41. *Electronic Spectra and Magnetic Properties of Some Isothiocyanate Complexes of Manganese and Iron.*

By D. FORSTER and D. M. L. GOODGAME.

Compounds containing complex anions of the types $M(NCS)_4^{2-}$ [M = Mn(II) or Fe(II)], and $M(NCS)_6^{n-}$ [M = Mn(II) or Fe(III)] have been prepared and their magnetic and spectral properties have been studied. The infrared spectra show that in all cases the thiocyanate groups are bonded to the metal ions through the nitrogen atoms. The electronic spectra show that the ions $M(NCS)_4^{2-}$ are essentially tetrahedral and, for the iron(II) complex, this is supported by isomorphism with the analogous cobalt(II) compounds. The $^5E \longrightarrow {}^5T_2$ band for the iron(II) complexes exhibited a larger splitting than would be predicted from simple spin-orbit coupling effects, and the possible reasons for this are discussed.

The electronic spectra of the compounds $HgM(NCS)_4$ [(M = Mn(II) or Fe(II)] have been obtained and are consistent with the presence of an essentially tetrahedral environment of nitrogen atoms for the iron(II) and manganese(II) ions.

THE thiocyanate group is a versatile ligand and is known to co-ordinate with transition-metal ions through the nitrogen atom or the sulphur atom and to function as a bridging ligand. The factors that determine whether N- or S-bonding will be preferred in a given complex are not well defined, although general trends may be recognized. For example, most " thiocyanate " complexes of first-series transition-metal ions are isothiocyanates, but some exceptions are known, such as dithiocyanato-bis(triphenylphosphine)cobalt(II) [1] and -tetramminecopper(II).[2]

Although numerous complex " thiocyanato "-anions of first-series transition-metal ions are reported in the older literature,[3] hardly any of these have been subjected to detailed study. Moreover, many of the compounds described by earlier workers are hydrated, and the presence of water molecules in a compound [4] such as $(enH)_2Fe(NCS)_4,4H_2O$ presents an additional complication in the elucidation of the stereochemistry of the metal ion. Hitherto, the most fully characterized complex " thiocyanato "-anion of first-series transition metals appears to be the tetrahedral tetraisothiocyanatocobaltate(II) ion. The structures of compounds containing this anion have been determined,[5] and the electronic spectrum and magnetic properties have been reported.[1,6]

In order to provide more information about the stoicheiometry, the structures and the mode of bonding of the NCS groups in " thiocyanato "-complex anions of first-series transition metals, we have prepared and studied compounds with anions of this type. We report here the results of magnetic, spectral, and *X*-ray studies on the complexes of manganese(II), iron(II), and iron(III). Some of the compounds examined are listed in Table 1, together with figures for their electrolytic conductance and magnetic moments. The preparations were carried out in non-aqueous solvents and this, together with the use of large, quaternary ammonium or phosphonium cations, permitted the isolation of products free from " water of crystallization."

The electrolytic conductances of the compounds in nitrobenzene or nitromethane are in the ranges expected for the ionic formulæ given in Table 1. The infrared absorption spectra of the compounds (Table 2) indicate that the NCS groups are N-bonded, since the C–S stretching frequencies occur [7] in the range 820—830 cm.$^{-1}$.

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[1] Cotton, Goodgame, Goodgame, and Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.

[2] Poraj-Kosic, 6th Internat. Congress and Symposia of the Internat. Union of Crystallography, Rome, 1963, *Acta Cryst.*, Suppl., 1963, *A*, **42**, abstract 4·72.

[3] See, *e.g.*, Williams, " Cyanogen Compounds," Edward Arnold, 2nd edn., 1948.

[4] Grossmann and Schück, *Z. anorg. Chem.*, 1906, **50**, 21.

[5] Zhdanov, Tishchenko, and Zvonkova, *Zhur. fiz. Khim.*, 1950, **24**, 1338.

[6] Holm and Cotton, *J. Chem. Phys.*, 1960, **32**, 1158.

