Iron(II) and Copper(I) Complexes with Some Substituted 1,2-Dithiole-3-thiones

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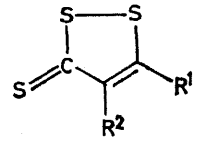
The ligand 1,2-dithiole-3-thione and some derivatives substituted in the 4- and/or 5-positions yield complexes of the type FeX_2L_2(X = Cl, Br, or I). Iron(III) chloride is reduced, to give $FeCl_2L_2$, and copper(II) salts yield copper(I) complexes of the types $CuXL_2$ (X = Cl, Br, or NO_3) or $CuXL_3$ (X = Cl, Br, or ClO_4). Physical studies, particularly electronic and Mössbauer spectra, show that the iron(II) compounds have pseudotetrahedral structures.

THERE is appreciable interest in the compounds of iron with sulphur donors, as these ligands often stabilise the lower oxidation states and produce systems with unusual magnetic behaviour or co-ordination geometry. This interest has been heightened by the recognition that the iron atoms in some electron transfer proteins, such as the ferrodoxins, are surrounded by a tetrahedral array of sulphur atoms.



	R^1	R^2	Formula
(I)	H	H	$C_3H_2S_3$
(II)	Me	H	$C_4H_4S_3$
(III)	Me	Me	$C_5H_6S_3$
(IV)	C_4H_3S	H	$C_7H_4S_4$
(V)	Ph	H	$C_9H_6S_3$
(VI)	C_7H_7O	H	$C_{10}H_8OS_3$

During studies [1,2] of the co-ordination chemistry of 1,2-dithiole-3-thione (I) and of some of its derivatives (II—VI) it has been found that these sulphur ligands reduce iron(III) to iron(II) and induce iron to adopt a tetrahedral geometry. We report here the results of physical studies on these compounds and on some copper(I) complexes obtained from attempts to isolate the related copper(II) compounds.

RESULTS AND DISCUSSION

Iron Compounds.—Compounds of stoicheiometry FeX_2L_2 were obtained quite readily from the calculated quantities of iron(II) halide and the thiones in mixtures of acetone and alcohols, with the addition of 2,2-dimethoxypropane to remove water. Attempts to obtain iron(III) complexes always resulted in the formation of iron(II) compounds in pure form. I.r. evidence suggested that in reducing the iron(III) to iron(II) the 1,2-dithiole-3-thione is converted to the corresponding 3-ketone.

The room temperature magnetic moments of the complexes (Table 1) show that they all contain high-spin iron(II): the moments are 5·1—5·5 B.M.

Good evidence for the presence of a tetrahedral co-ordination geometry is afforded by the electronic spectra of the solid compounds (Table 1), as the *d–d* bands are all at very low energies ($\leqslant$6280 cm^{-1}). Departures from strict T_d symmetry should result in a splitting of both the ^5E ground state and the $^5T_2$ excited state. Except for the compounds $FeBr_2(C_3H_2S_3)_2$, $FeBr_2(C_9H_6S_3)_2$, and $FeI_2(C_9H_6S_3)_2$ two *d–d* bands were observed in each case. For systems of C_{2v} symmetry, the highest formal symmetry for FeX_2L_2 compounds of approximately tetrahedral geometry, three bands are expected but usually [3] only one or two bands are resolved at instrumentally convenient frequencies.

The compounds $FeX_2(C_3H_2S_3)_2$ (X = Cl or Br) and $FeBr_2(C_7H_4S_4)_2$ show a shoulder in the 15 000—19 000 cm^{-1} region, possibly attributable to a spin-forbidden transition. There are also bands in this region in the other compounds, but these absorptions are much more intense, and they are probably electron-transfer bands.

