2$O	144	20.2	19.4	4.3	4.3	23.6	23.2		
trans-[Rh(en)$_2$(*S*CN)$_2$](NCS) · H$_2$O		20.2	19.7	4.3	4.2	23.6	23.2		

[a] Molar conductivities (Ω^{-1} cm^2 mol^{-1}) for *ca* 10^{-3} M solutions at 293 K; *trans*-[Rh(en)$_2$Cl$_2$]Cl gave $\Lambda = 116\ \Omega^{-1}$ cm^2 mol^{-1}.

[b] By Volhard titration.

Table 3. IR absorption bands associated with the thiocyanate ligand in complexes of rhodium(III) (cm^{-1})

Compound	ν_{CN}	ν_{CS}	δ_{NCS}	Reference
[Rh(NH$_3$)$_5$(*N*CS)](ClO$_4$)$_2$	2145(s,b)	815(s)		[a]
trans-[Rh(en)$_2$(*N*CS)Cl](ClO$_4$)		835		[b]
cis-[Rh(cyclam)(*N*CS)$_2$](ClO$_4$)	2100	835		[c]
	2080	820		
cis-[Rh(en)$_2$(*N*CS)$_2$]Cl	2125(sh)	820(w)	—	[d]
cis-[Rh(en)$_2$(*N*CS)$_2$](NCS)	2125(s)	820(w)	485(w)	[d]
trans-[Rh(en)$_2$(*N*CS)$_2$](NCS)	2110(vb,s)	835(m)	470(m)	[d]
	2045(vb,s)	710(w)	430(w)	
cis-[Rh(en)$_2$(*N*CS)(*S*CN)]Cl	2120(s)	830(vw)	450(m)	[d]
		735(vw)	430(sh)	
		700(vw)		
cis-[Rh(en)$_2$(*N*CS)(*S*CN)](NCS)	2140	835(w)	470(sh)	[d]
	2120(sh)	750(w)	460(m)	
	2060(s)	730(w)		
trans-[Rh(en)$_2$(*N*CS)(*S*CN)](NCS)	2140(s)	835(w)	470(m)	[d]
	2060(s)	735(m)	455(m)	
		710(w,b)	450(sh)	
			420(vw)	
			400(vw)	
trans-[Rh(cyclam)(*S*CN)$_2$](ClO$_4$)	2090	830		[c]
[Rh(NH$_3$)$_5$(*S*CN)](ClO$_4$)$_2$	2115(s,sp)	730(w,b)		[a]

[a] Reference 38.

[b] Reference 36.

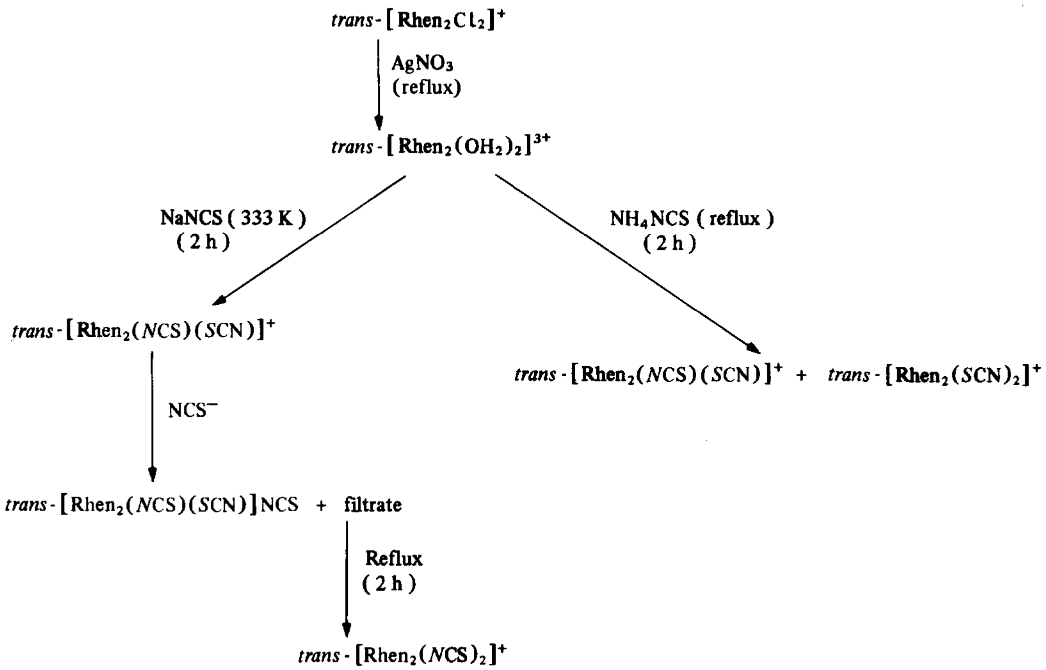
[c] Reference 37.

[d] This work; the range of such frequencies is well known, but may be exemplified by isomers of [Os(NCS)$_6$]$^{3-}$ studied by W. Preetz and G. Peters, *Z. Naturforsch.* 1979, **34b**, 1243.