[7] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

As well as the ionic complexes, the compounds MHg(SCN)$_4$ where M = Mn(II) or Fe(II), described by Rosenheim and Cohn[8] have been reprepared and their electronic spectra studied. It is convenient to discuss the results of the magnetic and electronic spectral measurements on the basis of the nature of the central metal ion.

Manganese(II) *Complexes*.—The magnetic moment (5·92 B.M.) of n-butyltriphenylphosphonium tetraisothiocyanatomanganate is in the region expected for a spin-free manganese(II) complex. The electronic spectrum of the compound has been obtained by reflectance for the solid, and for acetonitrile solutions (Table 3, and Fig. 1). There is a broad, intense band at ~35,000 cm.$^{-1}$, which may be a charge-transfer band or, more probably, an internal transition of the thiocyanate group.[9] This band obscures the much weaker *d–d* bands of manganese(II) above 28,000 cm.$^{-1}$. However, the *d–d* bands that can be observed are very similar, both in energies and intensities, to those found for tetrahedral MX$_4^{2-}$ ions and, in particular, the tetrahedral tetraisocyanatomanganate(II) ion.[10]

TABLE 1.

Electrolytic conductances and magnetic values for some isothiocyanate complexes.

	Electrolytic conductances *		Magnetic values			
Compound	Solvent	Λ_m ohm^{-1}	T(°K)	$10^6 . \chi_m$ † (c.g.s.u.)	μ_{eff} ‡ B.M.	θ § (°K)
(Bu^{n}Ph$_3$P)$_2$[Mn(NCS)$_4$]	PhNO$_2$	51	296·0	14,660	5·92	*a*
	CH$_3$NO$_2$	172				
(Me$_4$N)$_2$[Fe(NCS)$_4$]	CH$_3$NO$_2$	154	*a*	*a*	*a*	*a*
(Et$_4$N)$_2$[Fe(NCS)$_4$]	*a*	*a*	294·0	12,370	5·42	—15
(Me$_4$N)$_3$[Fe(NCS)$_6$]	PhNO$_2$	74	295·0	14,707	5·92	*a*

* 10^{-3}M-Solutions at 20—25°. † Corrected for diamagnetism. ‡ Calc. from $\mu_{eff} = 2{\cdot}84\ (\chi_m T)^{\frac{1}{2}}$.
§ Weiss constant. *a*, Not measured.

TABLE 2.

Infrared frequencies (cm.$^{-1}$) of the isothiocyanate groups.

Compound	State	C–N stretch	C–S stretch
(Bu^{n}Ph$_3$P)$_2$[Mn(NCS)$_4$]	Mull *	2050vs	—
	CH$_3$CN	—	825vw
(C$_9$H$_8$N)$_4$[Mn(NCS)$_6$]	Mull	2066vs, 2045vs	†
(Me$_4$N)$_2$[Fe(NCS)$_4$]	Mull	2053vs	830vw
	CH$_3$NO$_2$	—	825vw
(Me$_4$N)$_3$[Fe(NCS)$_6$]	Mull	2075vs, 2057vs, 2026vs	828vw

* In Nujol. † Region contains bands due to cation.

TABLE 3.

Electronic absorption spectra of the complexes.

Compound	State	Absorption max. (cm.$^{-1}$) (ε for solns.)
(Bu^{n}Ph$_3$P)$_2$[Mn(NCS)$_4$]	Solid †	~35,000vbr; 27,030; 25,190; 22,730; 21,740; ~19,600sh; 16,000 *
	CH$_3$·CN (0·0399M)	*a*; 27,030 (0·18); 25,500 (0·83); 22,730 (1·9); 21,740 (2·2); ~19,700sh; 15,900 (0·55) *
HgMn(NCS)$_4$	Solid	22,900; 22,000; ~20,000sh; 16,700 *
(Me$_4$N)$_2$[Fe(NCS)$_4$] ...	Solid (mull)	5800; 4650
	CH$_3$NO$_2$ (0·042M)	5780 (142); 4650 (126)
(Et$_4$N)$_2$[Fe(NCS)$_4$]	Solid	~5700; 4300 ‡
	CH$_3$NO$_2$ §	5900; ~4600
	CH$_3$CN §	5900; ~4550
	Acetone §	5800; ~4600
HgFe(NCS)$_4$	Solid (mull)	6250; 5000
Me$_4$N)$_3$[Fe(NCS)$_6$] ...	Solid	~21,400vbr; ~17,500br, 10,640

