Solvent Effects on the Mode of Co-ordination of the Thiocyanate Ion: a Study on Some Bis(dimethylglyoximato)thiocyanatocobalt(III) Complexes

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The preparation and structure of some 20 complexes of the type $[Co(dh)_2L(SCN)]$ (dh = dimethylgloximato; L = various pyridines and anilines, H_2O, NH_3, $Me_2N{\cdot}CHO$, Ph_3P), $H[Co(dh)_2X(SCN)]$ (X = Cl^-, Br^-, or SCN^-), or $Et_4N[Co(dh)_2NO_2(NCS)]$ are described. It is shown that, for the substituted pyridine and aniline complexes, the equilibrium $[Co(dh)_2L(SCN)] \rightleftharpoons [Co(dh)_2L(NCS)]$ exists in solution, and that it lies to the right for solvents with higher dielectric constants, and to the left for solvents with lower dielectric constants. This behaviour is explained in a way which also reconciles the reverse behaviour of thiocyanato-complexes of class ' b ' metals.

SINCE Turco and Pecile [1] first recognised that changing the ligands in complexes of the type $[PdL_2(CNS)_2]$ † could affect the mode of co-ordination of the thiocyanate group, there has been much discussion concerning the nature of the changes (see refs. 2 and 3). Although the importance of steric effects in these particular compounds was recognised at an early stage,[4] it is only recently that their full significance has become apparent. *X*-Ray studies of a series of palladium(II) thiocyanate complexes with phosphine ligands [5] or with triphenyl phosphite [6] suggest that where *N*-thiocyanato-co-ordination occurs it is due primarily to steric inhibition of S-bonding rather than electronic effects. Conversely the bonding in $[Pd(Ph_2PCH{=}CHPPh_2)(SCN)_2]$ [7] is accounted for by the compact five-membered metal-chelate ring which holds back the phenyl groups and allows room for S-co-ordination.

Steric effects are not present in the octahedral complexes *trans*-$[Co(dh)_2L(CNS)]$ (dh = dimethylglyoximato), so that any ligational effects on thiocyanate co-ordination must be electronic in origin. The fact that these effects on a class ' a ' metal have different consequences than those on a class ' b ' metal has been well documented, and two explanations have been put forward,[8,9] which will be discussed later.

The nature of the solvent is also known to influence the mode of thiocyanate co-ordination. Burmeister *et al.*[10] have reported that solvents with high dielectric constants favour M–SCN bonding (M = class ' b ' metal), while the opposite is observed for solvents with low dielectric constants. We have communicated [11] the fact that the opposite effect (*i.e.* solvents of high dielectric constant favouring M–NCS bonding) occurs for octahedral complexes of a class ' a ' metal, as exemplified by the behaviour of the linkage isomers of $[Co(dh)_2(py)(CNS)]$.[12] Burmeister [13] challenged these results but it later transpired that his samples contained traces of paramagnetic impurities so that his conclusions are unreliable.[14] The behaviour of the cobalt(III) complexes reported earlier was confirmed by Marzilli.[14-16]

Here we describe the preparation of some 20 complexes of the type $[Co(dh)_2L(CNS)]$ and their behaviour in a number of solvents. In addition we offer a possible explanation for this behaviour *vis-à-vis* that of some class ' b ' metals.

EXPERIMENTAL

Methods of Preparation.—(I) Most of the complexes were prepared by adding the appropriate ligand to the solution obtained by warming together equimolecular amounts of aquabis(dimethylglyoximato)nitrocobalt(III) and potassium thiocyanate in water. According to Ablov and his co-workers,[17] the aquanitro-complex reacts with potassium thiocyanate as follows:

$$[Co(dh)_2(NO_2)(H_2)] + KSCN \longrightarrow K[Co(dh)_2(NO_2)(SCN)] + H_2O$$

The nitrothiocyanato-complex which was not isolated, presumably, reacts with the ligand according to the reaction:

$$K[Co(dh)_2(NO_2)(SCN)] + L \longrightarrow [Co(dh)_2(SCN)L] + KNO_2$$

(II) Complexes with moderately basic ligands, *e.g.* ammonia and pyridine, were prepared by the reaction of the dithiocyanato-complex with the ligand:

$$H[Co(dh)_2(SCN)_2] + 2L \longrightarrow [Co(dh)_2(SCN)L] + LH^+SCN^-$$

The ammonia-complex was obtained by Ablov and Samus [18]

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† M–NCS and M–SCN represent N- and S- thiocyanato-groups respectively, while M–CNS indicates that the mode of thiocyanate co-ordination is unspecified.

[1] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.

[2] W. Beck and W. P. Fehlhammer, *MTP Internat. Rev. Sci.: Inorg. Chem., Series One*, 1972, vol. 2, p. 253.

[3] A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, in the press.

[4] J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587.

[5] G. L. Palenik, W. L. Steffen, M. Matthew, M. Li, and D. W. Meek, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 125.

[6] S. Jacobson, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1974, 520.

[7] K. K. Chow and C. A. McAuliffe, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1031.

[8] A. H. Norbury, *J. Chem. Soc.* (*A*), 1971, 1089.

[9] R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

[10] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Comm.*, 1970, 679; *Inorg. Chem.*, 1971, **10**, 2032.

[11] A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, *Chem. Comm.*, 1970, 1080.

[12] A. H. Norbury and A. I. P. Sinha, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 617.

[13] J. L. Burmeister and R. J. Hassel, *Chem. Comm.*, 1971, 568.

[14] L. G. Marzilli, *Inorg. Chem.*, 1972, **11**, 2504.

[15] L. A. Epps and L. G. Marzilli, *J.C.S. Chem. Comm.*, 1972, 109.

