Preparation and Study of Some Dithiolylium Salts

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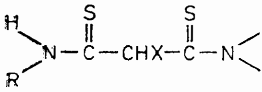
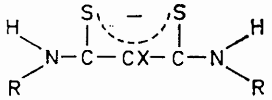
The salts 3,5-diamino- or 3,5-di(methylamino)-1,2-dithiolylium perchlorate or bromide and 4-chloro-(or 4-bromo-)3,5-diamino- or 3,5-di(methylamino)-1,2-dithiolylium chloride or bromide have been prepared by oxidation of dithiomalonamide or *NN'*-dimethyldithiomalonamide. Conductivity, molecular-weight, ^{1}H n.m.r., u.v., i.r., and polarographic measurements are reported. The removal of a proton from the CH_2 group of the dithiomalonamides gives a five-membered ring with pseudo-aromatic character. All the experimental data support considerable π bonding between the sulphur atoms, and this confers great stability on the disulphide group. The stability of the 3,5-diamino- or 3,5-di(methylamino)-1,2-dithiolylium salts is greater than that of the 4-chloro-3,5-diamino- or 3,5-di(methylamino)-1,2-dithiolylium salts. The reduction of these salts occurs in one two-electron wave. Mono- and bis-dithiolylium salts of tetrachloro-ferrate(III), -cobaltate(II), -niccolate(II), and -cuprate(II) have also been prepared. Their magnetic moments and electronic and i.r. spectra suggest a tetrahedral configuration for the $[FeCl_4]^-$ anions and a distorted tetrahedral configuration for the $[MCl_4]^{2-}$ (M = Co, Ni, or Cu) anions, and absence of co-ordination of the dithiolylium ions which act as cations.

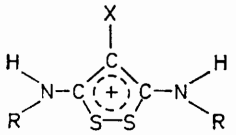
THE co-ordination properties of dithiomalonamides, (I), have been previously studied. Dithiomalonamides are structurally analogous to β-dithioketones, with the advantage of being isolable ligands which can be compared with their complexes. Previously, we have demonstrated that in neutral media dithiomalonamide, (Ia), *NN'*-dimethyldithiomalonamide, (Ib), and *NN'*-diphenyldithiomalonamide, (Ic), give *SS'*-co-ordinated complexes $[ML_2]$ [M = Ni[1,2] and Pd[3,4]; L = (IIa), (IIb), or (IIc)] and $[AuL_2X]$ [L = (IIa) or (IIc), X = Cl; L = (IIb), X = $[AuCl_4]^-$[5]], and in acid media *NS*-co-ordinated cationic complexes of the types $[ML_2]X_2$ (M = Ni[1,2] and Pd[3,4]) and $[NiL_3]X_2$,[1,2] and neutral complexes of the type $[PdLX_2]$[3,4] [L = (Ia), (Ib), or (Ic)].



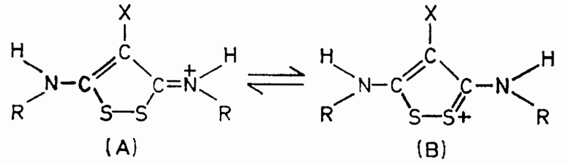
	R	X
(Ia)	H	H
(Ib)	Me	H
(Ic)	Ph	H



	R	X
(IIa)	H	H
(IIb)	Me	H
(IIc)	Ph	H



	R	X
(IIIa)	H	H
(IIIb)	H	Cl
(IIIc)	H	Br
(IIId)	Me	H
(IIIe)	Me	Cl
(IIIf)	Me	Br



In this work we examine the capacity of these ligands to form cations through oxidation. The cations are unsaturated five-membered cyclic disulphides and pseudo-aromatic systems,(III), the stability of which may be attributed to resonance stabilization involving structures (A) and (B). The major interest in compounds of this class has been in the dye industry.[6] Their use as cationic dyes and intermediates for synthetic fibres has been studied by a number of investigators.[7-9] Quiniou and his co-workers[10,11] have prepared and studied a great number of 1,2-dithiolylium derivatives. Of the compounds reported in this work, only 3,5-diamino-1,2-dithiolylium perchlorate has been previously studied, by Jensen *et al.*[12] who also prepared 3,5-diamino-1,2-dithiolylium chloride, the radioprotective properties of which have been recently investigated.[13]

EXPERIMENTAL

The ligands were prepared as previously described.[1,2] The following concentrations were used: $MeCO_2H$, glacial; $HClO_4$, 70%; HCl 37%; HBr, 58%; and H_2O_2, 35%. All reagents were of pure chemical grade.