a, Strong absorption >28,000 cm.$^{-1}$. * Band due to cobalt(II) impurity, see text. † By reflectance unless stated otherwise. ‡ Vibrational overtone. § Concentration not determined.

The bands in the spectrum of the tetraisothiocyanatomanganate(II) ion may be assigned on the basis of a tetrahedral structure, as follows: $^6A_1 \longrightarrow {}^4T_1\ (G)$ at ~19,600 cm.$^{-1}$;

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[8] Rosenheim and Cohn, *Z. anorg. Chem.*, 1901, **27**, 280.

[9] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, 1962, p. 196.

[10] Forster and Goodgame, *J.*, 1964, 2790.

$^6A_1 \longrightarrow {}^4T_2$ (*G*) at 21,740 cm.$^{-1}$; $^6A_1 \longrightarrow {}^4E$, $^4A_1$ (*G*) at 22,730 cm.$^{-1}$; $^6A_1 \longrightarrow {}^4T_2$ (*D*) at 25,500 cm.$^{-1}$; $^6A_1 \longrightarrow {}^4E$ (*D*) at 27,030 cm.$^{-1}$. Because the transitions lying above ~28,000 cm.$^{-1}$ could not be observed, it was not thought worth while to attempt a detailed quantitative analysis of the spectrum to obtain values of the ligand field-strength parameter Δ and the interelectronic-repulsion parameters, *B* and *C*. However, as in the case of the tetraisocyanatomanganate(II) ion,[10] the energy level diagram for the tetrabromomanganate(II) ion [11] was used to obtain an approximate value of Δ for $Mn(NCS)_4^{2-}$. Due allowance was made for the very small differences in the $^6A_1 - {}^4E$, $^4A_1$, (*G*) and $^6A_1 - {}^4E$ (*D*) separations for the two cases. On this basis, a Δ value of ~4700 cm.$^{-1}$ was found, which may be compared with the value of ~4600 cm.$^{-1}$ for the tetraisocyanatomanganate(II) ion.[10]

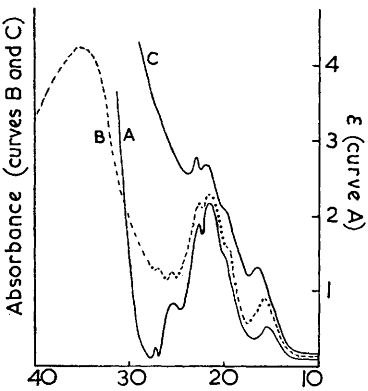

FIG. 1.

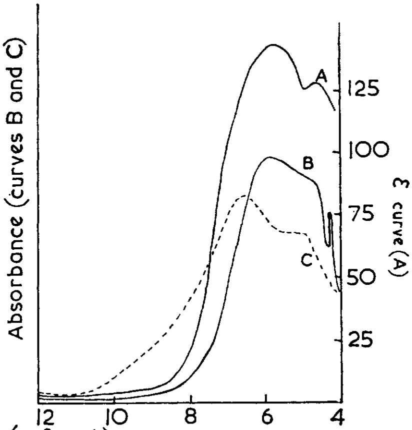

FIG. 2.

FIG. 1. Spectra of manganese(II) complexes: A, $(Bu^nPh_3P)_2Mn(NCS)_4$, 0·039M in $CH_3{\cdot}CN$; B, $(Bu^nPh_3P)_2Mn(NCS)_4$, solid by reflectance; C, $HgMn(NCS)_4$, solid by reflectance.