[16] L. G. Marzilli, R. C. Stewart, L. A. Epps, and J. B. Allen, *J. Amer. Chem. Soc.*, 1973, **95**, 5796.

[17] A. V. Ablov, N. M. Samus, and M. S. Popov, *Doklady Akad. Nauk. S.S.S.R.*, 1956, **106**, 665.

[18] A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, 1959, **4**, 790.

by method (I) from an aqueous alcoholic solution; the pyridine, β-picoline, and γ-picoline complexes have been prepared in this work by both methods (I) and (II).

Standard methods were used for the preparation of compounds (1),[19] (2),[17] (3),[17] (5),[17] (7),[18] and the isomers $[Co(dh)_2(py)(SCN)]$ and $[Co(dh)_2(py)(NCS)]$.[12] The analytical data for these and the new compounds described herein are listed in Table 1.

Tetraethylammonium bis(dimethylglyoximato)isothiocyanatonitrocobaltate(III). Aquabis(dimethylglyoximato)nitrocobalt(III) (3·5 g) and potassium thiocyanate (0·97 g) were warmed with water (100 ml) on a water-bath until the aquanitro-complex dissolved. The solution was cooled and filtered, and the filtrate was treated with a saturated aqueous solution of tetraethylammonium chloride when a crystalline precipitate slowly formed. After *ca.* 1 h the precipitate was filtered off. A second crop of crystals could be obtained from the filtrate. The solid thus obtained was extracted with a small quantity of dry acetone and any insoluble material was filtered off. The filtrate was evaporated to dryness on a water-bath and the solid extracted with dichloromethane. The extract was filtered and the filtrate was evaporated to dryness when brown-red crystals were obtained; yield 2·4 g.

TABLE 1

Analytical data

	Observed					Theoretical					I.r. bands (in cm^{-1}) between 700 and 2200 cm^{-1}					
	Co	C	H	N	S	Co	C	H	N	S						
(1) $H[(A)SCN]$	14·7	29·55	4·2	20·4		14·51	29·53	3·69	20·6		720m, w	962m	1080s	1230s	1540m	2112s
(2) $H[(A)Cl]$	15·2					15·39					735m, br		1080s	1240s	1550sh	2112s
(3) $H[(A)Br]$	13·4					13·80					722m	975m	1080s	1240s		2115s
(4) $Et_4N[(A)NO_2]$	11·35	38·45	6·65	18·25	6·1	11·26	39·03	6·56	18·75	6·11	725m	980w	1090ms	1240s	1560s	2130s, br
(5) $[(A)H_2O]\cdot H_2O$	15·6					15·38					725m	980s	1090s	1245s	1565s	2116s
(6) $[(A)NH_3]\cdot H_2O$	15·55	28·5	4·75	22·05	8·25	15·41	28·28	5·01	21·99	8·37	725m	980s	1090s	1245s	1565s	2116s
(7) [(A)(3-Mepy)]	13·45	40·9	4·9	18·0	6·65	13·38	40·93	4·82	19·09	7·27	722m	982m	1098s	1245s	1560s, br	2110s
(8) [(A)(4-Mepy)]	13·45	41·0	4·4	19·55	6·35	13·38	40·93	4·82	19·09	7·27	718m	980m	1072s	1240s	1557s, br	2110s
(9) [(A)(3-Clpy)]	13·2	36·1	3·95	18·3	6·5	12·79	36·49	3·93	18·25	6·95	722m	980m	1098s	1242s	1566s	2110s
(10) [(A)(3-Brpy)]		33·15	3·65	16·85	6·1		33·27	3·58	16·64	6·33	725m	980m	1100m			
(11) $[(A)(4\text{-}NH_2py)]$		37·25	4·8	22·2	6·05		38·10	4·57	22·23	7·25	725m	980m	1095s	1243s	1570s, br	2110s
(12) [(A)(4-CNpy)]		38·05	4·0	21·55	6·15		39·92	4·02	21·72	7·09	725m	980w	1095s	1240s	1570s	2120s
(13) [(A)(pip)]	13·3	38·45	5·65	19·75	8·05	13·63	38·81	5·83	19·44	7·40	722m	978m	1095s	1242s	1560s	2118s
(14) [(A)(an)]	13·45					13·38					726m	980m	1092s	1248s	1573s, br	2120s
(15) [(A)(3-Mean)]	12·65					12·97					722m	982m, br	1088s	1245s	1560s	2118s
(16) $[(A)(3\text{-}NO_2an)]$		37·1	4·3	20·1	7·15		37·13	4·15	20·21	6·59	724m	976w, br	1096s	1245s	1570s	2120s
(17) [(A)(4-Clan)]		37·65	4·3	17·65	7·1		37·95	4·25	17·71	6·74	724m	980m, br	1098s	1245s	1560s	2120s
(18) $[(A)Ph_3P]$		53·2	4·75	11·3			53·2	4·79	11·49			980w	1080s	1245s	1560s	2110s
(19) [(A)dmf]	13·5					13·9										
(20) $[Co(dh)_2(py)_2]NCS$	11·0					11·5										
(21) $[Co(dh)_2(py)_2][(A)SCN]$	13·45					13·82					722m	990m, br	1150s	1242vs	1575s	
$Ni(dh)_2$											710m	980vs	1020m	1145s		
Hdh											725sh					

A = $[Co(dh)_2SCN]$; dh = dimethylglyoximato-; py = pyridine; pip = piperidine; an = aniline; dmf = dimethylformamide.