Table 4. IR absorption bands for isomers of [Rh(en)$_2$(*N*CS)$_2$](NCS)

Isomer	X	Y	Z	ν_{NH_2}	ν_{CH_2}	$\delta_{d(NH_2)}$	$\nu_{bend(NH_2)}$	$\delta_{s(NH_2)}$	$\nu_{wag(CH_2)}$	$\nu_{twist(CH_2)}$	$\nu_{C\text{—}N}$	Others
cis-	*N*CS	*S*CN	NCS	3280(s) 3220(s) 3120(s)	2980(s) 2940(m) 2880(m)	1580(s) 1560(sh) 1545(sh)	1460(sh) 1450(m) 1440(sh)	1390(m) 1365(m,sp) 1360(sh)	1315(m) 1285(m,s) 1270(sh)	1145(sh) 1130(s) 1120(s)	1055(s)	1220(m)
trans-	*N*CS	*S*CN	NCS	3290(s) 3210(s) 3120(s)	2990(sh) 2945(s,sp) 2925(s,sp) 2855(s,sp) 2780(w)	1580(s) 1560(sh)	1450(m)	1395(m) 1385(w) 1380(m) 1360(m)	1315(m) 1290(m,sp) 1270(w)	1130(s) 1110(sh)	1060(s,sp)	1215(m)
trans-	*S*CN	*S*CN	NCS	3260(sh) 3220(s,b) 3120(s,b)	2980(m) 2970(m) 2950(m) 2880(w) 2800(w)	1605(m) 1585(s,b)	1445(m)	1400(m) 1385(m) 1362(m) 1367(m)	1320(sh) 1315(m-w) 1285(m,sp) 1280(sp)	1145(sh) 1130(s) 1115(sh)	1055(s,sp)	1210(m)
cis-	*N*CS	*N*CS	NCS	3200(s,b) 3100(s,b)	2960(m) 2900(sh)	1580(sh) 1570(s,b) 1560(sh)	1450(m)	1400(m) 1370(m)	1320(m) 1300(m)	1160(sh) 1150(s) 1120(m) 1110(sh)	1055(s)	1220(m) 1210(m)
trans-	*N*CS	*N*CS	NCS	3140(s,b)	2980 2950 2890(sh) 2790(sh)	1570(s,b)	1445(s) 1360(m)	1390(m) 1285(s,sh) 1280(sh)	1320(m)	1125(s,b)	1050(s)	1210(s)

KBr pellets. (s) = strong; (m) = medium; (w) = weak; (sp) = sharp; (b) = broad; (sh) = shoulder.



Scheme 4. Formation of linkage isomers of *trans*-$[Rh(en)_2(NCS)_2]^+$.

mark on separately,[35] is the Christiansen filter effect commonly found in these (and other) thiocyanato complexes. Because of this, care is needed to establish numbers and positions of vibrational bands in the ν_{CN} region.

Johnson and Basolo showed[36] that the reaction of *trans*-$[Rh(en)_2Cl_2](NO_3)$ with NaNCS gives *trans*-$[Rh(en)_2Cl(NCS)]^+$ and no disubstituted product. We therefore started here with silver-promoted aquation to *trans*-$[Rh(en)_2(OH_2)_2]^{3+}$: this, with an excess of NaNCS at 333 K, gives mainly *trans*-$[Rh(en)_2(NCS)(SCN)]^+$ (isolated as its thiocyanate). Further reaction of the mother liquor gives *trans*-$[Rh(en)_2(NCS)_2]^+$. Scheme 4 summarizes the *trans* isomers.

Among the *cis* isomers, we have made two, one being the known compound obtained by following the method[36] of Johnson and Basolo. Here, the major product was the thiocyanato–isothiocyanato thiocyanate.

$$cis\text{-}[Rh(en)_2Cl_2](NO_3) + KNCS \longrightarrow cis\text{-}[Rh(en)_2(NCS)(SCN)](NCS). \quad (11)$$

This analysed well (Volhard: cf. Table 2) for ionic thiocyanate. Using the chloride of the chloro factor, under reflux with an excess of KNCS, we obtained a new isomer:

$$cis\text{-}[Rh(en)_2Cl_2]Cl + KNCS \longrightarrow cis\text{-}[Rh(en)_2(NCS)_2](NCS). \quad (12)$$

In general, salts of our S-bonded isomers are more water soluble than the isomeric isothiocyanato complex salts. In the same way, the solid chlorides of the thiocyanato salts are hygroscopic, but their N-bonded isomers are not.

The IR spectra, 250–1000 cm^{-1}, recorded in Table 5, give further good evidence for the retention of *cis* or *trans* geometry in products and need no further discussion. (Diagrams are available.)[1(a)] Among other properties of these isomeric $[Rh(en)_2(NCS)_2]^+$ ions, we studied isomerizations (Scheme 4), addition of mercury(II), and oxidations by trioxoiodate(V) in acidic solution (i.e. iodic acid). These, being slow at room temperature, go to completion in a few hours at 333 K. Essentially (see Experimental) $[Rh^{III}—NCS]^{2+} \rightarrow [Rh^{III} \rightarrow NH_3]^{3+}$ + some $[Rh(CN)]^{2+}$; whereas $[Rh—SCN]^{2+}$ is unreactive.