FIG. 2. Near-infrared spectra of some iron(II) thiocyanate complexes: A, $(Me_4N)_2Fe(NCS)_4$ 0·042M in CH_3NO_2; B, $(Me_4N)_2Fe(NCS)_4$, solid by mull technique; C, $HgFe(NCS)_4$, solid by mull technique.

The reflectance spectrum of the compound $HgMn(NCS)_4$ shows only three bands assignable as *d–d* transitions. All *d–d* bands above ~24,000 cm.$^{-1}$ were masked by a strong band, probably due to an internal transition of a thiocyanate group, in the ultraviolet region. However, the three bands observed correspond very closely in energy to the three transitions of lowest energy in the spectrum of the tetraisothiocyanatomanganate(II) ion. Therefore, it seems very probable that in the compound $HgMn(NCS)_4$ the manganese ion is surrounded by four nitrogen atoms in an approximately tetrahedral array, as in the cobalt(II) analogue.[12] However, the compounds $HgMn(NCS)_4$ and $HgCo(NCS)_4$ are not isomorphous, although their powder patterns are rather similar. Single-crystal *X*-ray-diffraction photographs show that n-butyltriphenylphosphonium tetraisothiocyanatomanganate(II) and its cobalt(II) analogue are also not isomorphous.

The electronic spectra of both of the manganese(II) compounds show the presence of traces of the analogous cobalt(II) complexes. This is apparent from the weak bands at 16,700 and 16,000 cm.$^{-1}$ in the spectra of $HgMn(NCS)_4$ and the ionic complex, respectively. These bands arise from the highest spin-allowed transition, $^4A_2(F) \longrightarrow {}^4T_1(P)$ of cobalt(II) in a tetrahedral ligand field. From the optical density of the band at 16,000 cm.$^{-1}$ in the

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[11] Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1962, **84**, 167.

[12] Jeffery, *Nature*, 1947, **159**, 610; 6th Internat. Congress and Symposia of the Internat. Union of Crystallography, Rome, 1963, *Acta Cryst.*, *Suppl.*, 1963, *A*, **66**, abstract 6.6.

spectrum of the tetraisothiocyanatomanganate(II) ion and the known molar extinction coefficient of this band for pure complexes containing the $[Co(NCS)_4]^{2-}$ ion, it appears that the cobalt(II) impurity is present only to the extent of about one part in 3500.

Neither of the tetrahedral manganese(II) isothiocyanate complexes showed, in ultra-violet radiation, even at ~80°K, the yellow-green fluorescence that has been observed with some other tetrahedral manganese(II) complexes.[13]

The pink quinolinium hexaisothiocyanatomanganate(II) described by Grossman and Hünseller [14] was prepared again in order to obtain a value of Δ for the octahedral ligand field of NCS groups around manganese(II). However, the reflectance spectrum of this compound contained a very strong band at ~28,000 cm.$^{-1}$, probably due to the cation, and all the *d–d* bands, except one at 19,700 cm.$^{-1}$, were hidden. The *d–d* bands for octahedral manganese(II) complexes are usually very weak. Solutions of the compound in organic solvents such as nitromethane are greenish-yellow and, from the electronic spectra, appear to contain mainly the tetrahedral tetraisothiocyanatomanganate(II) ions. We have confirmed, by *X*-ray powder photographs, the observation made by Grossman and Hünseller [14] that the compounds $(C_9H_8N)_4M(NCS)_6$, (M = Mn or Ni), are isomorphous.

Iron(II) *Complexes*.—The tetraisothiocyanatoferrate(II) ion has been obtained in the form of tetramethyl- and tetraethyl-ammonium salts. Both compounds are very readily oxidized in air. *X*-Ray powder photographs show that the compounds are isomorphous with their cobalt(II) analogues, and hence the ions $[Fe(NCS)_4]^{2-}$ are tetrahedral. The *X*-ray powder results for the tetraethylammonium salts are given in Table 4.

TABLE 4.