Amminebis(dimethylglyoximato)thiocyanatocobalt(III) *monohydrate*. Bis(dimethylglyoximato)dithiocyanatocobaltic acid (1 g) was dissolved in water (40 ml) by warming. To a cooled filtered solution of the above, a few drops of conc. ammonia were added when a precipitate at once appeared. The precipitate was filtered off, washed with water, and dried at room temperature; yield 0·8 g.

The aforesaid reaction was also carried out by Ablov and Syrstova[19] who thought that the precipitate was $[Co(dh)_2(SCN)H_2O]\cdot H_2O$ and reported the following analyses: Co, 15·40; SCN, 15·33; S, 8·61; H_2O, 4·81. However, the nitrogen content which is essential in order to differentiate between $[Co(dh)_2(SCN)H_2O]\cdot H_2O$ and $[Co(dh)_2(SCN)NH_3]\cdot H_2O$ was not determined by these authors. The complete analysis in Table 1 shows that the compound is, in fact, an ammine complex.

Bis(dimethylglyoximato)(β*-picoline)thiocyanatocobalt*(III) *and related compounds*. Aquadimethylglyoximatonitrocobalt(III) (1·75 g) and potassium thiocyanate (0·49 g) were warmed with water (50 ml) on a water-bath until dissolution was complete. To a cooled filtered solution of the above, β-picoline (0·47 g) was added when a precipitate appeared. This was filtered off, washed successively with water, alcohol, and ether, and dried at room temperature; yield 1·3 g.

A similar method was used to prepare the compounds $[Co(dh)_2L(SCN)]$ (L = γ-picoline, 3-chloropyridine, 3-bromopyridine, 4-aminopyridine, 4-cyanopyridine, and piperidine).

Bis(dimethylglyoximato)(p*-toluidine)thiocyanatocobalt*(III). This compound was obtained by the method of Ablov and Samus[16] using *p*-toluidine in place of *o*-toluidine.

p-*Chloroanilinebis(dimethylglyoximato)thiocyanatocobalt*-(III). Aquabis(dimethylglyoximato)nitrocobalt (1·75 g) and potassium thiocyanate (0·49 g) were warmed with water (50 ml) on a water-bath until dissolution was complete. The solution was cooled and filtered and the filtrate was treated with an alcoholic solution of *p*-chloroaniline (0·638 g) when a precipitate gradually formed. This was filtered off, washed successively with water and alcohol and ether, and was then dried at room temperature; yield 1·2 g.

Bis(dimethylglyoximato)(m*-nitroaniline)thiocyanatocobalt*-(III). This compound was obtained in the same way as that described above.

Bis(dimethylglyoximato)thiocyanato(triphenylphosphine)-cobalt(III). Aquabis(dimethylglyoximato)thiocyanatocobalt(III) (1·42 g) was suspended in dry acetone (150 ml) and treated with a solution of triphenylphosphine (1·32 g) in acetone and 2,2-dimethoxypropane. The mixture was then refluxed for *ca.* 0·5 h when a dark red solution was obtained. The solution was concentrated to *ca.* 25 ml by distilling off the liquid. The concentrate was cooled and any undissolved material was filtered off. The filtrate was evaporated to dryness on a water-bath and the residue was extracted with a small amount of chloroform. The extract was filtered and the filtrate concentrated by evaporation when a viscous mass was obtained. On cooling, the residue was triturated with dry ether when a solid was obtained. This was further recrystallised from

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[19] A. V. Ablov and G. P. Syrstova, *Zhur. obshchei. Khim.*, 1955, **25**, 1304.

a very small amount (5 ml) of chloroform and the above procedure was repeated to give a dark brown mass; yield 0·3 g.

Bis(dimethylglyoximato)bis(pyridine)thiocyanatocobalt(III). Cobalt(II) acetate (2·5 g), dimethylglyoxime (2·2 g), and pyridine (2·7 g) were dissolved in methanol (200 ml) and air was drawn through the mixture for 14 h. A solution of potassium thiocyanate (40%) was added and the resultant precipitate filtered off and dried in air.

Bis(dimethylglyoximato)bis(pyridine)cobalt(III) *bis(dimethylglyoximato)dithiocyanatocobaltate*(III). Bis(dimethylglyoximato)dithiocyanatocobalt was added to the above solution in the presence of base. The precipitate was filtered off and dried in air.

Analyses.—Cobalt was determined gravimetrically as anhydrous cobalt(II) sulphate. Carbon, hydrogen, nitrogen, and sulphur were analysed by Beller Micro-analytical Laboratory, Göttingen, Western Germany, and Drs. Weiler and Strauss, Oxford, England.

General Properties.—All the complexes are brown solids. The complexes $H[Co(dh)_2(SCN)X]$ ($X = Cl$ or Br) are sensitive to moisture and almost insoluble in most organic solvents except dimethylformamide and dimethyl sulphoxide. The dithiocyanato-complex is slightly soluble in water and acetone, and moderately soluble in dimethylformamide and dimethyl sulphoxide but insoluble in dichloromethane or chloroform. Tetraethylammonium (dimethylglyoximato)isothiocyanatonitrocobaltate(III) is moderately soluble in acetone, nitromethane, dimethylformamide, and dimethyl sulphoxide and highly soluble in dichloromethane. Of the neutral complexes $[Co(dh)_2(SCN)L]$, the complexes with L = water, ammonia, 4-aminopyridine, and aniline or its derivatives, are not soluble in chloroform or dichloromethane and slightly so in acetone but are moderately soluble in dimethylformamide or dimethyl sulphoxide; complexes with L = pyridine and its derivatives, and triphenylphosphine, are soluble in all the above-mentioned organic solvents.

Physical Measurements.—Molar conductances were measured using either an Electronic Switchgear, Mark III, conductance bridge or a Wayne Kerr Autobalance Universal bridge B641.