Addition of aqueous mercury(II) chloride to aqueous *cis*-$[Rh(en)_2(NCS)_2]^+$ gave the clear-cut results of Fig. 6: similar findings for the *trans* species are given in Fig. 7. Additions of mercury(II) and silver(I) ions to pendant pseudo-halide (e.g. cyanides) or sulphur atoms of coordinated isothiocyanates, have been well studied.[41,42] Mercury ions also promote the solvolysis in water of halo–rhodium bonds, and the *cis*-$[M(en)_2Cl_2]^+$ ions (M = Co, Rh) show[43] a kinetic pattern arising from a long-lived stable chloride-bridged dinuclear intermediate, as in eq. (13).

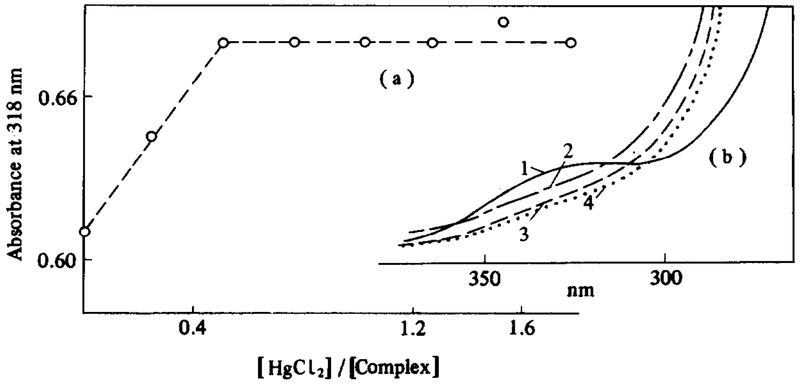


Fig. 6. Effect on the electronic absorption spectrum (———) of *cis*-$[Rh(en)_2(NCS)_2]^+$ of adding aqueous $HgCl_2$: (a) absorbance at 318 nm as f $[HgCl_2]$: [complex ion]; (b) addition in excess: 10 M (—·—·—), 20 M (— — — —), 30 M (····).

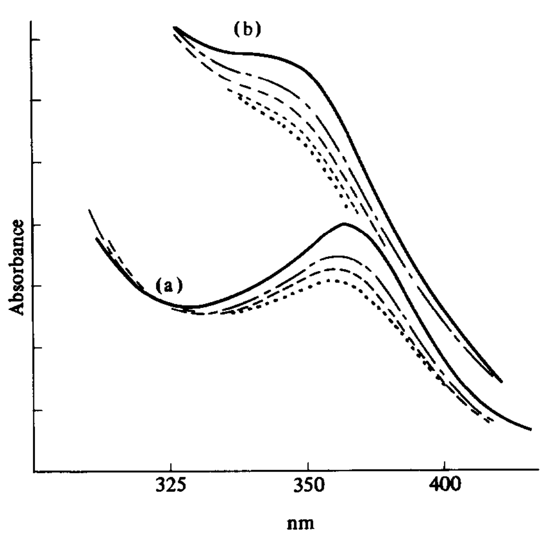


Fig. 7. Effect of adding an excess of aqueous $HgCl_2$ (a) *trans*-$[Rh(en)_2(NCS)(SCN)]^+$ (———) with: 5 M $HgCl_2$ (—·—·—), 10 M (— — — —) and 15 M (····); (b) *trans*-$[Rh(en)_2(NCS)_2]^+$ (———) with: 5 M $HgCl_2$ (—·—·—), 10 M (— — — —) and 15 M (····).

$$\textit{cis}\text{-}[Rh(en)_2Cl_2]^+ + Hg^{2+} \longrightarrow \textit{cis}\text{-}[Rh(en)_2Cl_2Hg]^{3+} \longrightarrow \text{products.} \quad (13)$$

After periods ranging from several hours to several days, all the complexes studied, whether S-bonded (thiocyanate–metal complexes), or N-bonded (isothiocyanate–metal complexes), exhibit the same triplet signal in TFA centred at $\delta \sim 6.6$ ppm due to NH_4^+. In addition, the signals from other ligands appear (e.g. from bipy in the Pd compounds, and at δ 3.3 and 5 ppm from the ethylenediamine ligands of Rh^{III} complexes, Fig. 8). Clearly, in TFA, the complexes solvolyse; thiocyanate groups dissociated from the complexes eventually produce NH_4^+. This finding requires amplification (in a kinetic framework) to be useful in studies of linkage isomerism, but is directly useful in the analysis of N-isotopic abundance in thiocyanates, via the ^{14}N : ^{15}N coupling method.[14]

Larsson showed[16] that *cis*-$[Co(en)_2(NCS)_2]ClO_4$, dissolved in concentrated sulphuric acid, produces *cis*-$[Co(en)_2(NCSH)_2]^{4+}$, responsible for the colour change from red to bright yellow. Similar protonation is also observed[16] for $[Co(NH_3)_5NCS](ClO_4)_2$. The lifetime of the species are unknown, although Gillard and Maskill were able[17] to measure circular dichroism spectra for the resolved ion (+)-$[Co(en)_2(NCSH)_2]^{4+}$ in such solutions, so that racemization is slow and salts can indeed be crystallized.