Preparations of Dithiolylium Salts.—3,5-*Diamino*-1,2-*dithiolylium perchlorate*, [(IIIa)][ClO$_4$]. Compound (Ia)

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[10] F. Clesse, J. P. Pradere, and H. Quiniou, *Bull. Soc. chim. France*, 1973, 586 and refs. therein.

[11] J. P. Guemas and H. Quiniou, *Bull. Soc. chim. France*, 1973, 592 and refs. therein.

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[13] G. N. Alekseeva, A. V. El'tsov, M. B. Kolesova, L. I. Maksimova, and A. M. Rusanov, *Zhur. farm. Khim.*, 1972, **6**, 23.

(0.625 mmol) was dissolved in a mixture of water (15 cm^3), perchloric acid (5 cm^3), and hydrogen peroxide (2 cm^3). The warm solution was cooled and pale yellow crystals precipitated.

3,5-*Diamino*-4-*chloro*-1,2-*dithiolylium chloride*, [(IIIb)]Cl. On cooling a warm solution containing (Ia) (0.625 mmol) in HCl (15 cm^3) and H_2O_2 (1.5 cm^3), pale yellow crystals were obtained. The compound was recrystallized from ethanol and diethyl ether.

3,5-*Diamino*-4-*bromo*-1,2-*dithiolylium bromide*, [(IIIc)]Br. Hydrogen peroxide (2 cm^3) was added dropwise to a filtered warm solution containing (Ia) (0.625 mmol) in water (40 cm^3) and HBr (8 cm^3). Yellow crystals were obtained on cooling.

3,5-*Di*(*methylamino*)-1,2-*dithiolylium perchlorate or bromide*, [(IIId)][ClO_4] *or* [(IIId)]Br. Iron(III) perchlorate hexahydrate or iron(III) bromide hexahydrate (0.7 mmol) in water (5 cm^3) was added to a warm solution containing (Ib)(0.625 mmol) in water (40 cm^3). The white crystalline compound was obtained on cooling.

4-*Chloro*-3,5-*di*(*methylamino*)-1,2-*dithiolylium chloride*, ([IIIe)]Cl. Pale yellow crystals separated after some hours from a mixture of (Ib) (12.5 mmol) in HCl (30 cm^3) and H_2O_2 (4 cm^3).

4-*Bromo*-3,5-*di*(*methylamino*)-1,2-*dithiolylium bromide*, ([IIIf)]Br. Hydrogen peroxide (2 cm^3) was added dropwise to a filtered warm solution containing (Ib) (0.625 mmol) in water (40 cm^3) and HBr (8 cm^3). A yellow compound was obtained instantaneously.

All the compounds, except [(IIIb)]Cl, were recrystallized from water.

Preparation of Metal Salts.—3,5-*Diamino*-1,2-*dithiolylium and* 4-*chloro*-3,5-*di*(*methylamino*)-1,2-*dithiolylium tetrachloroferrate*(III), [(IIIa)][$FeCl_4$] *and* [(IIIe)][$FeCl_4$]. Iron(III) chloride hexahydrate (6 mmol) and (Ia) [or (Ib)] (3 mmol) were dissolved in HCl (5 cm^3), water (2 cm^3), and H_2O_2 (2 cm^3). The solution was shaken vigorously and warmed until a clear solution was obtained. Red crystalline salts separated out on cooling.

Bis(3,5-*diamino*-1,2-*dithiolylium*) *tetrachlorocobaltate*(II), [(IIIa)]$_2$[$CoCl_4$]. Cobalt(II) chloride hexahydrate (15 mmol) was added to a warm solution containing (Ia) (7.5 mmol) in HCl (15 cm^3), H_2O_2 (1.5 cm^3), and water (2.5 cm^3). Blue-green crystals were obtained on cooling to 0 °C.