Infrared spectra were obtained on Perkin-Elmer 457 and Unicam SP 200G spectrophotometers. Mulls in both Nujol and halocarbon oil were measured, and no anion-exchange with the windows was observed. Integrated intensities were measured and calculated as described previously.[20]

Nuclear magnetic resonance spectra were measured on a Varian Instruments A60 or by P.C.M.U., Harwell, using a Varian Instruments HA100.

Separation of isotopic species was achieved on Whatman's No. 1 chromatography paper and detected by a Pannax Paper Chromatography Scanner RCMS 2 fitted with a windowless scintillation counter using an anthracene crystal.

RESULTS

Conductivity Measurements.—All complexes of the type $[Co(dh)_2L(SCN)]$ show molar conductivities corresponding to non-electrolytes. These are neutral species therefore and not, for example, the dimeric isomers $[Co(dh)_2L]$-$[Co(dh)_2(SCN)_2]$. The anionic complexes $H[Co(dh)_2(SCN)X]$ ($X = Cl^-$, Br^-, or SCN^-), $Et_4N[Co(dh)_2(NO_2)(NCS)]$, and $[Co(dh)_2(py)_2][Co(dh)_2(SCN)_2]$ all have conductivities corresponding to those of a 1 : 1 electrolyte in dimethylformamide[21] (80 Ω^{-1} cm^2) and nitromethane[22] (100 Ω^{-1} cm^2), respectively.

Infrared Spectra.—The frequencies of the main infrared bands observed in the mull spectra of the complexes are recorded in Table 1. The bands at 2120 cm^{-1} may be assigned to the C–N stretching mode of the thiocyanate group. There is no regular trend in the variation of these frequencies with the nature of the ligand. However, two notable points emerge from an inspection of the mull spectra data: (i) the C–N stretching frequency of $Et_4N[Co(dh)_2(NCS)(NO_2)]$ is higher than those of the other compounds, (ii) the C–N stretching bands of the complexes with L = 3-chloropyridine or 3-bromopyridine are split. The solution spectra, on the other hand, do not show either of the above mentioned anomalies so that the latter may be due to solid-state effects. The bands at 1560 cm^{-1} may be assigned[23] to the ring-vibrations of the dimethylglyoximato-part of the complex; this band appears to be sensitive to the nature of the axial ligand L but again there is no regular pattern in its behaviour. In the complexes $H[Co(dh)_2(SCN)X]$ ($X = Cl$, Br, or SCN) these bands appear as weak shoulders; this is probably due to the fact that these complexes have a different type of structure, $[Co(dh)_2(dh)(SCN)X]^0$, in a solid state, as suggested by Gillard and Wilkinson[24] for the complexes usually formulated as $H[Co(dh)_2X_2]$. A comparison of the spectra of the free ligand, dimethylglyoxime, and the complex $[Ni(dh)_2]$ shows that while the former has no band at 1240 cm^{-1} there is a very strong band in the latter at 1242 cm^{-1}, similar to the bands observed at 1240 cm^{-1} in all the complexes studied in this work. If the 1145 cm^{-1} band in dimethylglyoxime is tentatively assigned to the N–O stretching mode, it has been shifted on co-ordination to 1240 cm^{-1} in these complexes. Previously[12] the 1245 cm^{-1} band in $[Co(dh)_2(py)(SCN)]$ was assigned to a vibration of the pyridine molecule; it is quite probable that in this complex the band due to pyridine and the band of the dimethylglyoximato-fragment in this region overlap and obscure each other. The bands at 1080, 980, and 720 cm^{-1} in the complexes correspond to largely N–O stretching modes in the former case, and to skeletal modes in the two latter cases.[23]

The infrared bands of the thiocyanate group may be used to determine its mode of co-ordination. The problems associated with these assignments have been summarised.[8,25] As the weak C–S stretching frequencies at 700—850 cm^{-1} are obscured by the presence of various ligand bands in the complexes it is not possible to draw any reliable conclusions regarding the mode of linkage of the thiocyanate group on the basis of the mull spectra. However, the position of the C–N stretching frequency confirms that the thiocyanate group is indeed co-ordinated in every case: NCS^- absorbs at 2060 cm^{-1}. Similarly, the possibility of Co–NCS–Co bridges being formed is precluded since such a grouping would be expected to have its C–N stretching frequency above 2200 cm^{-1}. The high value of this frequency for $[Et_4N][Co(dh)_2(NO_2)(CNS)]$ suggests that this compound

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[20] A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc.* (*A*), 1968, 1598.

[21] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, 1955, **59**, 16.

[22] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

[23] A. Bigotto, G. Costa, V. Galasso, and G. de Alti, *Spectrochim. Acta*, 1970, **26A**, 1939.

[24] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 6041.

[25] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

may have a different structure from the remaining compounds, which are remarkable only for the similarity of the values observed.

Infrared and N.m.r. Measurements on Solutions of the Isomers $[Co(dh)_2(py)(SCN)]$ *and* $[Co(dh)_2(py)(NCS)]$.—The integrated intensities of the CN stretching frequency have characteristic values depending on whether the thiocyanate group is N- or S-bonded. Values 3×10^4 l mol^{-1} cm^{-2} are indicative of the latter, and 10×10^4 l mol^{-1} cm^{-2} of the former modes of bonding.[26] The results recorded in several different solvents for $[Co(dh)_2(py)(SCN)]$ are given in Table 2, where it is seen that the values increase over a period of 3 days, especially in solvents with high dielectric constants (the values ceased to change appreciably after 48 h, so all measurements were taken as soon as possible after the preparation of the solution, and then again after 3 days). Conversely, the N-isomer, in spite of its decreased solubility which prevented measurements being taken in most solvents, showed a decrease from 11·3 to $6·57 \times 10^4$ l mol^{-1} cm^{-2} in dimethylformamide. In solution, the small difference between the positions of the CN stretching frequencies observed in the two solid isomers[12] is no longer apparent.

