HORDVIK, A. & KJØGE, H. M. (1965). *Acta Chem. Scand.* **19**, 935–946.
HORDVIK, A. & SLETTEN, E. (1966). *Acta Chem. Scand.* **20**, 1874–1884.
International Tables for X-ray Crystallography. (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.
KNAUER, K., HEMMERICH, P. & VAN VOORST, J. D. W. (1967). *Angew. Chem. Int. Ed.* **6**, 262–263.
LEVY, H. A. & BUSING, W. R. (1957). *Acta Cryst.* **10**, 180–182.
MACFARLANE, A. J. & WILLIAMS, R. J. P. (1969). *J. Chem. Soc.* (*A*), pp. 1517–1520.
MASON, R., MCKENZIE, E. D., ROBERTSON, G. B. & RUSHOLME, G. A. (1968). *Chem. Commun.* pp. 1673–1674.
MASON, R., ROBERTSON, G. B. & RUSHOLME, G. A. (1974). *Acta Cryst.* B**30**, 894–905.
MASON, R. & ZUBIETA, J. A. (1973). *Angew. Chem. Int. Ed.* **12**, 390.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 2nd ed., p. 260. Ithaca: Cornell Univ. Press.
PAULING, P. (1966). *Inorg. Chem.* **5**, 1498–1505.
PROUT, C. K. & MURRAY-RUST, P. (1969). *J. Chem. Soc.* (*A*), 1520–1525.
PROUT, C. K. & WRIGHT, J. D. (1968). *Angew. Chem. Int. Ed.* **7**, 659–667.
RAE, A. D. (1965). *Acta Cryst.* **19**, 683–684.
RAE, A. D. & BLAKE, A. B. (1966). *Acta Cryst.* **20**, 586.
SIEKER, L. C., ADMAN, E. & JENSEN, L. H. (1972). *Nature Lond.* **235**, 40–42.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TRINH-TOAN, & DAHL, L. F. (1971). *J. Amer. Chem. Soc.* **93**, 2654–2666.
WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DI VAIRA, M.| & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565–574.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1974). B**30**, 894

The Crystal Structures of Bis-(3,5-diphenyl-1,2-dithiolium) Tetrachloroferrate(II) and of Bis-(3,5-diphenyl-1,2-dithiolium) Tetrachloromercurate(II)

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The crystal structure analyses are based on three-dimensional diffractometer data with least-squares refinement of the scattering model. Crystals are triclinic, space group $C\bar{1}$, with two formula units per asymmetric unit ($Z=4$). Cell dimensions, with values for the tetrachloromercurate isomer given in parentheses, are $a=16{\cdot}22$ (16·26), $b=22{\cdot}28$ (22·31), $c=16{\cdot}95$ (17·12) Å, $\alpha=94{\cdot}9$ (94·5), $\beta=82{\cdot}7$ (82·8) and $\gamma=100{\cdot}4$ (99·6)°. Terminal R values for the two analyses are 0·047 (4621 reflexions) and 0·044 (4079 reflexions) respectively. In both complexes, similarly located tetrachlorometallate ions show marked, but very similar, angular distortions from tetrahedral symmetry. Both the angular distortions and M–Cl bond-length inequivalences are related to local Cl···S(dithiolium) charge transfer interactions. Some comments are made regarding the possible relevance of such anion–cation interactions to non-valence interactions and mechanisms of electron transfer in metalloenzymes.

Introduction

As discussed in the preceding paper (Freeman, Milburn, Nockolds, Mason, Robertson & Rusholme, 1974), interest in the structural chemistry of the supposed iron-thiol complexes, $(R_2C_3HS_2)_2FeCl_4$ [R = Me, Ph], arose largely from their possible mimicry of the redox chromophore in the mononuclear iron-sulphur protein, rubredoxin. Subsequently, this possibility was firmly ruled out by spectroscopic and X-ray diffraction analyses of $(Me_2C_3HS_2)_2FeCl_4$ (Mason, McKenzie, Robertson & Rusholme, 1968; Freeman, Milburn, Nockolds, Hemmerich & Knauer, 1969; Heath, Martin & Stewart, 1969), which showed the intense absorption at *ca.* 500 nm to result from $(FeCl_4)^{2-}$ to $(Me_2C_3HS_2)^+$ charge transfer rather than Fe–SS coordination. Ion–ion charge transfer bands are also observed, though with differing intensities and wavelengths, in the diffuse reflectance spectra of $(PhMeC_3HS_2)_2FeCl_4$ and $(Ph_2C_3HS_2)_2FeCl_4$ [bands centred at 516 and 741 nm respectively: *cf.* 500 nm for $(Me_2C_3HS_2)_2FeCl_4$] (Rusholme, 1970). Spectra of each of these complexes, together with that of the tetrachloromercurate(II) isomorph of $(Ph_2C_3HS_2)_2FeCl_4$, are collected in Fig. 1.

Because of the manifest dependence of spectral properties on the nature of both the tetrachlorometallate ion and the substituent groups in the organic ligand.

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it seemed desirable to follow our X-ray diffraction study of $(Me_2C_3HS_2)_2FeCl_4$ with similar studies of the tetrachloroferrate(II) complexes of the diphenyl-substituted dithiolium cations.

In the event, solution of the $(Ph_2C_3HS_2)_2FeCl_4$ structure was only accomplished *via* prior analysis of the isomorphous tetrachloromercurate(II) derivative, and the supposed 'yellow isomer' of the dark-green tetrachloroferrate(II) derivative was shown, more or less concurrently, to be a tetrachloroferrate(III) analogue, $(Ph_2C_3HS_2)_2(FeCl_4)Cl$ (Mason, Robertson & Rusholme, 1974). Unexpectedly, and for reasons quite different from those initially envisaged, the present analyses of the bis-(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate(II) and tetrachloromercurate(II) complexes are of interest in relation to studies of electron transfer mechanisms in both haem and non-haem iron proteins.

Synthetic procedures, together with data relating to structural polymorphism in the series $(Ph_2C_3HS_2)_2MCl_4$, are detailed by Mason *et al.* (1974). Reaction products occasionally included a small amount of free sulphur. In the case of the $(HgCl_4)^{2-}$ complexes some contamination by metallic mercury was also observed. Crystals of $(PhMeC_3HS_2)_2PeCl_4$, prepared by the same route but with benzoylacetone as the parent β-diketone, always occurred as badly aggregated very thin plates, and could not be obtained in a form suitable for X-ray diffraction studies. Freshly prepared crystals were green, but on standing slowly acquired a brownish-black coloration with concomitant changes in their reflectance spectra (Rusholme, 1970).