Further evidence for the pseudo-tetrahedral geometry of the FeX_2L_2 compounds comes from their low frequency i.r. spectra (Table 2). For a co-ordination arrangement FeX_2S_2 of C_{2v} symmetry two ν(Fe–X) and two ν(Fe–S) i.r. active bands are expected. The ν(Fe–X) bands were identified by comparing the spectra of the complexes in which X was varied but L was kept unchanged. The ν(Fe–X) bands were found in the following ranges: X = Cl 292—350, X = Br, 215—270, and X = I, 200—231 cm^{-1}. The ν(Fe–S) absorptions were observed as a pair of bands (or, in four cases, as one band) in the region 278—320 cm^{-1}. The frequencies of the ν(Fe–S) bands varied with the identity of the thione present, as expected, but the X-dependence of the ν(Fe–S) bands for a given thione was rather small. For the compounds $FeX_2(C_3H_2S_3)_2$ there was a strong band at 206—209 cm^{-1} which was X-independent, and which may be due to δ(Fe–S–C) or a combination band.

The presence of solvate methanol in a compound which analysed as $FeBr_2(C_3H_2S_3)_2,\frac{1}{2}MeOH$ was confirmed by i.r. bands at 3500 and 1600 cm^{-1}.

Confirmation of the proposed pseudotetrahedral geometry was obtained by Mössbauer studies. The spectra at 77 K (or in one case at 100 K) consisted of a

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[1] F. Petillon and J. E. Guerchais, *Bull. Soc. chim. France*, 1971, 2455.

[2] F. Petillon and J. E. Guerchais, *Canad. J. Chem.*, 1971, **49**, 2598.

[3] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 454.

quadrupole split doublet with quadrupole splitting (Q.S.) values of 2·79—3·24 mm s^{-1} and chemical isomer shifts (I.S.) of +0·75 to +0·81 mm s^{-1}, relative to natural iron (Table 1). The spectra of $FeCl_2(C_3H_2S_3)_2$ and $FeBr_2(C_7H_4S_4)_2$ each showed a weaker, additional doublet.

The I.S. values are much lower than those found[4] for six-co-ordinate, high-spin iron(II) compounds, either monomeric or polymeric. Comparison may be made with I.S. values of +1·14 mm s^{-1} for six-co-ordinate $FeCl_2$(thiourea)$_4$[5] and of +0·81 to +0·91 for some other tetrahedral FeX_2L_2 compounds with sulphur donor ligands.[5] As may be seen in Table 1, changing the halide ion in the FeX_2L_2 complexes reported here has little effect on the I.S. values.