X-Ray powder results (*d*) for $[Et_4N]_2[M(NCS)_4]$, where M = Fe or Co.

Fe	9·50w,br	7·17w	6·57vw	6·03w	4·98vs	4·75s	4·17w	3·99m	3·80s,br		3·19vw	3·04s
Co	9·52m	7·13m		6·02w	4·98vs	4·72s	4·19w	4·00w	3·82m	3·71s	3·18vw	3·04s

The electronic spectra of the complexes have been obtained in the near-infrared and the visible region for the solids, by reflectance or by transmission, using the mull technique, and for solutions in nitromethane, acetone, or acetonitrile. The numerical results are listed in Table 3 and some typical spectra are shown in Fig. 2. All the spectra contain a strong band in the near-infrared region, with maxima at ~5800 and ~4600 cm.$^{-1}$. This band can be assigned as the transiton $^5E \longrightarrow {}^5T_2$ of iron(II) in a ligand field of T_d symmetry. From this a Δ value of 5200 ± 200 cm.$^{-1}$ is obtained for the tetraisothiocyanatoferrate(II) ion. The intensity of the band ($\varepsilon_{\text{molar}} = 142$ and 126 for the higher- and the lower-energy maxima, respectively, in nitromethane) is also in accord with a tetrahedral structure and is about one hundred times as large as those of the bands due to the transition $^5T_{2g} \longrightarrow {}^5E_g$ for octahedral iron(II) complexes.[15] The molar extinction coefficients are approximately double those reported [16] for the ions FeX_4^{2-} (X = Cl or Br). A similar relation has been observed [1,17] for the analogous complexes of cobalt(II).

The sharp bands observed on the low-energy side of the main absorption band in the solid-state spectra are probably combination bands from vibrational fundamentals of the NCS groups.

The separation observed for the components of the electronic band is of interest. Under the influence of spin–orbit coupling the $^5T_2$ upper level of iron(II) in a ligand field of T_d symmetry splits into six sublevels, which form three multiplets: T_2, $E + T_2$, and $A_1 + E + T_1$. The separation between the highest- and lowest-energy components is predicted to be $5\lambda'$ where λ' is the effective spin–orbit coupling constant for iron(II) in the compound being considered. The free-ion value of λ for iron(II) is -100 cm.$^{-1}$,[18] and

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[13] Goodgame and Cotton, *J.*, 1961, 3735, and refs. therein.
[14] Grossmann and Hünseller, *Z. anorg. Chem.*, 1905, **46**, 361.
[15] Cotton and Meyers, *J. Amer. Chem. Soc.*, 1960, **82**, 5023.
[16] Furlani, Cervone, and Valenti, *J. Inorg. Nuclear Chem.*, 1963, **25**, 159.
[17] Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1963, **83**, 4690.
[18] Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

therefore the three multiplets should be spread over an energy range no greater than 500 cm.$^{-1}$. In fact, a splitting of less than this value would be expected, since the effective spin–orbit coupling constants in complexes are generally smaller than the free-ion values. However, with the tetraisothiocyanatoferrate(II) ion, although only two components are resolved, the splitting of the band due to $^5E \longrightarrow {}^5T_2$ is ~1100 cm.$^{-1}$. Low and Weger [19] also report a large splitting (900 cm.$^{-1}$) in the $^5E \longrightarrow {}^5T_2$ band of iron(II) doped into sphalerite (ZnS). Splittings of electronic spectral bands larger than those predicted from simple spin–orbit coupling effects are, of course, not uncommon and may arise from one or more of several effects. In the solid state, crystal forces may cause a lowering of the site symmetry of the central metal ion. However, the splitting of the $^5E \longrightarrow {}^5T_2$ band for the tetraisothiocyanatoferrate(II) ion is much the same in solution as it is in the solid state. Hence, static distortions due to crystal effects do not seem to be of importance in this case.