Bis(3,5-*diamino*-1,2-*dithiolylium*) *tetrachlorocuprate*(II), [(IIIa)]$_2$[$CuCl_4$]. A warm solution of (Ia) (1.5 mmol) in $MeCO_2H$(42 cm^3) and HCl (3 cm^3) was added to a warm solution of Cu[O_2CMe]$_2$·H_2O (4.5 mmol) in $MeCO_2H$ (22 cm^3) and HCl (6 cm^3). Red crystals were obtained on cooling the green solution at 0 °C for 1 h.

[*Bis*(4-*chloro*-3,5-*di*(*methylamino*)-1,2-*dithiolylium*] *tetrachlorocobaltate*(II), [(IIIe)]$_2$[$CoCl_4$]. A solution of $CoCl_2$·$6H_2O$ (7 mmol) in HCl (10 cm^3) was added to a warm solution of (Ib) (3.5 mmol) in HCl (15 cm^3), water (2 cm^3), and H_2O_2 (1.5 cm^3). Blue-green crystals were obtained on cooling the solution at 0 °C for some hours.

Bis[4-*chloro*-3,5-*di*(*methylamino*)-1,2-*dithiolylium*] *tetrachloroniccolate*(II), [(IIIe)]$_2$[$NiCl_4$]. A mixture of $NiCl_2$·$6H_2O$ (4 mmol) and (IIIe) (2 mmol) was dissolved in methylcellusolve (mcs) (15—20 cm^3) and concentrated until the mcs was completely evaporated. Acetic acid (50 cm^3) was rapidly added to the green crystals thus obtained. The insoluble salt was filtered off and washed with $MeCO_2H$ and diethyl ether.

Bis[4-*chloro*-3,5-*di*(*methylamino*)-1,2-*dithiolylium*] *tetrachlorocuprate*(II), [(IIIe)]$_2$[$CuCl_4$]. A solution of (Ib) (3.5 mmol) in HCl (10 cm^3), water (2 cm^3), and H_2O_2 (2 cm^3) was added to a solution of Cu[O_2CMe]$_2$·H_2O (7 mmol) in $MeCo_2H$ (50 cm^3) and HCl (5 cm^3). Red crystals were obtained from the olive-green solution on cooling and shaking at 0 °C.

None of the salts could be recrystallized.

All the compounds were analyzed by conventional methods. Physical measurements were made as previously described.[1] Deuteriated compounds were prepared by repeated exchange with D_2O until the N–H stretching frequencies had largely disappeared from the infrared spectra. ^1H N.m.r. spectra were obtained with a Jeolco model C-60 HL spectrometer for solutions in deuterioacetone and D_2O, using $SiMe_4$ and dds, respectively, as internal standards. Polarographic curves were recorded with an AMEL multipurpose model 563–551/SU polarograph at different temperatures. A standard calomel electrode (s.c.e.) was used as reference, and the potential values were corrected for the junction potential. Aqueous solutions were used with 0.1 mol dm^{-3} [NEt_4][ClO_4] as supporting electrolyte. Molecular weights were determined with a Mechrolab Inc. vapour-pressure osmometer or by the cryoscopic method.

RESULTS AND DISCUSSION

Dithiolylium Salts.—By reaction of dithiomalonamide, (Ia), and *NN*′-dimethyldithiomalonamide, (Ib), in HX (X = Cl or Br) and hydrogen peroxide we obtained compounds of the types (IIIb) and (IIIe) and (IIIc) and (IIIf), while by reaction in aqueous solution with $FeBr_3$·$6H_2O$ or Fe[ClO_4]$_3$·$6H_2O$ we obtained compounds of the types (IIIa) and (IIId). Table 1 lists the compounds and their analyses, molar conductivities, molecular weights, and melting points.