TABLE 2

Changes in the integrated intensity (A $\times 10^4$ l mol^{-1} cm^{-2}) of the thiocyanate group in $[Co(dh)_2(py)(SCN)]$

Solvent	Dielectric constant[a]	A (initially)	A (after 3 days)
$CHCl_3$	4·8	1·90	1·90
CH_2Cl_2	9·08	1·79	2·13
$(ClCH_2)_2$	10·65	1·63	2·29
$MeNO_2$	35·9	1·74	2·24
DMF	36·7	1·92	6·30
DMSO	46·6	0·92	10·05

[a] From A. L. McClelland, Tables of Experimental Dipole Moments, W. H. Freeman and Co., San Francisco and London, 1963.

TABLE 3

Comparison of ^1H n.m.r. results at different frequencies

Sample	Peaks at 100 MHz (τ)		Peak separation (Hz)	Peaks at 60 MHz (τ)		Peak separation (Hz)
$[(A)(PPh_3)]$	7·95	8·00	1·8	7·94	7·97	1·8
$Et_4N[(A)NO_2]$	7·59	7·63	6·0	7·59	7·65	3·6
[(A)(4-CNpy)]	7·61	7·65	4·7	7·61	7·66	3·0
[(A)(3-Brpy)]	7·61	7·64	3·2	7·62	7·66	2·4

Changes are also observed in the n.m.r. spectra of the two isomers. The resonance position of the methyl protons of the bis(dimethylglyoximato)-moiety is known to be sensitive to the nature of the axial ligand,[27] and this fact has already been utilised in assigning the two linkage isomers.[12]

$[Co(dh)_2(py)(SCN)]$ Resonates at τ 7·67 and 7·63 in $[^2H_6]$dimethyl sulphoxide (DMSO-d_6) and $[^2H_7]$dimethylformamide (DMF-d_7) respectively, while $[Co(dh)_2(py)(NCS)]$ resonates at τ 7·62 and 7·59 in the same two solvents: lack of solubility, particularly of the latter isomer, prevented further measurements being made. When either isomer was left for a period of time, peaks at τ 7·67 and 7·62 (in DMSO-d_6) or at 7·63 and 7·59 (in DMF-d_7) are observed, and it has been confirmed that these are due to separate chemical entities (see later, and results in Table 3).

There are several possible changes which could be taking place in solution, and which could account for these results, although the existence of bridged thiocyanato-species can be excluded directly from the positions of the infrared bands (see earlier). These other alternatives will be discussed in turn and may be represented by the following equations:

$$trans\text{-}[Co(dh)_2(py)(SCN)] \longrightarrow cis\text{-}[Co(dh)_2(py)(NCS)] \quad (1)$$

$$2[Co(dh)_2(py)(SCN)] \longrightarrow [Co(dh)_2(py)_2][Co(dh)_2(SCN)_2] \quad (2)$$

$$[Co(dh)_2(py)(SCN)] + S' \longrightarrow [Co(dh)_2S'(NCS)] + py \quad (3)$$

$$[Co(dh)_2(py)(SCN)] + S' \longrightarrow [Co(dh)_2(py)S']NCS \quad (4)$$

$$[Co(dh)_2(py)(SCN)] \longrightarrow [Co(dh)_2(py)(NCS)] \quad (5)$$

$$S' = \text{solvent}$$

The question of whether the products are in thermodynamic equilibrium with the reactants, or with any subsequent products will be deferred for the present.

Ablov and his co-workers[28] have reported the existence of *trans*-$[Co(dh)_2H_2O(SCN)]$ and *cis*-$[Co(dh)_2H_2O(NCS)]$, but the latter compound requires alkaline conditions for its formation, whereas normal conditions lead to *trans*-bis(dimethylglyoximato)cobalt(III) compounds.[24] Not only do such alkaline conditions not prevail in this study, but also the integrated intensities of the CN stretching frequencies in DMF, which are intermediate between typical N- and S-bonded values, suggest a mixture of reactant and product. If this were the case, the n.m.r. would show a single resonance due to the *trans*-species together with two peaks of equal intensity, which might be coupled due to the *cis*-isomer. The observation of two peaks of different intensities precludes the possibility of simultaneous geometric and linkage isomerism, so that equation (1) does not apply, and all the products may be regarded as *trans*-complexes.

The conductivities of the solutions do not change significantly with time so that equations (2) and (4) are not applicable. Lest ion-pairing should be particularly prevalent, $[Co(dh)_2(py)_2][Co(dh)_2(SCN)_2]$ and $[Co(dh)_2(py)_2]$SCN were prepared and shown to behave like normal 1 : 1 electrolytes (it was not possible to synthesise $[Co(dh)_2(py)(dmf)]$NCS). Further, the n.m.r. spectrum of the former compound showed the expected two peaks of equal intensity at τ 7·74 and 7·67 in DMF corresponding to the cation and anion respectively, while the infrared spectrum of $[Co(dh)_2(py)_2]$NCS has a clear peak at 2060 cm^{-1} due to the unco-ordinated thiocyanate ion, a peak which was not observed in any of the other compounds studied.

In order to exclude possibility (3), the compound $[Co(dh)_2(dmf)(SCN)]$ was prepared and found to have

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[26] S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, 1962, **16**, 447; C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

[27] H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. (A)*, 1969, 554.