Then we may consider the possibility of Jahn–Teller distortions, involving raising the degeneracies of the ^5E ground state or the $^5T_2$ excited state. Any static distortion arising from Jahn–Teller splitting of the ^5E level appears to be very small for tetrahedral iron(II) complexes. Compounds containing the ions FeX_4^{2-} (X = Cl or Br) are known [20] to be isomorphous with the analogous compounds of other first-series transition-metal ions which would not be expected to show any appreciable distortion of this type. Certainly, with the compound $(Me_4N)_2MCl_4$ (M = Co or Zn) the anions are very little distorted from T_d symmetry.[21] As mentioned above, the tetraisothiocyanatoferrate(II) salts that we have studied are isomorphous with their cobalt(II) analogues. Moreover, the results of infrared spectral studies [22] on the compounds containing the ions FeX_4^{2-} (X = halogen) or NCO [23] provide no indication for any pronounced departure from T_d symmetry in these cases.

The possibility arises that the splitting of the electronic band in the spectrum of the tetraisothiocyanatoferrate(II) ion is due to a dynamic Jahn–Teller effect involving a lifting of the degeneracy of the $^5T_2$ excited state. However, it is known that broadening of bands in electronic spectra can be caused, at least in part, by the presence of vibrational fine structure arising from differences in the geometry of ground and excited states of the molecules, due to *d*-electron rearrangement.[24] Therefore, interpretation of the splitting observed must await a study of the spectrum at low temperatures.

The magnetic susceptibility of tetraethylammonium tetraisothiocyanatoferrate(II) follows the Curie–Weiss Law over the range 294—100°K, with a Weiss constant of $-15°$. The effective magnetic moment, 5·42 B.M. at room temperature, is higher than would be expected for iron(II) with a ^5E ground state. Orbital contribution from the $^5T_2$ excited state should give magnetic moments of ~5·1 B.M. if we assume a free-ion value of λ and $\Delta = 5000$ cm.$^{-1}$. The presence of iron(III) as an impurity would increase the magnetic susceptibility. However, although we cannot rule out the presence of trace amounts of iron(III) in the samples studied, precautions were taken to minimize any oxidation. Some 35% of the iron would have to be in the tervalent state for all of the increase in the magnetic susceptibility to be attributed to this, which seems unlikely. High magnetic moments have also been reported for the tetrahalogenoferrate(II) ions.[16,20] Since the high moments cannot be explained by ferric impurity or the orbital contribution, they still pose a major problem in interpretaion.

An ion with a ^5E ground state should obey the Curie law. A negative Weiss constant could be caused by antiferromagnetic interactions or by small deviations from T_d symmetry.

[19] Low and Weger, *Phys. Rev.*, 1960, **118**, 1130.

[20] Gill, *J.*, 1961, 3512.

[21] Morosin and Lingafelter, *Acta Cryst.*, 1959, **12**, 611.

[22] Clark and Dunn, *J.*, 1963, 1198; Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189; Sabatini and Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

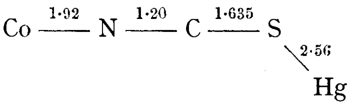
[23] Forster and Goodgame, preceding Paper.

[24] Weakliem, *J. Chem. Phys.*, 1962, **36**, 2117; Ferguson, *ibid.*, 1963, **39**, 116.

The temperature-independent contribution to the susceptibility from the second-order Zeeman effect is quite small, ~200 × 10^{-6} c.g.s.u., and allowance for this alters the Weiss constant by only ~1°. The origin of the observed temperature-dependence may well be related to the unexpectedly high magnetic moment.

The transmission spectrum of a mull of the compound $HgFe(NCS)_4$ is similar to that of the tetraisothiocyanatoferrate(II) ion. The broad, strong band in the near-infrared region has distinguishable maxima at 6250 and 5000 $cm.^{-1}$ (Fig. 2). The spectrum provides good evidence for an essentially tetrahedral environment for iron(II) in this compound, and the band may be assigned as the $^5E \longrightarrow {}^5T_2$ transition. From the position of this band the value of Δ is 5600 ± 200 $cm.^{-1}$, which is somewhat larger than the Δ value for the tetraisothiocyanatoferrate(II) ion. A similar situation has been found [1] for the analogous compounds of cobalt(II), for which the values of Δ are: $HgCo(NCS)_4$ 4880 and $Co(NCS)_4^{2-}$ 4550 $cm.^{-1}$.