In compounds (IIIa) and (IIId) the halide ion was directly titrated by the Volhard method (X_{free} in Table 1), while in the other compounds (III) only one halide atom was directly titrated (X_{free} in Table 1); the determination of the second halide atom was obtained only after decomposition of the compounds, suggesting that the second halide atom is strongly bonded in the dithiolylium cation. The molar conductivities and the molecular weights of both sets of compounds in water suggest that they are 1 : 1 electrolytes.[14] In our compounds the disulphide group is perfectly planar,[15–17] indicating an absorption in the electronic spectrum at *ca.* 330 nm.[18] The actual absorption was at 290—310 nm (Table 2). This behaviour is explained, as in the case of the thiuret cation,[18] if the two p_π electron pairs on the sulphur atoms form part of a conjugated system with the remainder of the ring. The stability of the disulphide group in compounds (IIIa) and IIId) may be greater than that in other compounds (III) as suggested by the absorption at shorter wavelengths found for the former compounds.

The ^1H n.m.r. results (Table 2) are strictly consistent with the structure formulated for (III). The pseudo-

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aromatic character of the dithiolylium salts is confirmed by the great downfield shift of the proton of C^4 which appears in the ranges of olefinic and of aromatic protons [19] in (IIIa) and (IIId), with respect to the CH$_2$ protons of the free ligands (I). The absence of a CH proton resonance in the spectra of the remaining compounds (III) indicates that the hydrogen atom on C^4 has been substituted by a halide atom.

TABLE 1

Analyses, molar conductivities, melting points, and molecular weights of the dithiolylium salts

Compound	Analysis [a] (%)				Λ_m/S cm^2 mol^{-1}	M.p. (θ_c/°C)	M [b]
	C	H	X$_{free}$	X$_{tot}$			
[(IIIb)]Cl	17.4 (17.75)	2.20 (2.00)	17.55 (17.45)	35.0 (34.9)	109	150 (decomp.)	121 (203)
[(IIIc)]Br	12.25 (12.35)	1.75 (1.40)	27.2 (27.35)	54.3 (54.7)	110	200—203 (decomp.)	
[(IIIa)][ClO$_4$] [c]				15.35 (15.25)	113	190—191	126 (233)
[(IIIe)]Cl	25.95 (25.85)	3.85 (3.90)	15.45 (15.35)	30.05 (30.55)	113	226—230 (decomp.)	118 (232)
[(IIIf)]Br	18.3 (18.75)	2.70 (2.50)	24.1 (24.95)	51.2 (49.95)	97	230—234 (decomp.)	
[(IIId)]Br	24.3 (24.8)	4.10 (4.15)	33.3 (33.0)		117	260—264 (decomp.)	139 (242)
[(IIId)][ClO$_4$] [d]				13.85 (13.55)	112	225—228 (decomp.)	128 (262)

[a] Calculated values are given in parentheses. [b] Values calculated for undissociated salts are in parentheses. [c] S, 28.0 (27.55%). [d] N, 10.65 (10.7%).

TABLE 2

Electronic spectra [a] of dithiomalonamides, (I), and their dithiolylium salts, (III), in aqueous solution, and polarographic data [b] and ^{1}H n.m.r. results for (III)

Compound	Electronic spectra				$E_{\frac{1}{2}}$/V	I/A	δ/p.p.m.		
							NH$_2$	CH$_2$	
(Ia)	340 (sh) (190)	266 (18 940)		202 (9 600)			9.30 [c]	4.04 [c]	
[(IIIb)]Cl		302 (20 590)	280 (sh) (11 610)	197 (13 930)	−0.31	2.8			
[(IIIc)]Br		300 (13 840)	280 (sh) (8 250)		−0.32	2.8			
[(IIIa)][ClO$_4$]		290 (18 300)		200 (7 240)	−0.45	3.2	8.62 [c]	6.46 [c]	
							NH	CH$_2$	NCH$_3$
(Ib)	325 (sh) (220)	263 (18 900)					9.42 [c]	4.07 [c]	3.12 [c]
[(IIIe)]Cl		310 (27 350)	270 (7 970)		−0.31	3.2			3.25 [d]
[(IIIf)]Br		310 (19 910)	273 (5 660)		−0.32	2.8	8.81 [c]		3.10 [c]
[(IIId)]Br		299 (19 210)	272 (sh) (12 170)		−0.36	2.9		6.05 [d]	3.09 [d]
[(IIId)][ClO$_4$]		300 (26 130)	270 (sh) (11 690)		−0.37	3.1	8.87 [c]	6.37 [c]	3.23 [c]

[a] In nm with absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) in parentheses. [b] $E_{\frac{1}{2}}$ against s.c.e. drop time, 1.5 s; 25 °C; scan rate, 1.7 × 10^{-3} V s^{-1}; 10^{-3} mol dm^{-3} solutions in water using 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. [c] In perdeuterioacetone. [d] In D$_2$O.