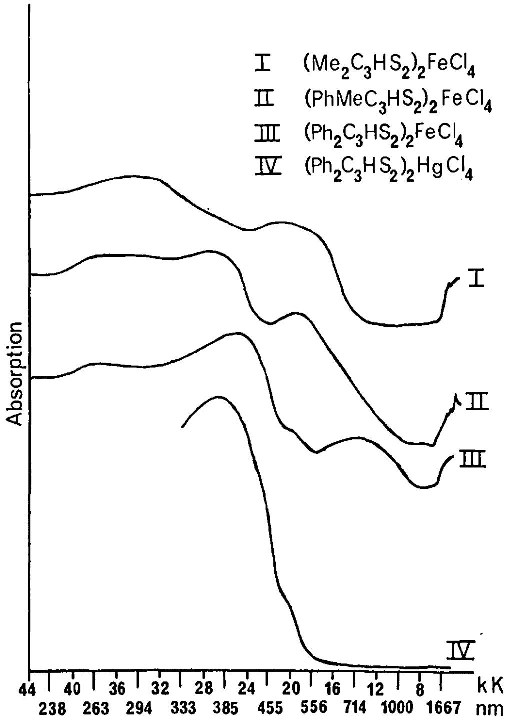

Fig. 1. Reflectance spectra of some dithiolium complexes of tetrachlorometallate dianions.

Experimental

I. *Bis-*(3,5*-diphenyl-*1,2*-dithiolium*)*tetrachloroferrate*(II), $C_{30}H_{22}S_4Cl_4Fe$

Crystals of $(SbzSbz)_2[FeCl_4]$ occur as well-formed dark-green needles, having a roughly octagonal cross section and elongated along the arbitrarily assigned a axis. Weissenberg and precession photographs show the Laue group to be C_i ($\bar{1}$) with systematic absences $\{hkl\}$, $h+k=2n+1$ of the non-standard face-centred triclinic spacegroups, $C1$ or $C\bar{1}$. Subsequent structure analysis has confirmed the centrosymmetric choice ($C\bar{1}$). Dimensions of the centred cell estimated from high-angle (Mo $K\alpha$) precession data are: $a=16·22$ (1), $b=22·28$ (1), $c=16·95$ (1) Å, $\alpha=94·9$ (1), $\beta=82·7$ (1), $\gamma=100·4$ (1)°, $V_c=5965$ Å^3. The crystal density measured by flotation in benzene–1,1,2,2-tetrabromoethane [1·57 (1) g cm^{-3}] is identical with the value calculated for eight formula units per cell (1·57 g cm^{-3}).

Reflexion intensities were collected on a PAILRED automatic diffractometer using a well-formed crystal of dimensions 0·51 × 0·22 × 0·20 mm elongated along **a**. With the crystal aligned so that the needle axis (a) and instrumental ω axis were coincident, all unique data within the range $6° \leq 2\theta \leq 60°$ for the reciprocal levels $\{0kl\}$ to $\{18kl\}$ were recorded using crystal-monochromated Mo $K\bar{\alpha}$ radiation (Si crystal; $2\theta_m=13·02°$; $\bar{\lambda}=0·7107$ Å). Data were measured by the ω-scan technique, with a constant scan velocity of 2·5° min^{-1}, and scan ranges varying from 2·0° for the zero level to 4·4° for the $\{18kl\}$ level. All data were recorded in the equi-inclination mode. Backgrounds were measured at each extreme of the ω scan for 20 s with both crystal and counter stationary, and were assumed to vary linearly over this range.

Reflexion intensities were corrected in the usual way for incoherent background contributions and for Lorentz and polarization effects. Appropriate formulae are collected below. Those reflexions with $\Delta(B)/\sigma(B) > 3·0$ or $I/\sigma(I) < 3·0$ were rejected. The remaining 4621 unique non-zero data were used for solution and refinement of the structure. The statistical discrepancy index for this data set, defined as $\sum\sigma(F_o)/\sum|F_o|$, is 0·039. No corrections were applied for specimen absorption effects.

Crystal data

$C_{30}H_{22}S_4Cl_4Fe$. M.W. 708·46. Analysis: calc: C 50·8; H 3·1; S 18·1; Cl 20·0; Fe 7·9%, found: C 50·5; H 3·4; S 18·0; Cl 20·0%. Colour dark green. Triclinic, space group $C\bar{1}$ [non-standard setting of $P\bar{1}$, (C_i^2, No. 2)]. Cell dimensions: $a=16·22$ (1), $b=22·28$ (1), $c=16·95$ (1) Å; $\alpha=94·9$ (1), $\beta=82·7$ (1), $\gamma=100·4$ (1)°; $V_c=5964$ Å^3 ($t=20\pm2$ °C). $D_m=1·57$ (1), $D_c=1·57$ g cm^{-3}, $Z=4$. μ(Mo $K\bar{\alpha}$) = 11·6 cm^{-1}. $F(000)=1440$. Delaunay reduced cell: $a'=12·54$, $b'=14·92$, $c'=$

21·92 Å; $\alpha'=113{\cdot}7$, $\beta'=110{\cdot}8$, $\gamma'=108{\cdot}2°$; $V_c'=2982$ Å^3.

Data reduction formulae

$|F_o|^2=I\times \mathrm{Lp}$; $I=[PK-(t_p/\mathrm{t}_b)\ (B_1+B_2)]$; $\mathrm{Lp}=(1+\cos^2 2\theta_m)\sin\gamma\cos^2\nu/\{(1+\cos^2 2\theta_m)-\cos^2 2\theta_m\sin^2\gamma\times\cos^2\nu-(\cos^2\nu-\cos^4\nu)\ (1+\cos\gamma)^2\}$; $\sigma(I)=[PK+(t_p/t_b)^2\ (B_1+B_2)]^{1/2}$; $\sigma(F_o)=\mathrm{Lp}\times\sigma(I)/2|F_o|$; $\Delta(B)=|B_1-B_2|$; $\sigma(B)=(B_1+B_2)^{1/2}$. *PK* is the scan count, t_p and t_b are scan and total background times respectively, and B_1, B_2 are individual background counts. θ_m is the monochromator Bragg angle, ν $(=\mu)$ is the inclination angle and $\gamma=2$ arc cos $(\cos\theta/\cos\nu)$.