TABLE 1

Some physical data for the complexes

Complexes	Λ/Ω^{-1} mol^{-1} cm^2 [a]	μ/B.M.	Mössbauer parameters [b] δ(Fe)/mm s^{-1}	Mössbauer parameters [b] Δ/mm s^{-1}	Absorptions/cm^{-1} $^5E \rightarrow {}^5T_2$	Absorptions/cm^{-1} Charge transfer or spin-forbidden bands	Found (Calc.) % C	H	S	Metal	Halogen or N
$FeCl_2(C_3H_2S_3)_2$	54	5·18	0·80 [c]	2·95 [c]	4680sh, 6050	17 670sh	18·8 (18·25)		47·8 (48·65)	14·1 (14·15)	18·2 (17·95)
$FeBr_2(C_3H_2S_3)_2$	47	5·24	0·81	3·18	5675	17 330sh	15·7 (14·9)		38·3 (39·7)	11·7 (11·55)	33·7 (33·0)
$FeBr_2(C_3H_2S_3)_2,\frac{1}{2}MeOH$							16·9 (15·6)	1·15 (1·2)	38·4 (38·45)	11·5 (11·15)	32·3 (31·95)
$FeI_2(C_3H_2S_3)_2$	39	5·36			4410sh, 5000	16 500	12·9 (12·45)		33·2 (33·25)	9·6 (9·65)	43·6 (43·9)
$FeCl_2(C_4H_4S_3)_2$	54	5·35	0·80	3·00	4935sh, 5720	18 050	22·5 (22·7)		45·3 (45·45)	13·3 (13·2)	17·2 (16·75)
$FeBr_2(C_4H_4S_3)_2$	45	5·34			4480sh, 5700	17 980	18·7 (18·75)	1·7 (1·55)	35·4 (35·75)	11·8 (10·9)	30·9 (31·2)
$FeCl_2(C_5H_6S_3)_2$	51	5·17	0·79	2·84	5070sh, 5980	18 800	26·9 (26·6)		42·2 (42·6)	12·4 (12·35)	15·5 (15·7)
$FeBr_2(C_5H_6S_3)_2$	42	5·36	0·80	3·10	4450sh, 5680	18 315	22·2 (22·25)	2·25 (2·25)	35·0 (35·6)	10·7 (10·35)	29·4 (29·6)
$FeI_2(C_5H_6S_3)_2$	44	5·32	0·75	3·24	4440sh, 5540	17 420	18·9 (18·95)	2·0 (1·9)	29·0 (30·35)	9·4 (8·8)	38·8 (40·0)
$FeBr_2(C_7H_4S_4)_2$	40	5·40	0·77 [d]	3·03 [d]	4630sh, 5640	15 410sh	26·5 (25·95)	1·45 (1·25)	37·6 (39·5)	8·7 (8·6)	24·4 (24·65)
$FeI_2(C_7H_4S_4)_2$	56	5·50	0·79	3·24	4290sh, 5320		22·3 (22·65)	1·25 (1·1)	32·7 (34·55)		33·5 (34·2)
$FeCl_2(C_9H_6S_3)_2$		5·22	0·81 [b]	2·79 [b]	4390sh, 5840	18 350, 16 310	39·5 (39·5)	2·35 (2·2)	34·0 (35·15)	10·1 (10·2)	13·2 (12·95)
$FeBr_2(C_9H_6S_3)_2$		5·11			5380	18 450, 16 120	33·9 (33·95)	2·05 (1·9)	30·2 (30·25)	9·2 (8·75)	25·0 (25·1)
$FeI_2(C_9H_6S_3)_2$		5·32	0·78	3·03	4810	17 860	29·7 (29·6)	1·85 (1·65)	25·6 (26·35)	7·9 (7·65)	34·6 (34·75)
$FeCl_2(C_{10}H_8OS_3)_2$	41	5·10			4980sh, 6280	18 450, 16 260	39·5 (39·55)	2·65 (2·65)	30·6 (31·65)	9·4 (9·2)	12·3 (11·65)
$FeBr_2(C_{10}H_8OS_3)_2$	46	5·30	0·79	3·00	4220sh, 5850	18 720, 16 080	34·5 (34·5)	2·3 (2·3)	25·6 (27·6)	8·7 (8·0)	
$FeI_2(C_{10}H_8OS_3)_2$		5·35	0·77	3·02	4780sh, 5710	18 180 ,15 410	30·4 (30·4)	2·2 (2·05)	23·5 (24·35)	7·9 7·05)	31·7 (32·1)
			Infrared spectral assignments δ(C=S)	Infrared spectral assignments ν(Cu–S)							
$CuCl(C_3H_2S_3)_2$	35 [e]; 3·7 [f]	0·3	366w, 353mw	310sh, 288s		17 980, 10 290sh	19·3 (19·6)	1·1 (1·1)	52·3 (52·35)	14·8 (17·3)	10·2 (9·65)
$CuBr(C_3H_2S_3)_2$	48 [e]: 1·4 [f]	0·3	364w, 353mw	310w, 290s		18 650, 12 640sh	17·6 (17·5)	1·0 (1·0)	46·1 (46·85)	14·6 (15·4)	19·4 (19·4)
$CuCl(C_4H_4S_3)_2$	69 [e]; 7 [f]	0·3	333w	308mw, 278s		10 530sh	24·3 (24·3)	2·05 (2·05)	48·3 (48·65)	15·0 (16·05)	9·2 (8·95)
$CuCl(C_7H_4S_4)_3$	62 [g] ; 3 [f]	Diamagn.		274m [h]		16 030	33·8 (33·7)	1·6 (1·6)	51·4 (51·45)	8·7 (8·5)	4·5 (4·75)
$CuBr(C_7H_4S_4)_3$	0·9 [f]	0·3		272s [i]		16 800	31·4 (31·8)	1·45 (1·55)	46·2 (48·55)		10·2 (10·1)
$CuCl(C_9H_6S_3)_2$	56 [e]; 2·3 [f]	Diamagn.	369m	307mw [j]		17 070	42·5 (41·6)	2·35 (2·35)	37·0 (37·0)	12·5 (12·25)	7·0 (6·8)
$CuBr(C_9H_6S_3)_2$	52 [e]; 2·1 [f]	0·1	368s	309m		17 060	38·7 (38·3)	2·2 (2·15)	32·8 (34·1)		14·2 (14·2)
$CuNO_3(C_9H_6S_3)_2$	5 [k]	0·6	355w	303w		17 210, 10 920sh	40·3 (39·6)	2·25 (2·2)	35·6 (35·2)	10·6 (11·65)	2·45 (2·55)
$\{Cu(C_9H_6S_3)_3\}ClO_4$	102 [g]; 19 [k] 24 [f]	0·6	359w	301mw		17 510	41·4 (40·85)	2·4 (2·3)	35·8 (36·35)	8·0 (8·0)	4·45 (4·45)