No polarographic reduction of the free ligands (I) was observed in water solution in the range 0 to −1.7 V. The reduction of the dithiolylium salts (III) occurs with one reversible two-electron wave (Table 2) [the total number of electrons added ($n = 2$) being calculated from the Ilkovic equation [20]] as shown by potentiometric titrations with Na$_2$[S$_2$O$_8$] and confirmed by comparison with the reduction current of a 10^{-3} mol dm^{-3} solution of Cd^{2+} under the same experimental conditions. We therefore suggest a formation reaction of the type:

$$\text{(Ia)} \rightleftharpoons \text{(IIIa)} + H^+ + 2e^-$$

Plots of the limiting current against the drop time and concentration show that the reduction wave is diffusion-controlled for cations (IIIa), (IIIb), and (IIIc), while for (IIId), (IIIe), and (IIIf) the adsorption of the reduction products on the electrode alters the overall process which is diffusion-controlled only for low drop times (the $E_{\frac{1}{2}}$ values in Table 2 are recorded under such experimental conditions). The greater stability of the disulphide group in compounds (IIIa) and (IIId) is confirmed by the more negative $E_{\frac{1}{2}}$ values.

The i.r. assignments given for (Ia) by Jensen and Nielsen,[21] the normal-co-ordinate analysis of the 3,5-dimethyl-1,2-dithiolylium cation,[17] the proposed assignments for the thiuret cation,[18] and the comparison with the spectra of previously studied complexes [1-5] are taken

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[19] E. D. Becker, 'High Resolution NMR,' Academic Press, New York, 1970, p. 65.

[20] D. R. Crow, 'Polarography of Metal Complexes,' Academic Press, London, 1967, p. 24.

[21] K. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, 1966, **20**, 597.

as a guide in the interpretation of some bands in the i.r. spectra of our compounds. The complete i.r. spectra of the compounds and of the deuteriated compounds are deposited as Supplementary Publication No. SUP 21672 (4 pp.).* The constancy of ν(NH), the increase in ν(CN), and the strong decrease in ν(CS) in the cations with respect to the free ligands (I) indicate a cyclization by means of a sulphur–sulphur bond with concomitant removal of a proton from the C^4H_2 group, which gives a pseudo-aromatic character to the five-membered ring.

TABLE 3

Analyses, molar conductivities, and magnetic moments of the metal salts

Complex	Colour	Analysis [a] (%) M	C	H	Cl	Λ_M S cm² mol⁻¹	μ_{eff} [b] B.M.
$[(IIIa)][FeCl_4]$	Red		10.6 (10.9)	1.55 (1.50)	43.1 (42.85)	681	5.64
$[(IIIa)]_2[CoCl_4]$	Greenish blue	12.3 (12.55)	15.85 (15.4)	2.35 (2.15)	29.95 (30.4)	451	4.97
$[(IIIa)]_2[CuCl_4]$	Red	13.25 (13.4)	15.65 (15.2)	2.45 (2.60)	29.1 (29.95)	400	2.00
$[(IIIe)][FeCl_4]$ [c]	Red				44.35 (44.95)	696	6.01
$[(IIIe)]_2[CoCl_4]$	Greenish blue	9.15 (9.90)	20.25 (20.2)	2.90 (3.05)	35.3 (35.8)	293	4.81
$[(IIIe)]_2[NiCl_4]$	Green	9.05 (9.90)	21.2 (21.2)	3.30 (3.05)	35.2 (35.8)	397	3.51
$[(IIIe)]_2[CuCl_4]$	Red	10.6 (10.6)	19.6 (20.05)	3.15 (3.05)	34.7 (35.55)	470	1.92

[a] Calculated values are given in parentheses. [b] At room temperature; 1 B.M. ≈ 9.27×10^{-24} A m². [c] S, 16.45 (16.25%).