II. *Bis*-(3,5-*diphenyl*-1,2-*dithiolium*) *tetrachloromercurate*(II), $C_{30}H_{22}S_4Cl_4Hg$

Well-formed crystals of $(SbzSbz)_2[HgCl_4]$ isomorphous with $(SbzSbz)_2[FeCl_4]$ were isolated from a mixture of polymorphs by microscopic examination. Crystals are orange but of similar morphology to the iron isomorph. Structural isomorphism was confirmed by Weissenberg and precession photography. Reflexion intensities were measured on a Hilger and Watts computer-controlled four-circle diffractometer. The specimen crystal, of dimensions 0·35 × 0·23 × 0·20 mm (elongated along **a**), was aligned with its *a* axis approximately coincident with the instrumental φ axis. Cell parameters and crystal oriention matrix were derived, following the method of Busing & Levy (1967), by least-squares analysis of the instrumental 2θ, ω, χ and φ values for 12 carefully centred high-angle reflexions (Mo $K\alpha_1$ radiation; $\lambda=0{\cdot}70926$ Å). Cell parameters determined in this way were equal, within 1σ, to the values derived from high-angle (Mo $K\alpha$) precession data. All unique data within the range $3° < 2\theta < 40°$ were recorded with molybdenum ($K\bar{\alpha}$) radiation using the method of balanced filters and *ca.* 95% discriminator band pass. Data were recorded in the θ–2θ scan mode, with constant 2θ scan velocity (0·86° min^{-1}) and scan width (1·2°). Backgrounds were measured in the stationary-crystal stationary-counter mode for $\frac{1}{6}$ of the total scan time at each extreme of the peak scan. Background variation over the scan range was assumed to be linear. Intensities of three reflexions, chosen as standards and monitored every 50 reflexions, showed no significant variation during the period of data collection.

Reflexion data were processed in the usual way and subject to the usual rejection criteria $\Delta(B)\geq 3{\cdot}0\sigma(B)$ or $I/\sigma(I)\leq 3{\cdot}0$. However, if $\Delta(B)\geq 3{\cdot}0$ *and* $I/\sigma(I)\geq 5{\cdot}0$, data were reprocessed with $B_{\min}$ [equal to twice the lower modulus of $\delta(B_1)$ or $\delta(B_2)$] replacing $\delta(B_1)+\delta(B_2)$ in the data reduction formulae (see below). After averaging equivalent forms, the resultant data set contained 4079 unique non-zero reflexions whose statistical discrepancy index $\{\sum\sigma(F_o)/\sum|F_o|\}$ is 0·028.

Crystal data

$C_{30}H_{22}S_4Cl_4Hg$. M.W. 853·22. Analysis: calc: C 42·2; H 2·5; S 15·0; Cl 16·6; Hg 23·6%; found: C 42·2; H 2·6; S 15·1%. Colour orange. Triclinic, space group $C\bar{1}$ [non-standard setting of $P\bar{1}$ (C_i^1, No. 2)]. Cell dimensions: $a=16{\cdot}26\ (1)$, $b=22{\cdot}31\ (1)$, $c=17{\cdot}12\ (1)$ Å; $\alpha=94{\cdot}5\ (1)$, $\beta=82{\cdot}8\ (1)$, $\gamma=99{\cdot}6\ (1)°$; $V_c=6065$ Å^3 ($t=20\pm 2$ °C). $D_m=1{\cdot}85$ (1) (flotation), $D_c=1{\cdot}86$ g cm^{-3}, $Z=4$. μ(Mo $K\bar{\alpha}$) = 55·4 cm^{-1}. $F(000)=1656$. Delaunay reduced cell: $a'=12{\cdot}66$, $b'=14{\cdot}86$, $c'=22{\cdot}08$ Å; $\alpha'=113{\cdot}3°$, $\beta'=110{\cdot}8$, $\gamma'=108{\cdot}1°$; $V_c'=3032$ Å^3.

Data-reduction formulae

$|F_o|^2=I\times \mathrm{Lp}$; $I=\{\delta(PK)-(t_p/t_b)[\delta(B_1)+\delta(B_2)]\}$; $\mathrm{Lp}=2\sin 2\theta/(1+\cos^2 2\theta)$; $\sigma(I)=\{S\{(PK)+(t_p/t_b)^2[S(B_1)+S(B_2)]\}^{1/2}$; $\sigma(F_o)=I\times \mathrm{Lp}/2|F_o|$; $\Delta(B)=|\delta(B_1)-\delta(B_2)|$; $\sigma(B)=[S(B_1)+S(B_2)]^{1/2}$. $\delta(PK)$ is the differential peak count, $\delta(B_1)$, $\delta(B_2)$ are differential background counts. $S(PK)$, $S(B_1)$ and $S(B_2)$ are summed rather than differential counts with alternate $K\beta$ (Zr) and $K\alpha$ (Y) filters.

Solution and refinement

Conventional and sharpened Patterson syntheses for the iron isomorph showed that all major vectors occur in pairs, related by translations of $u/2$, and reflecting the strong pseudo-halving of the *a* axis shown by the diffraction data [$\{hkl\}$, $h=2n+1$ weak; see structure-factor list]. However, consideration of relative peak heights in these two syntheses ($C\bar{1}$ assumed) led fairly straightforwardly to what ultimately were proven to be the correct iron-atom coordinates. Unit-weight block-diagonal least-squares refinement of the iron-only model gave a discrepancy index R $[=\sum||F_o|-|F_c||/\sum|F_o|]$ of 0·49. Fourier and difference syntheses phased on this model did not yield further atom coordinates. Patterson superposition and direct methods also proved unsuccessful and, consequently, data were collected for the mercury isomer where (i) the associated Patterson synthesis would be dominated by metal–metal and metal–ligand vectors and (ii) structure-factor phases would be governed to a much greater extent by metal-atom contributions.

Inspection of the Patterson synthesis for the mercury isomorph immediately confirmed the assignment of metal-atom coordinates. A difference synthesis with coefficients $[F_o-(F_{\mathrm{Hg1}}+F_{\mathrm{Hg2}})]$ showed the expected pseudo-symmetry (Hg at x,y,z and $\frac{1}{2}+x,y,z$ respectively), each metal atom being surrounded by two relatively inverted tetrahedra. Of the two possible scattering models consistent with this peak distribution, *viz.* parallel or anti-parallel tetrahedra, only the anti-parallel model resulted in sensible least-squares refinement. Subsequent difference syntheses, based on the extended (M + Cl) scattering models, revealed all non-hydrogen atoms of the four 3,5-diphenyl-1,2-dithiolium cations in stereochemically acceptable positions.