[a] 10^{-3}M in nitromethane unless stated otherwise. [b] At 77 K except $FeCl_2(C_9H_6S_3)_2$ which is at 100 K; errors in δ and Δ ±0·02 mm s^{-1}. [c] Additional weak doublet δ(Fe) +1·4, Δ 3·1 mm s^{-1}. [d] Additional weak doublet δ(Fe) +0·48, Δ 0·73 mm s^{-1}. [e] 5 × 10^{-4}M in acetonitrile. [f] 5 × 10^{-4}M in nitrobenzene. [g] 10^{-3}M in acetonitrile. [h] Other bands: ν(Cu–Cl) 202s, ν(Cu–S) + δ(ring) 560m, uncertain 303w, 233w cm^{-1}. [i] Other bands: ν(Cu–S) + δ(ring) 558m, uncertain 303mw, 233w cm^{-1}. [j] Other band ν(Cu–Cl) 244s cm^{-1}. [k] 10^{-3}M in nitrobenzene.

The Q.S. values are all quite large, reflecting appreciable distortions of the ligand field from T_d symmetry, comparable to those recently reported by Birchall and Morris[5] for tetrahedral iron(II) complexes with thioacetamide and thiourea derivatives. In contrast with the results for some tetrahedral FeX_2L_2 complexes with *N*-donor ligands,[6] for which Q.S. decreased in the order Cl > Br > I, the Q.S. values of the tetrahedral FeX_2S_2 systems increase along a series Cl < Br < I.

As stated above, two compounds gave a weak additional doublet in the Mössbauer spectrum. The complex $FeCl_2(C_3H_2S_3)_2$ had an extra pair of bands with parameters: I.S. +1·4 mm s^{-1}, and Q.S. 3·1 mm s^{-1}. One explanation of this is the presence of small amounts of a compound $FeCl_2(C_3H_2S_3)_4$ for which such parameters would be expected, but there is no evidence for this from the analytical results. The compound $FeBr_2(C_7H_4S_4)_2$ had an extra weak doublet with smaller Q.S. (0·73 mm s^{-1}) and a more negative I.S. (+0·48 mm s^{-1} relative to Fe), but an unambiguous identification of the likely impurity giving rise to this feature is not really possible.

Copper Compounds.—Although copper(II) salts were used as starting materials copper(I) complexes of stoicheiometry $CuXL_2$ or $CuXL_3$ were formed. These were little soluble in common organic solvents (alcohols, acetone, nitromethane, *etc.*) but they were quite soluble in acetonitrile and in nitrobenzene. From electrolytic conductance measurements (Table 1) the copper(I) perchlorate complex of stoicheiometry $Cu(C_9H_6S_3)_3(ClO_4)$ may be formulated as a 1 : 1 electrolyte $\{Cu(C_9H_6S_3)_3\}ClO_4$, or as a binuclear species $\{Cu(C_9H_6S_3)_3\}_2(ClO_4)_2$.