[28] A. V. Ablov, N. N. Proskina, C. A. Bologa, and N. M. Samus, *Russ. J. Inorg. Chem.*, 1970, **15**, 1245.

an integrated intensity for its CN stretching frequency of $3{\cdot}2 \times 10^4$ l mol^{-1} cm^{-2}, and one n.m.r. resonance at τ 7·64 (in deuteriated DMF), neither value of which changed with time, and which together indicated that only the S-bonded form prevailed with L = DMF. Further, there was no trace of free pyridine in the n.m.r. spectra of the two linkage isomers $[Co(dh)_2(py)(CNS)]$ in DMF-d_7.

The final possibility that both the N- and S-thiocyanato-isomers may be present in certain solutions is indicated by the foregoing discussion, and is confirmed by the correspondence between the increase in the integrated intensity of the CN stretching frequency for the S-isomer and the decrease for the N-isomer. The resonance positions of the new peaks after a period of time in the n.m.r. studies relative to the resonances for the two freshly prepared solutions also confirm equation (5).

TABLE 4

Spectroscopic data of bis(dimethylglyoximato)thiocyanatocobalt(III) complexes in different solvents

	Resonance positions (τ) of dimethylglyoximato-methyl protons [b]		Integrated intensities of absorption (A) of ν_{CN} per SCN ($\times 10^{-4}$ l mol^{-1} cm^{-2})		
Compound [a]	$CDCl_3$	$(CD_3)_2SO$	$CHCl_3$	CH_3NO_2	DMF
H[(A)SCN]		7·67			1·68
H[(A)Cl]		7·68			2·0
H[(A)Br]		7·68			2·0
$[Et_4N][(A)NO_2]$	7·60 7·65 (1 : 3)	7·67	6·8	7·87	12·1
$[(A)H_2O]$		7·68			2·5
$[(A)NH_3]$		7·68			1·84
[(A)(3-Mepy)]	7·61	7·62 7·67 (3 : 2)	1·73	1·68	5·45
[(A)(4-Mepy)]	7·61	7·61 7·66 (3 : 2)	1·45	1·65	5·5
[(A)(3-Clpy)]	7·60	7·61 7·66 (1 : 1)	1·58	1·63	7·76
[(A)(3-Brpy)]	7·60	7·62 7·66 (1 : 1)	1·54	1·67	7·4
$[(A)(4\text{-}NH_2py)]$		7·64 7·68			2·05
[(A)(4-CNpy)]	7·61	7·61 7·66 (2 : 1)	1·69	1·66	4·88
[(A)(pip)]	7·49	7·53 7·58 (3 : 1)	4·72	5·02	5·38
[(A)(an)]		7·78 7·88 (1 : 1)			4·58
[(A)(4-Mean)]		7·80			7·2
$[(A)(3\text{-}NO_2an)]$		7·69 7·74 (2 : 1)			6·33
[(A)(4-Clan)]		7·70 7·75 (3 : 2)			7·45
$[(A)(PPh_3)]$	7·94 7·97 (1 : 1)		2·9	3·82	4·5
[(A)(dmf)]					3·2

[a] A = $[Co(dh)_2SCN]$. [b] Relative intensities in brackets (approx.).

Burmeister *et al.*[10] attempted to show that the change from the S- to the N-bonded isomer was due to kinetic control of the thermodynamically less favoured S-thiocyanato-compound on the grounds that it isomerised in boiling $CHCl_3$ at an appreciable rate, although it did not do so at room temperature. We have found that a sample of the S-thiocyanato-complex first prepared four years ago is unchanged in its infrared and n.m.r. spectroscopic properties, and that we were unable to repeat Burmeister's results unless we added some Co^{II} species ($Co^{II} : Co^{III} = 1 : 200$). The effect of Co^{II} has been established unequivocally by Marzilli [14–16], so that Burmeister's conclusion can be discounted and equation (5) expressed in the form of the overall equilibrium

$$[Co(dh)_2(py)(SCN)] \rightleftharpoons [Co(dh)_2(py)(NCS)] \qquad (6)$$

in which the equilibrium position lies further to the right for solvents of high dielectric constant, and to the left for solvents with lower dielectric constants (it should be noted that here dielectric constant is used in a descriptive rather than an explanatory sense).

In an attempt to determine more of the nature of this equilibrium, and the mechanism by which the isomerisation was accomplished, the two isomers were separately treated with $KS^{14}CN$ in a mixed solvent containing different proportions of $CHCl_3$ and DMF (it was not possible to establish a pure solvent system which was adequate for all the steps in the experiment). The complex and the potassium thiocyanate were then separated by paper chromatography and the relative activities of the peaks were measured. Some exchange took place with each of the N- and S-isomers, and the amount of exchange was greater in both cases in the DMF-rich than in the $CHCl_3$-rich solvent mixture; the extent of exchange was also increased by the addition of catalytic amounts of Co^{II} to either isomer. The mechanism for isomerisation in the presence of Co^{II} has been discussed previously.[16] In the absence of Co^{II} these results suggest that a dissociative, ionic mechanism is involved in the isomerisation, but do not exclude the possibility of an associative mechanism also being involved. In fact, the small extent of isomerisation that occurs in the least polar solvents (see Table 2) suggests that the latter mechanism does have some part to play. The possibility of both mechanisms occurring has been mooted previously in the kinetic study of the reduction of $[Co(NH_3)_5NCS]^{2+}$ with $[Cr(H_2O)_6]^{2+}$. Initially, $[Cr(H_2O)_5NCS]^{2+}$ and $[Cr(H_2O)_5SCN]^{2+}$ were formed, the latter isomerising either by an intimate ion-pair mechanism or by the chromium 'sliding down' the π-orbitals of the thiocyanate group.[29]

The overall equilibrium constant for reaction (6) is small with $\Delta G \simeq 3{\cdot}1$ kJ mol^{-1}, $\Delta H = 26{\cdot}4$ kJ mol^{-1}, and $\Delta S = -78$ J K^{-1} at 298 K in chloroform.[30]

I.r. and N.m.r. Measurements on Solutions of $[Co(dh)_2L(CNS)]$.—Having established in some detail that an equilibrium exists between the linkage isomers for L = py, our attention was turned to the effect of varying the ligand *trans* to the thiocyanate group. Table 3 shows some n.m.r. results which establish without doubt that there are separate chemical species in solution, and no type of coupling is occurring which could account for the two

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[29] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1965, **87**, 4210; 1966, **88**, 434.