Block-diagonal least-squares refinements for atom coordinates, isotropic thermal parameters and overall scale (M, S, Cl and C atoms only) converged with

R values of 0·12 and 0·09 for the iron and mercury isomers respectively. Introduction of anisotropic thermal parameters for M, S and Cl atoms (only) reduced the R values to 0·089 and 0·061. At this stage of the refinement hydrogen-atom contributions were included in the scattering model. Coordinates were located by calculation (atoms on angle bisectors; C–H = 1·06 Å assumed) and B factors (6·5 Å^2, iron isomer; 7·5 Å^2, mercury isomer) estimated as 1 Å^2 greater than the mean isotropic thermal parameter averaged over all carbon atoms involved in C–H bonding. With inclusion of hydrogen-atom contributions (not subsequently refined) the R values corresponding to parameter reconvergence were 0·066 (Fe isomer) and 0·051 (Hg isomer). Correlation of observed and calculated structure factors for both isomers now indicated several reflexions with substantial disagreement $[\omega\Delta^2 \geq 20(\overline{\omega\Delta^2});\ \Delta = ||F_o - F_c||]$. These reflexions, 18 for the iron and 30 for the mercury isomer, apparently suffering from extinction effects were deleted from the data sets. No further corrections for extinction or for absorption, were applied to either data set. Both crystals had a near-regular octagonal cross-section in the b^*c^* plane and the linear absorption coefficient for the iron isomer is, in any case, small (μ = 11·6 cm^{-1}). For the mercury complex the absorption coefficient is substantial (μ = 55·4 cm^{-1}) but our interest in this isomer did not extend to a requirement for particularly precise bond-length or vibrational data.

Table 1. (SbzSbz)$_2$[FeCl$_4$] *and* (SbzSbz)$_2$[HgCl$_4$]: *atom coordinates and estimated standard deviations*

Hydrogen atom coordinates not refined.