^1H NMR spectra of these compounds in conc. H_2SO_4 were taken. Within 2 h of dissolution, hydrolysis had taken place and a triplet at δ 5.3 ppm was observed (see Fig. 9). The solvolysis of $[Co(NH_3)_5X]^{2+}$ ($X = CN^-$, ONO^-, NO_2^-, Cl^-, Br^-, F^-, NCS^-) by H_2SO_4 has been studied by ^1H NMR.[44–46] In every case, the anionic ligand is rapidly replaced by the $HOSO_3^-$ anion. However, the triplet signal for the particular case of the hydrolysis of $[Co(NH_3)_5NCS]^{2+}$ was not mentioned, and it may not have been observed because of quadrupolar relaxation.

The sharp triplet obtained here at 5.3 ppm and in TFA centred at $\delta = 6.6$ ppm, is due to the proton attached to the ^{14}N of NH_4^+, formed by solvolysis of N- or S-coordinated and free thiocyanate.

EXPERIMENTAL

Electronic spectra were recorded on a Pye-Unicam SP.8000 or on a Beckman DK-2A spectrophotometer. Values of pH were measured using

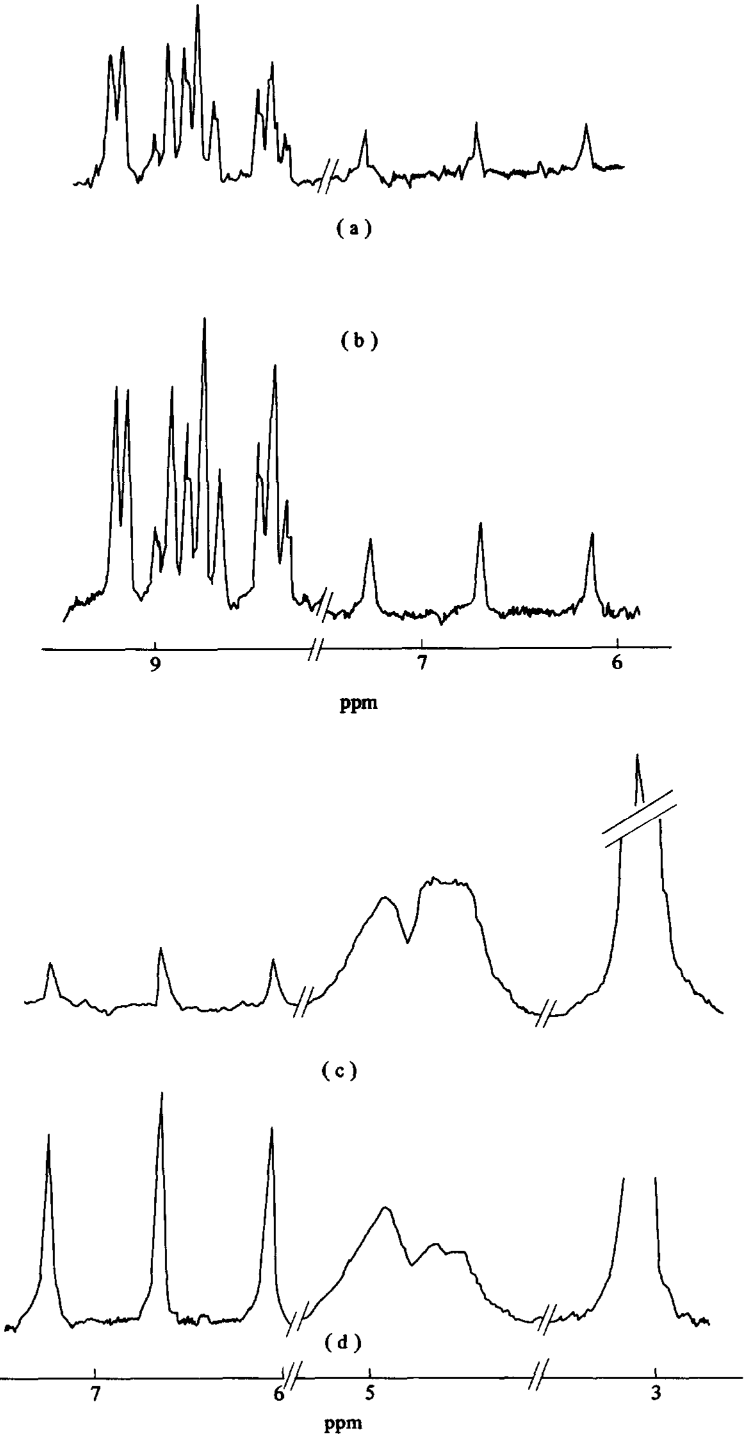


Fig. 8. Typical ^{1}H proton magnetic resonance spectra in TFA: (a) isothiocyanato species, Pd(bipy)(NCS)$_2$, after 1 day; (b) the same after 14 days; (c) thiocyanato species, *trans*-[Rh(en)$_2$(SCN)$_2$]X, X = Cl, after 1 day; (d) X = (NCS)$^-$, after 8 days.

a Corning digital pH-meter, model PT.15. IR spectra were recorded on a Perkin–Elmer 257 or Pye-Unicam SP200 spectrophotometer. Thermogravimetric analyses were performed using a Stanton–Redcroft TG-750 thermogravimetric balance. ^{1}H NMR spectra were obtained on a 90 MHz Perkin–Elmer R-32 spectrophotometer fitted with a digital signal analyser. Chemical shifts were measured relative to TSS [NaMe$_3$Si(CH$_2$)$_3$SO$_3$] or TMS (SiMe$_4$), as an internal standard. The temperature for ^{1}H NMR experiments was 35°C unless otherwise stated.