TABLE 4

Electronic spectra (nm) of the solid tetrachlorometallate salts

$[(IIIa)][FeCl_4]$					710					380	
$[(IIIe)][FeCl_4]$					720						
$[(IIIa)]_2[CoCl_4]$	1 910	1 810	1 635	900 (sh)	695	665 (sh)	635	610 sh	525		
$[(IIIe)]_2[CoCl_4]$	2 000	1 850	1 660	900 (sh)	690	670 (sh)	640	615 (sh)	530	495 (sh)	445 (sh)
$[(IIIe)]_2[NiCl_4]$	1 370	1 210 (sh)			860	705	660	615 (sh)	500 (sh)		
$[(IIIa)]_2[CuCl_4]$	1 400	1 000							405		
$[(IIIe)]_2[CuCl_4]$	1 115	870							400		

TABLE 5

Far-i.r. spectra (60—600 cm⁻¹) of the tetrachlorometallate salts

	ν_3	ν_4	Lattice modes	Other bands
$[(IIIa)][FeCl_4]$	366vs	144s	78w	518vs, b, 425w, 416w, 386 (sh), 304 (sh), 256w, 238s, 172 (sh), 133 (sh), 65w
$[(IIIe)][FeCl_4]$	362vs	143s	80 (sh)	522, 533 (sh), 384 (sh), 326 (sh), 226vw, 183w, 65w
$[(IIIa)]_2[CoCl_4]$	335s, 296vs	145m	80m	505vs, b, 426m, 396m, 336 (sh), 205m, 162s, 118w, 60m
$[(IIIe)]_2[CoCl_4]$	304vs, 294vs	138s	89m	537m, 521w, 397m, 385m, 225w, 187m, 145 (sh), 73m
$[(IIIe)]_2[NiCl_4]$	315 (sh), 286vs, 246m	120ms	91 (sh)	600m, 500 (sh), 390ms, 233m, 193 (sh), 165ms, 72m
$[(IIIa)]_2[CuCl_4]$	287vs, 270 (sh)	150mb, 114m		547mb, 527 (sh), 458mb, 425m, 416w, 315w 222m, 202wb, 70w
$[(IIIe)]_2[CuCl_4]$	286vs, 273 (sh)	157m, 123 (sh)	80s	568w, 547w, 533m, 395w, 385m, 372w, 210m 140ms, 60w

The results of the spectroscopic studies indicate that the disulphide group, participating in the conjugated π-electron ring system, confers a great stability on these compounds, which may be attributed to resonance stabilization involving structures (A) and (B).

Metal Salts.—We prepared salts of the types $[(IIIa)]_n[MCl_4]$ and $[(IIIe)]_n[MCl_4]$ (M = Fe, n = 1; M = Co,Ni, and Cu, n = 2) in the presence of metal (Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}) chlorides under conditions which favoured the formation of the dithiolylium salts. The salts are given in Table 3, with their colours, analyses, conductivity measurements, and magnetic moments.

The values of the conductivity measurements in water indicate that these salts decompose into M^{n+}, Cl^-, and dithiolylium cations. The magnetic moments of all the salts are ' normal ' for tetrahedral compounds,[22] and those of the tetrachloroferrate (III) salts are consistent with the presence of Fe^{III}.[22] The spectroscopic studies (Table 4) of our $[FeCl_4]^-$ salts were limited to poorly resolved room-temperature solid spectra, only one broad band being found at *ca.* 700 nm which may be assigned to a *d–d* transition. The electronic spectra of all the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[22] A. Earnshaw, ' Introduction to Magnetochemistry,' Academic Press, New York, 1968, p. 35.

solid salts (Table 4) exhibited *d–d* bands typical of tetrachlorometallate anions having a distorted tetrahedral symmetry.[23,24]

The i.r. and far-i.r. spectra of the salts closely resemble those of compounds (IIIa) and (IIId), except for some bands assignable to metal–chlorine vibrations (Table 5) in the far-i.r. region. This suggests that the nitrogen and sulphur atoms of the cations are not co-ordinated in any way to the metal atoms. The vibrational data (Table 5) of the $[FeCl_4]^-$ ions are in accord with a tetrahedral symmetry,[25] and those of the other $[MCl_4]^{2-}$ions agree with a distorted tetrahedral symmetry.[26–29]

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