Iron isomorph				Mercury isomorph		
x	y	z		x	y	z
0.19996(7)	0.11677(5)	0.25445(6)	M1	0.20404(4)	0.11544(2)	0.25405(3)
0.70695(7)	0.12440(5)	0.24248(6)	M2	0.70826(4)	0.12338(2)	0.24229(3)
0.2419 (2)	0.2057 (1)	0.3292 (1)	Cl1	0.2423 (3)	0.2099 (2)	0.3348 (2)
0.0530 (2)	0.1067 (1)	0.2721 (1)	Cl2	0.0458 (3)	0.1039 (2)	0.2743 (2)
0.2647 (2)	0.0428 (1)	0.2913 (2)	Cl3	0.2792 (4)	0.0366 (2)	0.2869 (3)
0.2317 (2)	0.1164 (1)	0.1180 (1)	Cl4	0.2336 (3)	0.1181 (2)	0.1088 (2)
0.6951 (2)	0.1214 (1)	0.3790 (1)	Cl5	0.6927 (3)	0.1213 (2)	0.3872 (2)
0.7174 (2)	0.02822(9)	0.1829 (1)	Cl6	0.7183 (3)	0.0199 (2)	0.1823 (2)
0.5831 (2)	0.1566 (1)	0.2197 (1)	Cl7	0.5732 (3)	0.1575 (2)	0.2175 (2)
0.8194 (2)	0.1918 (1)	0.1894 (1)	Cl8	0.8254 (3)	0.1965 (2)	0.1843 (2)
0.4463 (2)	0.1582 (1)	0.3858 (1)	S1	0.4469 (3)	0.1586 (2)	0.3846 (2)
0.4854 (2)	0.2432 (1)	0.3491 (1)	S2	0.4844 (3)	0.2431 (2)	0.3487 (2)
0.9341 (2)	0.1701 (1)	0.4038 (1)	S3	0.9325 (3)	0.1701 (2)	0.4052 (2)
0.9879 (2)	0.2400 (1)	0.3371 (1)	S4	0.9859 (3)	0.2387 (2)	0.3368 (2)
0.4547 (2)	0.05469(9)	0.1225 (1)	S5	0.4530 (2)	0.0546 (2)	0.1184 (2)
0.4712 (1)	0.13560(9)	0.0735 (1)	S6	0.4703 (2)	0.1358 (2)	0.0690 (2)
0.9522 (1)	0.00599(9)	0.1619 (1)	S7	0.9501 (3)	0.0047 (2)	0.1628 (2)
0.9503 (1)	0.08208(9)	0.1068 (1)	S8	0.9490 (3)	0.0804 (2)	0.1070 (2)
0.3432 (5)	0.1315 (4)	0.5212 (4)	C1	0.3475 (9)	0.1310 (6)	0.5186 (8)
0.3367 (6)	0.0704 (4)	0.4949 (5)	C2	0.3377(10)	0.0714 (7)	0.4920 (8)
0.3040 (7)	0.0252 (4)	0.5474 (6)	C3	0.3063(11)	0.0248 (7)	0.5412 (9)
0.2755 (7)	0.0401 (4)	0.6233 (5)	C4	0.2792(11)	0.0382 (7)	0.6190 (9)
0.2778 (8)	0.1004 (5)	0.6493 (5)	C5	0.2848(12)	0.0970 (8)	0.6452 (9)
0.3109 (7)	0.1464 (4)	0.5987 (5)	C6	0.3195(10)	0.1453 (6)	0.5962 (8)
0.3853 (5)	0.1792 (4)	0.4695 (4)	C7	0.3880 (9)	0.1782 (6)	0.4669 (8)
0.3842 (5)	0.2407 (3)	0.4828 (5)	C8	0.3865 (9)	0.2401 (6)	0.4818 (7)
0.4313 (5)	0.2786 (4)	0.4262 (5)	C9	0.4317 (8)	0.2783 (6)	0.4271 (8)
0.4373 (6)	0.3450 (4)	0.4268 (5)	C10	0.4368 (9)	0.3449 (6)	0.4276 (8)
0.3897 (6)	0.3758 (4)	0.4854 (6)	C11	0.3884(10)	0.3752 (7)	0.4875 (9)
0.3940 (7)	0.4384 (4)	0.4839 (6)	C12	0.3905(11)	0.4367 (8)	0.4872(11)
0.4459 (7)	0.4715 (4)	0.4265 (6)	C13	0.4420(13)	0.4705 (7)	0.4309(12)
0.4929 (8)	0.4413 (5)	0.3698 (6)	C14	0.4911(14)	0.4411 (8)	0.3719(11)
0.4910 (7)	0.3788 (4)	0.3693 (5)	C15	0.4900(11)	0.3792 (7)	0.3699 (9)
0.8321 (5)	0.1817 (3)	0.5409 (4)	C16	0.8319 (9)	0.1838 (6)	0.5419 (7)
0.8199 (7)	0.1179 (4)	0.5416 (5)	C17	0.8207(10)	0.1198 (7)	0.5425 (8)
0.7750 (7)	0.0880 (4)	0.6052 (5)	C18	0.7754(11)	0.0914 (7)	0.6084 (9)
0.7418 (6)	0.1211 (4)	0.6694 (5)	C19	0.7440(10)	0.1249 (7)	0.6711 (8)
0.7538 (6)	0.1843 (4)	0.6711 (5)	C20	0.7564(10)	0.1868 (7)	0.6714 (8)
0.7988 (5)	0.2141 (3)	0.6068 (5)	C21	0.8012 (9)	0.2164 (6)	0.6063 (8)
0.8827 (5)	0.2132 (3)	0.4747 (4)	C22	0.8832 (8)	0.2128 (6)	0.4735 (7)
0.8939 (5)	0.2746 (3)	0.4632 (4)	C23	0.8945 (8)	0.2749 (6)	0.4624 (7)
0.9453 (5)	0.2951 (3)	0.3960 (4)	C24	0.9432 (8)	0.2952 (7)	0.3945 (7)
0.9651 (5)	0.3579 (3)	0.3719 (4)	C25	0.9646 (8)	0.3577 (6)	0.3701 (7)
0.9501 (6)	0.4061 (4)	0.4253 (5)	C26	0.9517(11)	0.4044 (6)	0.4224 (9)
0.9716 (7)	0.4652 (4)	0.4032 (5)	C27	0.9756(12)	0.4649 (8)	0.3999(10)
1.0111 (6)	0.4775 (4)	0.3278 (6)	C28	1.0113 (9)	0.4755 (7)	0.3240 (9)
1.0276 (7)	0.4303 (4)	0.2751 (5)	C29	1.0208(11)	0.4275 (8)	0.2708 (8)
1.0045 (7)	0.3711 (4)	0.2959 (5)	C30	0.9996(10)	0.3700 (7)	0.2935 (8)
0.3724 (5)	-0.0516 (3)	0.0576 (4)	C31	0.3697 (8)	-0.0503 (6)	0.0513 (7)
0.3841 (6)	-0.0800 (4)	0.1238 (5)	C32	0.3812 (9)	-0.0795 (6)	0.1203 (8)
0.3587 (6)	-0.1432 (4)	0.1283 (5)	C33	0.3565(10)	-0.1410 (6)	0.1250 (8)
0.3214 (6)	-0.1776 (4)	0.0664 (5)	C34	0.3202 (9)	-0.1755 (6)	0.0624 (8)
0.3094 (6)	-0.1495 (4)	0.0004 (5)	C35	0.3088 (8)	-0.1461 (6)	-0.0022 (9)
0.3340 (5)	-0.0869 (4)	-0.0041 (5)	C36	0.3342 (9)	-0.0855 (5)	-0.0079 (7)
0.4000 (5)	0.0136 (3)	0.0504 (4)	C37	0.3990 (8)	0.0145 (5)	0.0471 (7)
0.3878 (5)	0.0474 (3)	-0.0105 (4)	C38	0.3883 (7)	0.0488 (5)	-0.0141 (7)
0.4197 (5)	0.1089 (3)	-0.0073 (4)	C39	0.4205 (8)	0.1103 (5)	-0.0111 (7)
0.4109 (4)	0.1523 (3)	-0.0634 (4)	C40	0.4125 (7)	0.1543 (5)	-0.0673 (7)
0.3419 (5)	0.1406 (4)	-0.1067 (5)	C41	0.3426 (8)	0.1425 (6)	-0.1106 (8)
0.3295 (6)	0.1828 (4)	-0.1563 (5)	C42	0.3301 (9)	0.1852 (6)	-0.1595 (8)
0.3857 (5)	0.2373 (4)	-0.1644 (4)	C43	0.3855 (9)	0.2401 (6)	-0.1662 (7)
0.4554 (5)	0.2481 (3)	-0.1241 (4)	C44	0.4556 (9)	0.2506 (6)	-0.1251 (8)
0.4684 (5)	0.2067 (3)	-0.0737 (4)	C45	0.4682 (8)	0.2084 (6)	-0.0757 (8)
0.8893 (5)	-0.1083 (3)	0.1077 (4)	C46	0.8886 (8)	-0.1086 (5)	0.1097 (8)
0.8979 (6)	-0.1272 (4)	0.1816 (5)	C47	0.8941(10)	-0.1270 (7)	0.1842 (9)
0.8830 (6)	-0.1884 (4)	0.1962 (6)	C48	0.8804(10)	-0.1877 (7)	0.1995 (9)
0.8599 (6)	-0.2315 (4)	0.1363 (6)	C49	0.8606 (9)	-0.2318 (7)	0.1392 (9)
0.8511 (5)	-0.2139 (3)	0.0625 (5)	C50	0.8543 (9)	-0.2137 (7)	0.0660 (9)
0.8665 (5)	-0.1530 (3)	0.0469 (5)	C51	0.8668 (9)	-0.1523 (6)	0.0499 (9)
0.9034 (5)	-0.0429 (3)	0.0926 (4)	C52	0.9035 (8)	-0.0438 (6)	0.0956 (7)
0.8838 (5)	-0.0171 (3)	0.0288 (4)	C53	0.8847 (8)	-0.0163 (6)	0.0301 (8)
0.9037 (5)	0.0462 (3)	0.0274 (4)	C54	0.9033 (8)	0.0447 (5)	0.0281 (7)
0.8897 (5)	0.0831 (3)	-0.0356 (4)	C55	0.8913 (8)	0.0819 (5)	-0.0345 (8)
0.8595 (6)	0.0558 (4)	-0.1060 (5)	C56	0.8597 (9)	0.0540 (6)	-0.1044 (8)
0.8520 (6)	0.0910 (4)	-0.1658 (5)	C57	0.8512(10)	0.0897 (8)	-0.1637 (9)
0.8726 (6)	0.1533 (4)	-0.1587 (5)	C58	0.8750(10)	0.1518 (7)	-0.1588 (8)
0.9023 (6)	0.1810 (4)	-0.0895 (5)	C59	0.9044 (9)	0.1789 (7)	-0.0915 (9)
0.9105 (6)	0.1468 (4)	-0.0285 (5)	C60	0.9127 (9)	0.1445 (6)	-0.0279 (8)

Table 1 (*cont.*)