Table 5. IR spectra (300–1000 cm^{-1}) of geometric isomers of $[\mathrm{Rh(en)_2}(\mathit{N}\mathrm{C}\mathit{S})_2]^+$

$[\mathrm{Rh(en)_2}(\mathit{N}\mathrm{CS})_2](\mathrm{NCS})$		$[\mathrm{Rh(en)_2}(\mathit{N}\mathrm{CS})_2]\mathrm{Cl}$		$[\mathrm{Rh(en)_2}(\mathit{S}\mathrm{CN})_2]\mathrm{X}$		
cis-	*trans-*	*cis-*	*trans-*	*cis-* (X = NCS)	*cis-* (X = Cl)	*trans-* (X = NCS)
	320(w)				335(w)	
	345(w)			348(m)	345(m)	345(m)
	370(w)					
				375(vw)	400(vw)	375(w)
			430(sh)	400(w)		400(wm)
400(wm)	430(wm)		445(mb)			420(w)
				460(m)	452(m)	450(sh)
				470(sh)		458(m)
455(sh)	450(sh)					470(m)
468(m)	460(m)					
485(w)	470(m)					
	480(sh)					
	502(ms)		500(ms)	505(ms)	503(ms)	500(ssp)
518(m)						
510(ws)	560(w)		555(mw)	560(wm)	558(wm)	558(wm)
578(ms)	570(sh)		575(mw)	580(ms)	518(ms)	580(msp)
	580(msp)					
			695(vw)		670(w)	
	710(w)		705(vw)		695(w)	700(wb)
730(w)	735(m)			732(w)	735(w)	735(m)
750(w)	740(ms)			750(sh)		
	750(m)					
785(mw)						
800(m)	790(sh)		800(mb)	800(m)	800(m)	800(m)
820(mw)	800(m)					
				835(w)	840(w)	835(m)
	835(w)					
	875(w)		878(m)	880(w)	880(w)	880(w)
	875(w)		878(m)	880(w)	880(w)	880(w)
875(m)	890(m)	890(sh)	895(w)	890(wm)	895(m)	
	895(wm)					
	920(wm)			930(w)		915(m)
970(w)	940(wm)			940(w)		935(m)
1010(mb)						
	1000(ms)		995(ms)	995(m)	100(m)	995(s)

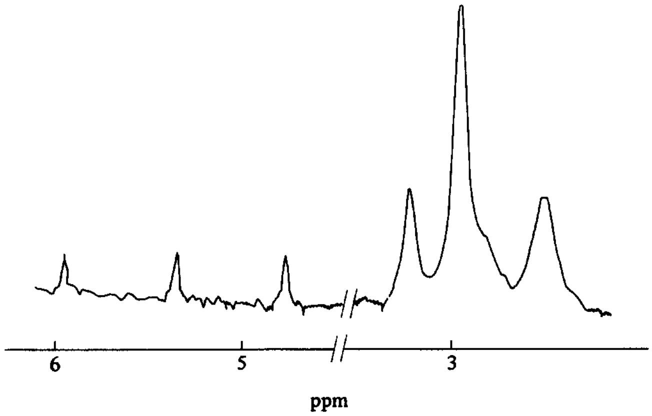


Fig. 9. Proton resonance of $[\mathrm{Co(NH_3)_5}(\mathit{N}\mathrm{CS})](\mathrm{ClO_4})_2$ in 98% H_2SO_4.

Purification of organic thiocyanates and isothiocyanates

Some minor impurities in phenyl isothiocyanate, C_6H_5NCS, and ethyl isothiocyanate, C_2H_5NCS, were observed by means of ^1H NMR spectroscopy in CCl_4. Purification was by distillation under reduced pressure (10–14 mm Hg). The purity was checked by ^1H NMR in CCl_4 and refractive indexes, at the sodium yellow lines, presented as: formula, literature[47] (20°C), observed (20.5°C): C_2H_5NCS: 1.5130, 1.5140; C_6H_5NCS: 1.6477, 1.6465; CH_3SCN: 1.4582, 1.4586; CH_3CH_2SCN: 1.4670, 1.4690; $C_6H_5CH_2SCN$: 1.5480, 1.5488.

^1H *NMR in* TFA

The ^1H NMR spectra of thiocyanate salts (Na^+, K^+, NH_4^+ etc.) were recorded on small amounts (15–20 mg) with about 0.5 cm^3 of TFA, and those of organic isothiocyanates were obtained by dissolving a small amount (~ 20 mg) of liquid in TFA; the spectra were recorded immediately and then at intervals. The concentrations in the reaction mixture of methyl isothiocyanate with TFA shown in Fig. 3 were deduced from the proton integration of the spectra.