[30] A. H. Norbury and S. Raghunathan, unpublished results.

peaks, except when L = PPh_3. Two peaks are observed for L = PPh_3 with J = 1·8 Hz at both 60 and 100 MHz, indicating P–H coupling as previously reported in other cobaloxime complexes.[27] The separations between the peaks observed at the two frequencies when L is a nitrogen donor are close to the 5 : 3 ratio so that here two distinct chemical entities are present in solution.

The n.m.r. results for a wide variety of complexes are given in Table 4. The data show that, except when L = NO_2^- and PPh_3, only one peak is observed in $CDCl_3$, whereas in many cases two peaks are observed in DMSO-d_6. The integrated intensity data for the CN stretching frequency for the same compounds are also included, and complement the n.m.r. data. From this Table it can be seen that the tendency to isomerise in solvents with higher dielectric constants extends to many, but not all, of the complexes. Substituted pyridine or aniline complexes isomerise in solution, but when L = PPh_3, H_2O, NH_3, Cl^-, Br^- or SCN^- there is no evidence that any N-thiocyanato-complex is formed. The case when L = SCN deserves further comment.

Epps and Marzilli [31] have isolated and characterised the S,S, the N,S, and the N,N isomers of $Ph_4As[Co(dh)_2(SCN)_2]$, and shown that although the S,S isomer is formed initially it isomerises in solution to give both other products. We have observed no such behaviour with the corresponding acid $H[Co(dh)_2(SCN)_2]$. It is quite clear that the S,S compound is formed initially from the results of both Epps and Marzilli, and those of Ablov *et al.*[19] $[NH_4][Co(dh)_2(SCN)_2],H_2O$ has been characterised by *X*-ray crystallography.[32] The fact that the acid remains unchanged may be due to the effect of the proton, which is believed to destroy the hydrogen bonding on one side of the bis(dimethylglyoximato)cobalt(III) fragment [24] in which case the system is no longer directly comparable with the complete planar array found in the neutral complexes. Alternatively, the tetraphenylarsonium cation may be decisive in affecting the solubilities of the different salts, and hence allowing the formation of the hitherto unknown species.

DISCUSSION

With the possible exception of the tetraethylammonium salt for L = NO_2^-, the compounds formed initially are $[Co(dh)_2L(SCN)]$. The reaction scheme proposed by Ablov [17] (see Experimental section) and the different conditions, especially the longer time in a solvent of high dielectric constant, used for the isolation of the above salt perhaps allows the isomerisation to the N-bonded form to take place. Nevertheless, the fact that many of the S-bonded products are prepared by displacing the nitro-group from the above complex, even though the latter was not isolated, suggests that the relative solubilities of the S- and N-bonded forms may be of over-riding importance in the isolation of a particular isomer. This point is reinforced by the fact that the preparations are carried out in ethanol, a protic solvent but nevertheless one with a relatively high dielectric constant which would thus be expected to favour the N-isomer. The presence of the nitro-group and the isolation of intermediates in our syntheses may also account for the difference in experimental results communicated by ourselves [11] and Burmeister *et al.*[13] This difference is due primarily to trace amounts of Co^{II} which catalyse the thiocyanate isomerisation [16] in the latter samples, but which have been removed in our samples, possibly by oxidation by the nitro-group.

The substituted pyridine and aniline ligands were chosen so as to span a wide range of pK_a values. Nevertheless, there is very little change in the position of the CN stretching frequency when any of these ligands are *trans* to the thiocyanate group, nor when they are replaced by PPh_3, NH_3, H_2O, or an anionic ligand. Ligational changes are known to modify the CN stretching frequency in some cases [3,25] so that in this case either lattice effects predominate, or the planar bis(dimethylglyoximato)-array over-rides such *trans*-effects as would be likely to change this frequency.

The compounds reported herein considerably extend the number of known S-thiocyanato-cobalt(III) complexes, and also of S-thiocyanato-complexes of class 'a' metals. These, unlike the complexes of class 'b' metals, are formed in the presence of ligands like dimethylglyoximato that are soft or have a π-accepting capacity.[3] The situation is summarised in Table 5, where the terms σ donor and π acceptor are intended to be descriptive about a type of ligand rather than carrying any explanatory implications.

TABLE 5

Effects of ligands and metal on thiocyanate co-ordination

Ligand / Metal	σ donor	π acceptor
Class 'a'	–NCS	–SCN
Class 'b'	–SCN	–NCS

Pearson [9] has put forward the concept of antisymbiosis to account for this behaviour. He extends the ideas of Chatt and Heaton [33] to imply that ligands with a large *trans*-effect induce bonding by the nitrogen atom, or the harder end of the thiocyanate group. Although the nitro-group fulfils this prediction in these compounds, it is the only one of a large number of ligands with varying *trans*-directing properties [34] so to do. Antisymbiosis does not appear to apply to this group of compounds, and it goes no way to explaining the consequences of the dimethylglyoximato-ligands. An overall explanation for the situation summarised in Table 5 has been put forward,[8] and the compounds reported here are in complete accord with that explanation.