Iron isomorph				Mercury isomorph		
x	y	z		x	y	z
0.3562	0.0614	0.4295	H1	0.3571	0.0603	0.4344
0.3009	-0.0237	0.5173	H2	0.3016	-0.0205	0.5202
0.2533	0.0025	0.6584	H3	0.2512	0.0015	0.6521
0.2561	0.1059	0.7050	H4	0.2629	0.1079	0.7020
0.3258	0.1932	0.6221	H5	0.3228	0.1902	0.6179
0.3508	0.3480	0.5297	H6	0.3478	0.3471	0.5318
0.3577	0.4647	0.5264	H7	0.3611	0.4631	0.5362
0.4527	0.5202	0.4257	H8	0.4432	0.5196	0.4253
0.5318	0.4668	0.3236	H9	0.5312	0.4707	0.3296
0.5311	0.3552	0.3254	H10	0.5324	0.3576	0.3225
0.8480	0.0933	0.4895	H11	0.8567	0.0965	0.4886
0.7671	0.0386	0.6050	H12	0.7555	0.0425	0.6151
0.7066	0.0984	0.7199	H13	0.7072	0.1042	0.7222
0.7277	0.2119	0.7206	H14	0.7298	0.2114	0.7243
0.8104	0.2637	0.6086	H15	0.8124	0.2670	0.6038
0.9206	0.3968	0.4845	H16	0.9268	0.3927	0.4819
0.9603	0.5022	0.4458	H17	0.9640	0.5036	0.4431
1.0255	0.5245	0.3114	H18	1.0342	0.5216	0.3008
1.0607	0.4397	0.2158	H19	1.0486	0.4386	0.2126
1.0143	0.3335	0.2531	H20	1.0121	0.3309	0.2480
0.4120	-0.0526	0.1720	H21	0.4090	-0.0529	0.1694
0.3698	-0.1655	0.1786	H22	0.3653	-0.1641	0.1750
0.2989	-0.2259	0.0709	H23	0.3075	-0.2261	0.0678
0.2807	-0.1762	-0.0494	H24	0.2781	-0.1716	-0.0504
0.3268	-0.0643	-0.0559	H25	0.3269	-0.0621	-0.0597
0.2991	0.0984	-0.1013	H26	0.2972	0.0998	-0.1056
0.2766	0.1727	-0.1910	H27	0.2801	0.1750	-0.1955
0.3762	0.2727	-0.2003	H28	0.3746	0.2746	-0.2014
0.4981	0.2900	-0.1358	H29	0.4959	0.2953	-0.1333
0.5233	0.2176	-0.0416	H30	0.5213	0.2178	-0.0421
0.9155	-0.0922	0.2279	H31	0.9143	-0.0942	0.2338
0.8894	-0.2035	0.2537	H32	0.8758	-0.2025	0.2579
0.8495	-0.2790	0.1471	H33	0.8547	-0.2782	0.1565
0.8322	-0.2489	0.0176	H34	0.8373	-0.2491	0.0183
0.8622	-0.1394	-0.0125	H35	0.8649	-0.1384	-0.0071
0.8410	0.0071	-0.1124	H36	0.8413	0.0038	-0.1090
0.8313	0.0668	-0.2201	H37	0.8221	0.0691	-0.2194
0.8669	0.1800	-0.2068	H38	0.8692	0.1793	-0.2089
0.9169	0.2298	-0.0869	H39	0.9180	0.2297	-0.0873
0.9343	0.1698	0.0251	H40	0.9397	0.1676	0.0264
0.3474	0.2589	0.5351	H41	0.3510	0.2580	0.5300
0.8671	0.3070	0.5053	H42	0.8650	0.3060	0.5010
0.3534	0.0254	-0.0607	H43	0.3560	0.0280	-0.0600
0.8541	-0.0444	-0.0181	H44	0.8587	-0.0442	0.0152

The mercury scattering factors were corrected for the real, but not the imaginary parts of the anomalous scattering contribution, and the scattering models were extended to include anisotropic thermal motion for all non-hydrogen atoms. After four additional (unit-weight) least-squares cycles the refinements converged to R values of 0·047(Fe) and 0·045(Hg). Refinement was continued with individual reflexion weights derived from a plot of $\overline{\Delta^2}$ *vs.* $|F_o|$ for small incremental $|F_o|$ ranges. In essence, this weighting scheme is similar to the σ^2 scheme proposed by Busing & Levy (1957) since, for PAILRED data at least, the $\overline{|F_o|}$ dependence of both $\overline{\Delta^2}$ and $\overline{\sigma^2(F_o)}$ is dissimilar only for the higher $|F_o|$ values (commonly *ca.* 30% of the 3σ data). Calculated parameter shifts for the terminal refinement cycles were uniformly less than one tenth of the corresponding parameter estimated standard deviation. Terminal R values for the iron and mercury isomorphs respectively were 0·047 and 0·044. Difference syntheses based on these parameters showed no maxima or minima greater than $\pm 0{\cdot}4$ e Å^{-3}.

All least-squares calculations were of the block-diagonal type. The function minimized was $\sum\omega||F_o|-|F_c||^2$ and parameter standard deviations were estimated in the usual way by inversion of the block-diagonal least-squares matrices. Atomic scattering factors for Fe, Hg, Cl, S and C were taken from *International Tables for X-ray Crystallography* (1972). For hydrogen, the bonded-atom scattering factors of Stewart, Davidson & Simpson (1965) were employed.

Table 2. $(SbzSbz)_2[FeCl_4]$ *and* $(SbzSbz)_2[HgCl_4]$: *anisotropic thermal parameters*

$$T = \exp -[h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+kl\beta_{23}+hl\beta_{13}+hk\beta_{12}].$$