TFA hardly dissolves most metal thiocyanate complexes. TFA was added to a capped sample bottle containing the metal complex, and the clear increasingly yellow solution was withdrawn from time to time to record spectra.

Rhodium^{III} *complexes*

trans-$[Rh(en)_2Cl_2]NO_3$. Following the method of Johnson and Basolo,[36] 2.0 g of $RhCl_3\cdot 3H_2O$ gave 0.98 g of *trans*-$[Rh(en)_2Cl_2]NO_3$. Found: C, 13.1; H, 4.5; N, 19.2. Calc. for $[Rh(en)_2Cl_2]NO_3$: C, 13.5; H, 4.5; N, 19.7%. λ 406 nm ($\varepsilon = 763$ mol^{-1} dm^2) and 286 nm ($\varepsilon = 1280$ mol^{-1} dm^2) literature:[36] λ (406, 750) and λ (288, 1300). The present SI units for ε differ from those usually given.

The preparations of the thiocyanato complexes of the bis(1,2-diaminoethane)/rhodium(III) moiety are given here in some detail because they deviate from the original method[36] of Johnson and Basolo, who obtained a substance of composition $[Rh(en)_2(NCS)_2](NCS)$ by refluxing $[Rh(en)_2Cl_2]^+$ in sodium thiocyanate. However, they reported[36] that their product failed Gladstone's test (giving no coloration with aqueous ferric ions). Our products, containing ionic thiocyanate gegen-ions, give the blood-red colour instantly. In the present context of substitution at rhodium(III) centres by thiocyanate, it is worth recalling the fact[48] that, despite forcing conditions, only one of the two chloro ligands of *cis*-α-$[Rh(trien)Cl_2]^+$ could be substituted.

Electronic spectra are given in Table 6, chiefly as a further means of characterization: the intensities for these isotropic absorptions are high, like those of other thiocyanatorhodium(III) species, whether N- or S-bonded.

Titration of ionic thiocyanate. The Volhard method was used. Typically 10 cm^3 of a 3.2×10^{-3} M solution of the complex was titrated with 0.1 M $AgNO_3$ using an acidic Fe^{2+} solution as the indicator. Values from the direct and back titration were taken.

trans-$[Rh(en)_2(NCS)_2]X$ (X = NCS, Cl). 0.620 g (1.7 mmol) of *trans*-$[Rh(en)_2Cl_2]NO_3$ in 50 cm^3 of H_2O and 0.590 g of $AgNO_3$ was set to reflux for 2 h, and the silver chloride formed was carefully removed. To the filtrate, which contained *trans*-$[Rh(en)_2(OH_2)_2]^{3+}$ (checked by visible spectrum), 1.5 g of NaNCS was added. The solution was heated (in a steam bath) at 70°C for about 2 h, during which time a new absorption band grew at *ca* 350 nm. The volume was reduced to about 20 cm^3, and all was cooled in ice. The solid obtained was collected, washed with ice-cold water, ethanol and ether. This solid is *trans*-$[Rh(en)_2(NCS)(SCN)](NCS)$; yield 0.11 g; λ 364 and 275 nm. IR spectroscopy shows strong sharp absorptions at 2140 and 2060 cm^{-1}.

The filtrate was again allowed to reflux for about 1 h, cooled and concentrated in vacuum to 10 cm^3 and finally kept overnight in the refrigerator. The resulting yellow precipitate was collected, washed with ice water, acetone and ether; yield 60 mg. Found: C, 19.6; H, 4.0; N, 22.8. Calc. for $[Rh(en)_2(NCS)_2](NCS)\cdot H_2O$: C, 20.2; H, 4.3; N, 23.6%. λ 340, 270 and 220 nm. IR: a strong sharp absorption at 2110 cm^{-1} was observed, characteristic of an N-bonded thiocyanate and at 2045 cm^{-1} due to ionic thiocyanate. *trans*-$[Rh(en)_2(NCS)_2]Cl$: *trans*-$[Rh(en)_2(NCS)_2](NCS)$ was suspended in water and moist anion-exchange resin (Amberlite IRA-400 in the chloride form) was added. The mixture was stirred (magnetically) until all dissolved. The solution was filtered several times and the yellow filtrate taken to dryness. IR shows only a single, broad, strong absorption at 2110 cm^{-1}.

trans-$[Rh(en)_2(SCN)_2]X$ (X = NCS, Cl). An aqueous solution (30 cm^3) of *trans*-$[Rh(en)_2Cl_2]NO_3$ (620 mg, 1.7 mmol) was refluxed with 590 mg (3.4 mmol) of $AgNO_3$ for 2 h and precipitated AgCl was removed by careful filtration. NH_4NCS (0.9 g) was added to the filtrate and the whole mixture was

Table 6. Electronic spectra in aqueous solution of some compounds of thiocyanate and rhodium(III), $[Rh(en)_2(NCS)_2]X$