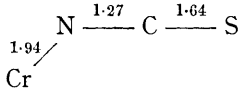
For cobalt(II) complexes, the difference in the ligand-field strengths of the NCS groups in the two types of compound may be rationalized on the basis of the structures. The compound $HgCo(NCS)_4$ contains bridging thiocyanate groups with the following dimensions: [12]



The grouping Co–N–C is virtually linear (∠CoNC = 178·6 ± 1·2°). However, in potassium tetraisothiocyanatocobaltate(II) the Co–N bond [5] is appreciably longer (2·15 Å) and ∠Co–N–C = 111°. The linearity of the Co–N–C group in the bridged compound permits Co–N π-bonding and a shorter Co–N bond and hence a larger Δ value than in the complex anion. A similar situation may well hold for the iron(II) compounds. However, it is generally found [25] that there is a wide range of M–N–C bond angles for co-ordinated isothiocyanate groups, and it is likely that in the solid state the geometry may be dictated very largely by crystal forces. For example, in Reinecke's salt [26] the Cr–N–C group is linear and the bond distances are:

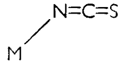
$$\mathrm{Cr} \overset{1\cdot97}{\text{———}} \mathrm{N} \overset{1\cdot14}{\text{———}} \mathrm{C} \overset{1\cdot80}{\text{———}} \mathrm{S}$$

and the pyridinium salt is very similar. But, in the corresponding choline salt, the isothiocyanate groups are bonded as follows: [26]



∠Cr–N–C = 155·5°.

These differences were attributed [26] to smaller polarization of the NCS groups by the choline cation (thus favouring the canonical form I) than those produced by the ammonium or pyridinium cations, which favour (II).

(I)


$M-\overset{+}{N}\equiv C-S^-$ (II)

Iron(III) *Complex*.—The red complex species formed by mixtures of ferric and thiocyanate ions in various solvents have been investigated by many workers as a means of determining iron colorimetrically.[27] Numerous "double salts" of ferric thiocyanate with alkali-metal thiocyanates have been described; [3] these are usually hydrated. We have obtained anhydrous tetramethylammonium hexaisothiocyanatoferrate(III) from alcohol. The magnetic moment of this compound is that expected for a high-spin d^5 complex. The reflectance spectrum has a very strong, broad charge-transfer band at

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[25] Hazell, *J.*, 1963, 5745.

[26] Takeuchi and Saito, *Bull. Chem. Soc. Japan*, 1957, **30**, 319.

[27] Vogel, "Quantitative Inorganic Analysis," 2nd edn., Longmans, Green and Co. Ltd., 1955, p. 645.

$\sim$21,400 cm.$^{-1}$. Two weak bands are also found at 10,640 and $\sim$17,500 cm.$^{-1}$ (the latter appears as a shoulder on the side of the charge-transfer band), which are probably due to the transitions $^6A_{1g} \longrightarrow {}^4T_{1g}$(G) and $^6A_{1g} \longrightarrow {}^4T_{2g}$(G), respectively.

Although the tetrahedral tetraisocyanatoferrate(III) ion has been obtained [23] attempts to prepare an analogous thiocyanato-complex have so far been unsuccessful.

EXPERIMENTAL

Preparation of the Compounds.—Compounds X^+NCS^-, where X = Me_4N, Et_4N, or Bu^nPh_3P, were prepared by metathetic reactions between the corresponding chlorides or bromides in ethanol and potassium thiocyanate in acetone, and were recrystallized from ethanol.