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Fe1	0.00349(5)	0.00127(2)	0.00219(4)	0.00002(5)	-0.00110(7)	0.00042(6)
Fe2	0.00310(5)	0.00140(2)	0.00195(4)	0.00019(5)	-0.00007(7)	0.00042(5)
C11	0.0053 (1)	0.00192(5)	0.00380(9)	-0.0018 (1)	-0.0024 (2)	0.0002 (1)
C12	0.0036 (1)	0.00288(6)	0.0047 (1)	-0.0024 (1)	0.0002 (2)	-0.0004 (1)
C13	0.0119 (3)	0.00227(6)	0.0063 (1)	0.0012 (2)	-0.0074 (3)	0.0040 (2)
C14	0.0051 (1)	0.00215(5)	0.00237(7)	-0.0005 (1)	-0.0006 (2)	-0.0001 (1)
C15	0.0084 (2)	0.00204(5)	0.00235(8)	0.0002 (1)	-0.0008 (2)	0.0024 (2)
C16	0.0053 (1)	0.00157(4)	0.00296(8)	-0.0003 (1)	-0.0007 (2)	0.0007 (1)
C17	0.0041 (1)	0.00350(7)	0.00369(9)	-0.0015 (1)	-0.0021 (2)	0.0029 (1)
C18	0.0043 (1)	0.00190(5)	0.0052 (1)	0.0010 (1)	0.0019 (2)	0.0000 (1)
S1	0.0046 (1)	0.00186(5)	0.00353(9)	-0.0001 (1)	0.0000 (2)	0.0020 (1)
S2	0.0042 (1)	0.00212(5)	0.00336(9)	0.0003 (1)	-0.0004 (2)	0.0015 (1)
S3	0.0053 (1)	0.00180(5)	0.00323(9)	-0.0001 (1)	0.0019 (2)	0.0012 (1)
S4	0.0053 (1)	0.00207(5)	0.00298(9)	-0.0000 (1)	0.0018 (2)	0.0011 (1)
S5	0.0045 (1)	0.00169(5)	0.00302(8)	0.0004 (1)	-0.0022 (2)	0.0009 (1)
S6	0.0039 (1)	0.00147(4)	0.00340(9)	-0.0003 (1)	-0.0021 (2)	0.0008 (1)
S7	0.0043 (1)	0.00136(4)	0.00319(6)	-0.0003 (1)	-0.0022 (2)	0.0004 (1)
S8	0.0044 (1)	0.00126(4)	0.00348(9)	-0.0004 (1)	-0.0025 (2)	0.0005 (1)
C1	0.0040 (4)	0.0020 (2)	0.0028 (3)	-0.0003 (4)	-0.0027 (6)	0.0009 (5)
C2	0.0065 (6)	0.0017 (2)	0.0037 (4)	0.0002 (4)	-0.0003 (7)	0.0008 (5)
C3	0.0069 (6)	0.0021 (2)	0.0049 (5)	0.0006 (5)	-0.0017 (8)	0.0013 (6)
C4	0.0070 (6)	0.0024 (2)	0.0038 (4)	0.0011 (5)	-0.0037 (8)	0.0001 (6)
C5	0.0084 (7)	0.0033 (3)	0.0030 (4)	-0.0005 (5)	0.0003 (8)	0.0007 (7)
C6	0.0068 (6)	0.0024 (2)	0.0039 (4)	-0.0009 (5)	-0.0002 (9)	-0.0001 (6)
C7	0.0033 (4)	0.0022 (2)	0.0027 (3)	-0.0003 (4)	-0.0019 (5)	0.0016 (4)
C8	0.0035 (4)	0.0017 (2)	0.0034 (3)	0.0001 (4)	-0.0017 (6)	0.0007 (4)
C9	0.0035 (4)	0.0019 (2)	0.0035 (3)	-0.0005 (4)	-0.0025 (6)	0.0012 (4)
C10	0.0045 (5)	0.0017 (2)	0.0033 (3)	-0.0003 (4)	-0.0031 (6)	-0.0001 (5)
C11	0.0045 (5)	0.0020 (2)	0.0055 (5)	0.0004 (5)	-0.0023 (7)	0.0013 (5)
C12	0.0059 (6)	0.0025 (3)	0.0069 (6)	-0.0013 (6)	-0.0022 (9)	0.0022 (6)
C13	0.0060 (6)	0.0021 (2)	0.0071 (6)	-0.0013 (6)	-0.0056 (9)	0.0014 (6)
C14	0.0084 (8)	0.0026 (3)	0.0054 (5)	0.0028 (6)	-0.0039 (9)	-0.0010 (7)
C15	0.0069 (6)	0.0021 (2)	0.0042 (4)	0.0001 (5)	-0.0020 (8)	0.0004 (6)
C16	0.0035 (4)	0.0016 (2)	0.0026 (3)	0.0006 (4)	-0.0014 (5)	0.0006 (4)
C17	0.0075 (6)	0.0021 (2)	0.0034 (4)	0.0001 (5)	0.0007 (7)	0.0028 (6)
C18	0.0082 (7)	0.0018 (2)	0.0038 (4)	0.0010 (5)	0.0006 (8)	0.0010 (6)
C19	0.0052 (5)	0.0026 (2)	0.0031 (4)	0.0022 (5)	0.0004 (7)	-0.0001 (5)
C20	0.0060 (6)	0.0023 (2)	0.0036 (4)	0.0001 (5)	0.0016 (7)	0.0012 (6)
C21	0.0039 (4)	0.0016 (2)	0.0034 (3)	0.0003 (4)	0.0005 (6)	0.0013 (4)
C22	0.0034 (4)	0.0019 (2)	0.0024 (3)	-0.0004 (4)	-0.0010 (5)	0.0004 (4)
C23	0.0033 (4)	0.0020 (2)	0.0020 (3)	-0.0001 (4)	0.0005 (5)	0.0011 (4)
C24	0.0029 (4)	0.0019 (2)	0.0029 (3)	-0.0001 (4)	-0.0011 (5)	0.0008 (4)
C25	0.0033 (4)	0.0017 (2)	0.0027 (3)	-0.0000 (4)	-0.0010 (5)	0.0004 (4)
C26	0.0063 (6)	0.0024 (2)	0.0034 (4)	0.0005 (5)	0.0005 (7)	0.0021 (6)
C27	0.0078 (7)	0.0023 (2)	0.0038 (4)	-0.0005 (5)	-0.0003 (8)	0.0016 (6)
C28	0.0048 (5)	0.0023 (2)	0.0051 (4)	0.0020 (5)	0.0007 (7)	0.0013 (5)
C29	0.0069 (6)	0.0029 (3)	0.0034 (4)	0.0016 (5)	0.0022 (8)	0.0023 (6)
C30	0.0066 (6)	0.0022 (2)	0.0041 (4)	0.0006 (5)	0.0031 (8)	0.0018 (6)
C31	0.0026 (4)	0.0018 (2)	0.0032 (3)	0.0000 (4)	0.0010 (5)	0.0007 (4)
C32	0.0045 (5)	0.0022 (2)	0.0026 (3)	0.0013 (4)	0.0002 (6)	0.0008 (5)
C33	0.0046 (5)	0.0022 (2)	0.0028 (3)	0.0012 (4)	0.0017 (6)	0.0023 (5)
C34	0.0043 (5)	0.0019 (2)	0.0039 (4)	0.0019 (4)	0.0023 (6)	0.0009 (5)
C35	0.0044 (5)	0.0019 (2)	0.0043 (4)	0.0007 (5)	-0.0009 (7)	-0.0008 (5)
C36	0.0040 (4)	0.0019 (2)	0.0034 (3)	0.0012 (4)	-0.0014 (6)	0.0007 (5)
C37	0.0029 (4)	0.0015 (2)	0.0023 (3)	-0.0001 (3)	0.0007 (5)	0.0007 (4)
C38	0.0028 (4)	0.0016 (2)	0.0032 (3)	0.0007 (4)	0.0006 (5)	0.0011 (4)
C39	0.0032 (4)	0.0012 (2)	0.0031 (3)	0.0002 (4)	-0.0001 (5)	0.0020 (4)
C40	0.0023 (3)	0.0012 (2)	0.0029 (3)	-0.0004 (3)	-0.0005 (5)	0.0010 (4)
C41	0.0027 (4)	0.0020 (2)	0.0033 (3)	0.0006 (4)	-0.0008 (5)	0.0013 (4)
C42	0.0035 (4)	0.0024 (2)	0.0038 (4)	0.0007 (5)	-0.0005 (6)	0.0017 (5)
C43	0.0038 (4)	0.0022 (2)	0.0026 (3)	0.0010 (4)	0.0020 (6)	0.0026 (5)
C44	0.0041 (4)	0.0013 (2)	0.0031 (3)	0.0001 (4)	0.0008 (6)	0.0003 (4)
C45	0.0034 (4)	0.0018 (2)	0.0028 (3)	-0.0002 (4)	-0.0001 (5)	0.0015 (4)
C46	0.0027 (4)	0.0013 (2)	0.0036 (3)	0.0003 (4)	-0.0006 (5)	0.0003 (4)
C47	0.0046 (5)	0.0017 (2)	0.0043 (4)	0.0006 (4)	-0.0037 (7)	-0.0008 (5)
C48	0.0051 (5)	0.0020 (2)	0.0054 (5)	0.0023 (5)	-0.0032 (8)	-0.0005 (5)
C49	0.0037 (4)	0.0016 (2)	0.0061 (5)	0.0014 (5)	-0.0005 (7)	0.0010 (5)
C50	0.0033 (4)	0.0013 (2)	0.0059 (5)	-0.0005 (5)	0.0010 (7)	0.0009 (4)
C51	0.0028 (4)	0.0017 (2)	0.0043 (4)	-0.0001 (4)	0.0007 (6)	0.0010 (4)
C52	0.0027 (4)	0.0014 (2)	0.0028 (3)	-0.0004 (4)	-0.0004 (5)	0.0010 (4)
C53	0.0026 (4)	0.0014 (2)	0.0033 (3)	-0.0002 (4)	-0.0009 (5)	0.0005 (4)
C54	0.0024 (3)	0.0018 (2)	0.0030 (3)	-0.0007 (4)	0.0000 (5)	0.0008 (4)
C55	0.0028 (4)	0.0018 (2)	0.0029 (3)	0.0001 (4)	-0.0004 (5)	0.0012 (4)
C56	0.0042 (5)	0.0019 (2)	0.0037 (4)	-0.0000 (4)	-0.0011 (6)	0.0010 (5)
C57	0.0048 (5)	0.0030 (3)	0.0030 (4)	-0.0005 (5)	-0.0020 (6)	0.0014 (6)
C58	0.0040 (5)	0.0023 (2)	0.0044 (4)	0.0009 (5)	-0.0005 (7)	0.0012 (5)
C59	0.0049 (5)	0.0021 (2)	0.0047 (4)	0.0014 (5)	-0.0016 (7)	0.0007 (5)
C60	0.0048 (5)	0.0018 (2)	0.0039 (4)	0.0007 (4)	-0.0019 (7)	0.0006 (5)