Compound	λ (nm)	$\nu(10^3\ cm^{-1})^a$	$\varepsilon(dm^2\ mol^{-1})^b$ $(\times 10^{-3})$
cis-$[Rh(en)_2(NCS)_2](NCS)\cdot H_2O$	318	31.45	8.8
	238(sh)	42.02	89.6
cis-$[Rh(en)_2(NCS)_2]Cl\cdot H_2O$	318	31.45	6.0
	238	42.02	119.3
	2.5(sh)	46.51	127.5
cis-$[Rh(en)_2(SCN)(NCS)](NCS)\cdot H_2O$	350	28.57	2.65
	274(sh)	36.50	21.1
	240(sh)	41.67	52.1
trans-$[Rh(en)_2(NCS)_2](NCS)\cdot H_2O$	340	29.41	4.1
	220	45.45	168.0
trans-$[Rh(en)_2(NCS)(SCN)](NCS)\cdot H_2O$	364	27.47	4.45
	275(sh)	36.36	28.7
	250(sh)	40.00	40.8
trans-$[Rh(en)_2(SCN)_2](NCS)\cdot H_2O$	400(sh)	25.00	1.1
	350	28.57	2.8
	275	36.36	105.0
trans-$[Rh(en)_2(NCS)Cl](NCS)$	363[c]	27.55	3.4

[a] The reciprocal of the measured wavelength (±1 nm).

[b] Note units.

[c] From ref. 36.

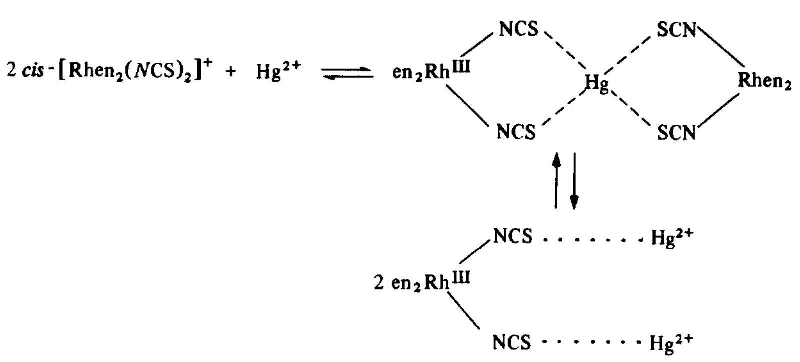
refluxed for about 1 h. The yellow solution was then reduced to about 10 cm^3 and left overnight in a refrigerator. The yellow–orange solid formed was collected, washed with ice-water, ethanol, ether and air-dried. This solid (140 mg) is again *trans*-$[Rh(en)_2(NCS)(SCN)](NCS)$, which was recrystallized from hot water. The volume of the filtrate F was reduced (*in vacuo*; 40°C) to about 5 cm^3 and it was left overnight in a refrigerator. The yellow solid obtained was collected, washed with ice–water, ethanol and ether; yield 70 mg. Found: C, 19.6; H, 4.2; N, 22.8. Calc. for *trans*-$[Rh(en)_2(SCN)_2](NCS)\cdot H_2O$: C, 20.2; H, 4.3; N, 23.3%. ν_{CN} at 2045(s, sp); 2110(s), 2130(s), 2140(sh). In an alternative treatment of F, it was taken to dryness, *in vacuo* at 40°C, and the product was redissolved in *ca* 3 cm^3 of hot water, allowed to cool to room temperature, and left at 2°C overnight. The yield was 95 mg.

The chloride salt was prepared by anion exchange as described previously. Its IR spectrum shows a single sharp strong absorption at 2110 cm^{-1} (ν_{CN}).

Isomerization of *trans*-$[Rh(en)_2(NCS)(SCN)]^+$ (*Scheme* 4). On refluxing a solution of *trans*-$[Rh(en)_2(NCS)(SCN)]^+$ in H_2O, the electronic spectrum changes to that of the *trans*-diisothiocyanate. The lower energy absorption band moves from 364 to around 340 nm, and two well defined shoulders are also observed at 270 and 220 nm. The product could not be isolated, although a few reactions have been studied.

Reactions with $HgCl_2(aq)$: adding $HgCl_2$ (aq) to aqueous *cis*-$[Rh(en)_2(NCS)_2]^+$ changed the electronic spectrum (Fig. 6). Absorbance at 318 nm increases linearly from $[HgCl_2]/[Complex] = 0–0.5$ and then stays constant (up to $[HgCl_2]/[Complex] = 1.8$); Fig. 6(a). When a large excess of $HgCl_2$ is added, the changes shown in Fig. 6(b) are observed. The first absorption band moves to higher energy and the intensity at 320 nm decreases.