Quinolinium hexaisothiocyanatomanganate(II) and nickelate(II) were prepared as described by Grossman and Hünseller.[14]

n-Butyltriphenylphosphonium tetraisothiocyanatomanganate(II). A solution of manganese(II) chloride tetrahydrate (0·75 g.) in ethanol (10 ml.) was mixed with one of potassium thiocyanate (0·74 g.) in acetone (20 ml.), and then filtered into a solution of n-butyltriphenylphosphonium thiocyanate (3·0 g.) in ethanol (15 ml.). The pale green solution was evaporated *in vacuo* to a volume of $\sim$10 ml., and then cooled to 0°. Pale green crystals separated, which were filtered off, washed with ether, and dried *in vacuo* (47%; m. p. 119°) (Found: C, 62·1; H, 6·0; N, 6·05. $C_{48}H_{48}MnN_4P_2S_4$ requires C, 62·3; H, 5·2; N, 6·05%). The *compound* is soluble in alcohols, nitrobenzene, nitromethane, acetone, and acetonitrile.

Tetramethylammonium and Tetraethylammonium Tetraisothiocyanatoferrate(II). Solutions of these complexes in acetone–ethanol were obtained in the same way as that of the previous compound. The *tetramethylammonium salt* was obtained by dissolving the tetramethylammonium thiocyanate in hot ethanol, and adding the ferrous thiocyanate solution. The iron(II) complex separated immediately as pale yellow crystals. The complex was filtered off, washed with ethanol, then ether, and dried *in vacuo* (56%, m. p. 215°) (Found: C, 33·4; H, 5·8; N, 18·5. $C_{12}H_{24}FeN_6S_4$ requires C, 33·0; H, 5·5; N, 19·3%). The *tetraethylammonium salt* was isolated from its acetone–ethanol solution by addition of ether until a slight turbidity appeared; the solution was then cooled to −40°; pale red crystals were formed; they were recrystallized twice from acetone–ethanol under nitrogen and dried *in vacuo* (70%; m. p. 100°) (Found: C, 43·4; H, 7·35; N, 14·6. $C_{20}H_{40}FeN_6S_4$ requires C, 43·8; H, 7·3; N, 15·3%). Both compounds are very readily oxidized in air.

Tetramethylammonium hexaisothiocyanatoferrate(III). This *complex* resulted from an attempt to prepare a compound containing the tetraisothiocyanatoferrate(III) ion. A solution of ferric thiocyanate, prepared by mixing solutions of ferric nitrate nonahydrate (5·6 g.) in ethanol (15 ml.) and potassium thiocyanate (4·0 g.) in acetone (30 ml.), was filtered into a hot solution of tetramethylammonium thiocyanate (2 g.) in ethanol (40 ml.). Dark green crystals (red when powdered) separated and were filtered off, washed with ether, and dried *in vacuo* (22%; m. p. 254°) (Found: C, 34·1; H, 5·7. $C_{18}H_{36}FeN_9S_6$ requires C, 34·5; H, 5·75%). The complex gives deep red solutions in alcohols, acetone, nitrobenzene, nitromethane, or acetonitrile.

Tetraisothiocyanatocobaltate(II) *salts.* The preparation of the tetramethylammonium salt has been reported previously.[1] The *tetraethylammonium* (*a*) and the *n-butyltriphenylphosphonium* (*b*) *salt* were prepared by a similar method and were recrystallized from acetone–ethanol [(*a*) Found: C, 43·75; H, 6·9. $C_{20}H_{40}CoN_6S_4$ requires C, 43·6; H, 7·3%. (*b*) Found: C, 62·3; H, 5·1. $C_{48}H_{48}CoN_4P_2S_4$ requires C, 62·0; H, 5·2%].

Compounds $HgMn(NCS)_4$ *and* $HgFe(NCS)_4$. These were prepared by the method of Rosenheim and Cohn.[8]

Physical Measurements.—The infrared spectra were obtained with a Grubb-Parsons Spectromaster grating spectrometer or with a Perkin-Elmer model 21 spectrometer with rock-salt or calcium fluoride optics. The other physical measurements were carried out as described previously.[10]

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INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7.

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