The low molar conductance values in nitrobenzene (Table 2) observed for most of the copper compounds suggest that they are non-electrolytes. In acetonitrile there is significant dissociation in most cases.

X-Ray powder photographs showed that the following pairs of compounds were isomorphous: (i) $CuX(C_7H_4S_4)_3$ (X = Cl or Br), (ii) $CuX(C_3H_2S_3)_2$ (X = Cl or Br), (iii) $CuX(C_9H_6S_3)_2$ (X = Cl or Br).

In an attempt to obtain further information concerning the structures of the complexes their low-frequency (200—400 cm^{-1}) i.r. spectra were measured (Table 1).

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[4] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971, ch. 6.

[5] T. Birchall and M. F. Morris, *Canad. J. Chem.*, 1971, **50**, 211.

[6] Ref. 4, p. 146.

$CuX(C_9H_6S_3)_2$ (X = Cl, Br, or NO_3).—Baldwin *et al.*[7] have assigned a band at 215 cm^{-1} in the spectrum of $(CuCl)_2$ (2,2′-azopyridine) as ν(Cu^I–Cl). A similar assignment may be made for a strong band at 244 cm^{-1} in the spectrum of $CuCl(C_9H_6S_3)_2$ as this is absent from the spectra of the isomorphous bromide and the nitrate.

TABLE 2

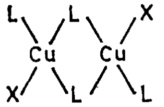
Infrared spectral assignments for the compounds FeX_2L_2/cm^{-1}

Compounds	ν(C=S) + ν(ring)	ν_s^{as}(Fe–X)	δ(C=S) or combination	ν(Fe–S)
$C_3H_2S_3$	1164s		354m	
$FeCl_2(C_3H_2S_3)_2$ [a]	1186 1180 } s	340s 292m	373m 369mw	320m 301m
$FeBr_2(C_3H_2S_3)_2$ [a, b]	1184 1180 } s	265s 221m	372m 367mw	318m 300m
$FeI_2(C_2H_3S_3)_2$ [c]	1173s	221vs	363mw	318mw 306m
$C_4H_4S_3$	1178s		316mw	
$FeCl_2(C_4H_4S_3)_2$	1188s	335s 308m	340sh	278s
$FeBr_2(C_4H_4S_3)_2$	1189s	270vs 221s	340mw	288mw
$C_5H_6S_3$	1162s		344m	
$FeCl_2(C_5H_6S_3)_2$	1156s	342vs 322m	357m	285s
$FeBr_2(C_5H_6S_3)_2$	1159s	270vs 223m	355m	298mw 286m
$FeI_2(C_5H_6S_3)_2$	1153s	231s 200m	355m	298w 284mw
$C_7H_4S_4$	1184s		347 343 } w	
$FeBr_2(C_7H_4S_4)_2$	1192s	270vs 224m	356 344 } vw	308mw 293m
$FeI_2(C_7H_4S_4)_2$	1207s	219s 203w	351 340 } w	308mw 296mw
$C_9H_6S_3$	1189s 1178s		344m	
$FeCl_2(C_9H_6S_3)_2$	1204m 1195s	348vs	368mw	314m 300s
$FeBr_2(C_9H_6S_3)_2$	1203m 1193s	268s 220m	362mw	310mw 301s
$FeI_2(C_9H_6S_3)_2$	1205m 1194s	229vs 204mw	360mw	315w 306s
$C_{10}H_8OS_3$	1192s			
$FeCl_2(C_{10}H_8OS_3)_2$	1201s	350m 320mw		300m
$FeBr_2(C_{10}H_8OS_3)_2$	1200s	269s 215w		315w 305m
$FeI_2(C_{10}H_8OS_3)_2$	1200s	230s		312w 298w

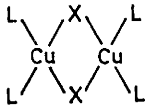
[a] δ(Fe–S–C) 206s cm^{-1}. [b] Spectrum of $FeBr_2(C_3H_2S_3)_2$,-½MeOH similar plus ν(OH) 3500s and δ(OH) 1600m cm^{-1}. [c] δ(Fe–S–C) 209vs cm^{-1}.