Reactions with IO_3^-: solid $NaIO_3\cdot H_2O$ (4.5 mg, 0.02 mmol) was added to 10 cm^3 of a solution of the complex (typically 2×10^{-3} M) previously acidified with $HClO_4$ (so that $[H^+] = 0.02$ M), at room temperature (when reaction was very slow) or at 333 K (reaction time *ca* 3 h) in a water bath. The I_2 formed was usually extracted with CCl_4. *cis*-$[Rh(en)_2(NCS)_2]^+$ with IO_3^- at room temperature gave a mixture of products, with, after anion exchange to the chloride, a new absorption at 2191 cm^{-1}, (CN^-) a broadening in the N—H stretching, bending and rocking regions (NH_3 ligand) and again the band at 2140 cm^{-1} (NCS^-). The lower energy absorption in the electronic spectrum moves to higher energies. Chromatography (cation ex-



Scheme 5. Adducts of mercury(II) with the *cis*-bis-isothiocyanate complex.

change resin, H$^+$ form) developed two main bands, one eluted with 0.1 M HCl {singly charged, *cis*-[Rh(en)$_2$(NCS)(CN)]$^+$} and the other with 0.5 M HCl {doubly charged, *cis*-[Rh(en)$_2$(NH$_3$)(*N*CS)]$^{2+}$, *cis*-[Rh(en)$_2$(NH$_3$)(CN)]$^{2+}$}.

The products from *cis*-[Rh(en)$_2$(*S*CN)(*N*CS)]$^+$ with IO$_3^-$, under the same conditions, were also analysed. On comparing the IR spectrum of the product (impure [Rh(en)$_2$(SCN)(NH$_3$)]$^{2+}$) with that of factor, there is no evidence for CN$^-$ (absorption at 2191 cm^{-1}), but the changed NH$_2$ vibrations also occurred here. The absorption around 2120 cm^{-1} (associated with C—N stretching of the thiocyanate ligand) was observed. Two new, broad, strong bands are observed at ~ 2450 and ~ 840 cm^{-1}. In the electronic spectrum, the main feature is a new well defined band at around 245 nm.

The reaction of *trans*-[Rh(en)$_2$(*N*CS)(*S*CN)]$^+$ with IO$_3^-$ at 333 K was followed: the products again involve coordinated NH$_3$, CN$^-$ and NCS$^-$ moieties. However, the reaction at room temperature produces no CN$^-$, although coordinated NCS$^-$ and NH$_3$ are still present: the mixture of products is more complex than in the reactions of the other isomers.

Addition of an excess of HgCl$_2$(aq) to solutions of *trans*-[Rh(en)$_2$(*N*CS(*S*CN)]$^+$ and *trans*-[Rh(en)$_2$(*N*CS)$_2$]$^+$ was followed in a similar way.

The results of the titration of *cis*-[Rh(en)$_2$(*N*CS)$_2$]$^+$ with HgCl$_2$(aq), Fig. 6(a), suggest that the first association between the rhodium(III) complex and the mercuric ions, probably involves two moles of complex to one of Hg^{2+}(aq). When this ion is then added in excess, it associates in a 2:1 ratio (Hg–Complex), Scheme 5. This would explain the increase in intensity observed in the quantitative titration [Fig. 6(a)], as a new chelate ring is formed around the rhodium(III) centre. In addition, at this concentration of Hg^{2+}, and also when Hg^{2+} is present in excess, there is a shift of the bands to lower energies, both in this instance and with the *trans* compound.

Cobalt(III) *complexes*

cis-[Co(en)$_2$(*N*CS)$_2$](ClO$_4$). This was prepared according to Gillard and Maskill.[17] Found: C, 17.0; H, 4.6; N, 19.9. Calc. for *cis*-[Co(en)$_2$(NCS)$_2$](ClO$_4$)·H$_2$O: C, 17.5; H, 4.4; N, 20.4%. IR spectra contain a single broad ν_{CN} at 2105 cm^{-1}. λ 508 and 314 nm correspond to published values.

[Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$. This was prepared as described in ref. 49 by reacting NaNCS with an aqueous solution of [Co(NH$_3$)$_5$H$_2$O]$^{3+}$ to form [Co(NH$_3$)$_5$NCS](NCS)$_2$. The perchlorate salt was prepared by dissolving the thiocyanate salt in water and a saturated solution of NaClO$_4$ was added. The resulting orange–red precipitate was collected, washed with water, ethanol, ether and sucked dry. Found: C, 3.0; H, 3.9; N, 19.3. Calc. for [Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$·H$_2$O: C, 2.9; H, 4.0; N, 20.1%. λ 496 and 306 nm correspond to known values.

Palladium(II) *complexes*

Pd(bipy)(*S*CN)$_2$. The compound (0.5 g) was prepared according to Basolo and Burmeister, from 0.84 g K$_2$Pd(*S*CN)$_4$. Found: C, 38.4; H, 2.3; N, 14.1. Calc. for Pd(bipy)(*S*CN)$_2$: C, 38.0; H, 2.1; N, 14.8%. IR spectra (Nujol) contain sharp, strong bands at 2114 and 2091 cm^{-1}.

Pd(bipy)(*N*CS)$_2$. The compound (0.21 g) was prepared from K$_2$Pd(SCN)$_4$ (0.84 g) with 0.32 g of 2,2′-bipyridyl. Found: C, 37.7; H, 2.4; N, 14.2. Calc. for Pd(bipy)(*N*CS)$_2$: C, 38.0; H, 2.1; N, 14.8%. IR spectra (Nujol) contain a single, broad, strong absorption at 2100 cm^{-1}.

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