The behaviour of these complexes in solution is of great interest because, like the isomers of $[Co(dh)_2(Bu^tpy)(CNS)]$,[14] they show the opposite effects to those reported for class 'b' solvents.[10] This affects and complicates the explanations that have been offered in the latter case in much the same way that the π-bonding explanation of Turco and Pecile [1] and the symbiosis

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[31] L. A. Epps and L. G. Marzilli, *Inorg. Chem.*, 1973, **12**, 1514.

[32] L. D. Samus, *Acta Cryst.*, 1966, **21**, A150.

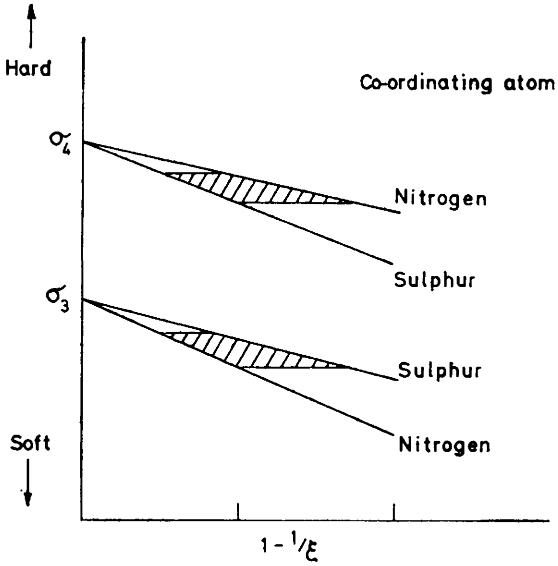
[33] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 2745.

[34] J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 375.

explanation of Jorgensen[35] applied to the effect of ligands on thiocyanate co-ordination for class ' b ' and class ' a ' complexes respectively but could not be applied the other way round. Similarly, Burmeister[10] has proposed that the solvent effects on the class ' b ' complexes may be accounted for using the concept of charge- and frontier-controlled reactions developed by Klopman.[36] Klopman's equations lead to the predictions that solvents with high dielectric constants tend to enhance frontier orbital-controlled (largely covalent) interactions whereas solvents with low dielectric constants favour charge-controlled (largely ionic) interactions as indeed was observed generally by Burmeister.[10] Clearly, the same explanation cannot be applied directly to these cobalt(III) complexes, and Marzilli[14] has supposed that, in such co-ordinatively saturated complexes, the major interaction is between the solvent and the unbonded atom of the thiocyanate group in contrast to the palladium system where the influence of the solvent on the metal-thiocyanate bond strength is of primary importance. It is not clear that these suppositions can be confirmed by experimental data, nor that they do represent different situations. Indeed the exchange studies already described in this paper suggest that the nature of the interaction between the thiocyanate group and cobalt is directly affected by changing the solvents, so that an alternative explanation must be sought.

An overall explanation of the differing aspects of the thiocyanate co-ordination summarised in Table 5 has been given by calculating the overall hardness/softness parameter ($E_d^‡$) for the nitrogen and sulphur atoms separately in each of the two highest occupied orbitals of the thiocyanate ion. Part of the calculation involves a term containing $1 - 1/\varepsilon$ (ε = the dielectric constant), and the Figure shows how variations in the dielectric constant of the solvent affect $E_d^‡$ for the four different situations outlined above. Thus, if attention is directed to the hatched portion of the diagram, it can be seen that, as ε increases, a class ' a ' metal which had previously interacted most strongly with the sulphur atom of σ_4 [as in the case with these bis(dimethylglyoximato)-S-thiocyanatocobalt(III) complexes] gradually changes its preference (*i.e.* moves horizontally across the diagram) as the dielectric constant of the solvent is increased. Conversely, a class ' b ' metal will show the opposite preference, as is observed experimentally. For the complexes described herein, the majority would appear to be susceptible to the effect of changing the solvent but a few (L = PPh_3, H_2O, NH_3, DMF; the acids) seem to be sufficiently stable to be unchanged in the solvents used (although in the presence of Co^{II} the PPh_3 complex does isomerise[16]). Thus, the solvent effect will only be apparent in circumstances where other ligational effects are approximately in balance, and is most likely where linkage isomers have been reported. Where the N-isomer is appreciably more stable than the S-isomer (or *vice versa*) no solvent effect is expected, nor found.[3] The small equilibrium constant[30] for reaction (6) suggests that $[Co(dh)_2(py)SCN]$ and related compounds are ideal for the observation of such effects.

The above discussion does not take into account the possible role of π-orbitals on the thiocyanate ion: Gutterman and Gray[37] interpreted some spectroscopic results to show that the thiocyanate group acted as a π-donor when it co-ordinated *via* the sulphur atom to a first-row transition element. Epps and Marzilli[31] suggest that when L is a good π-acceptor in $[Co(dh)_2L(CNS)]$ a Co-SCN bond should therefore be expected. Our results with L = NH_3 and H_2O where only S-bonded complexes are formed, even in solvents with high dielectric constants, and with L = substituted anilines which cannot act as π-acceptors and which show similar behaviour to complexes with substituted pyridines with corresponding basicities and π-accepting potential, suggest that the π-accepting nature of the ligand *trans* to the thiocyanate group is not of prime importance in the formation of Co-SCN bonds in these complexes, perhaps because of the over-riding *cis*-effects of the dimethylglyoximato-ligands.



Variation in softness character of donor centres on NCS^- with dielectric control

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[35] C. K. Jorgensen, *Inorg. Chem.*, 1964, **3**, 1201.

[36] G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

[37] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3364; *Inorg. Chem.*, 1972, **11**, 1727.