The presence of this absorption above 200 cm^{-1} strongly implies that the halogen atoms are non-bridging. Apart from this, all three compounds have a medium intensity band near 306 cm^{-1} which may be assigned as ν(Cu^I–S) of a terminal ligand. If copper(I) has four-co-ordination a likely structure is (A) with the metal atoms each adopting an approximately tetrahedral geometry (three-co-ordination cannot be ruled out, *a priori*,[8] but is less likely).

$CuX(C_3H_2S_3)_2$ (X = Cl *or* Br) *and* $CuCl(C_4H_4S_3)_2$.—These compounds show two bands in the region expected for ν(Cu^I–S) for a terminally bound ligand, but there are no bands attributable to ν(Cu^I–X) above 200 cm^{-1}. A structure of the type (B) may account for these observations, again with each metal atom having approximately tetrahedral geometry.



(A)



(B)

$CuX(C_7H_4S_4)_3$ (X = Cl *or* Br).—The structure of these compounds are very likely to be $CuXS_3$ tetrahedra. The strong band at 202 cm^{-1} for the chloride is absent in the spectrum of the isomorphous bromide, and may be assigned as ν(Cu^I–Cl). Two or three ν(Cu–S) bands would be expected for a distorted tetrahedral geometry. Although the medium-strong band near 273 cm^{-1} is clearly one of the ν(Cu–S) bands, the other assignments made in Table 1 are less certain because this sulphur ligand has two weak bands, at 215 and 295 cm^{-1}, which may shift and gain intensity on co-ordination.

EXPERIMENTAL

All compounds were dried in vacuum over P_2O_5. Analytical data are given in Table 1.

$FeCl_2L_2$.—(*a*) *From iron*(II) *chloride.* $FeCl_2,4H_2O$ (Merck) (0·04 mol) was dehydrated in acetone–2,2-dimethoxypropane containing iron powder. To the filtered solution was added the organic ligand (0·08 mol) in the minimum quantity of acetone. Concentration of the solution caused precipitation of the complexes, which were filtered off and washed with a little acetone (yields *ca.* 65%). Samples made from oven-dried iron(II) chloride were less pure than those obtained by the method outlined above.

(*b*) *From iron*(III) *chloride.* A solution of the organic ligand (0·12 mol) in acetone was added to one of iron(III) chloride (0·04 mol) in ethanol–2,2-dimethoxypropane. The mixture was refluxed for 1 h. Concentration of the solution gave a precipitate of the iron(II) complex.

$FeBr_2L_2$.—Hydrated iron(II) bromide (Roc-Ric reagent) (0·04 mol) was dehydrated as for the chloride and then treated with the organic ligand (0·08 mol) in acetone. Brown precipitates were obtained which were filtered off and washed with acetone. Dark green $FeBr_2(C_3H_2S_3)_2$,-½MeOH was obtained from methanol–2,2-dimethoxypropane solutions.

FeI_2L_2.—These were obtained essentially as for the chlorides starting from iron(II) iodide (K and K reagent).

$CuXL_2$, $CuXL_3$ (X = Cl *or* Br).—Anhydrous copper(II) halide (0·02 mol) and the organic ligand (0·07 mol) were

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[7] D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, 1969, **8**, 107.

[8] M. S. Weininger, G. W. Hunt, and E. L. Amma, *J.C.S. Chem. Comm.*, 1972, 1140.

refluxed in ethanol for 1 h to give a precipitate of the complex, which was collected and washed with ethanol.

$Cu(NO_3)(C_9H_6S_3)_2$ *and* $[Cu(C_9H_6S_3)_3]ClO_4$.—The copper (II) salt was dehydrated by refluxing with ethanol–2,2-dimethoxypropane and then treated as for the halogeno-complexes. Precipitation occurred on cooling, but sometimes it was found necessary to add some light petroleum.

Physical Measurements.—Mössbauer spectra were obtained at the P.C.M.U. Harwell. Other measurements were made as described previously.[1]

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