Table 2 (*cont.*)

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Hg1	0.00517(3)	0.00213(1)	0.00285(2)	0.00051(3)	-0.00093(4)	0.00105(3)
Hg2	0.00468(3)	0.00221(1)	0.00255(2)	0.00098(3)	0.00036(4)	0.00069(3)
C11	0.0065 (2)	0.00238(9)	0.0041 (2)	-0.0014 (2)	-0.0018 (3)	0.0005 (2)
C12	0.0048 (2)	0.0036 (1)	0.0049 (2)	-0.0016 (2)	0.0008 (3)	-0.0005 (2)
C13	0.0115 (4)	0.0030 (1)	0.0061 (2)	0.0024 (3)	-0.0051 (5)	0.0040 (3)
C14	0.0062 (2)	0.0030 (1)	0.0027 (1)	0.0002 (2)	-0.0002 (3)	0.0005 (2)
C15	0.0110 (3)	0.0027 (1)	0.0025 (1)	0.0007 (2)	-0.0002 (3)	0.0030 (3)
C16	0.0065 (2)	0.00207(8)	0.0031 (1)	0.0001 (2)	0.0001 (3)	0.0010 (2)
C17	0.0051 (2)	0.0043 (1)	0.0038 (2)	-0.0006 (2)	-0.0016 (3)	0.0035 (3)
C18	0.0051 (2)	0.0027 (1)	0.0053 (2)	0.0020 (2)	0.0024 (3)	-0.0001 (2)
S1	0.0055 (2)	0.0026 (1)	0.0037 (2)	0.0005 (2)	-0.0003 (3)	0.0019 (2)
S2	0.0051 (2)	0.0027 (1)	0.0039 (2)	0.0014 (2)	0.0000 (3)	0.0015 (2)
S3	0.0066 (2)	0.0027 (1)	0.0035 (2)	0.0004 (2)	0.0023 (3)	0.0009 (3)
S4	0.0066 (2)	0.0029 (1)	0.0034 (2)	0.0008 (2)	0.0022 (3)	0.0010 (3)
S5	0.0051 (2)	0.00238(9)	0.0032 (1)	0.0012 (2)	-0.0015 (3)	0.0009 (2)
S6	0.0049 (2)	0.00213(9)	0.0034 (1)	0.0009 (2)	-0.0012 (3)	0.0008 (2)
S7	0.0054 (2)	0.00213(9)	0.0038 (2)	0.0004 (2)	-0.0020 (3)	0.0012 (2)
S8	0.0053 (2)	0.00195(9)	0.0041 (2)	0.0003 (2)	-0.0016 (3)	0.0010 (2)
C1	0.0058 (8)	0.0020 (3)	0.0035 (6)	-0.0004 (7)	-0.003 (1)	0.0015 (8)
C2	0.0063 (9)	0.0037 (5)	0.0032 (6)	0.0014 (8)	0.000 (1)	0.003 (1)
C3	0.009 (1)	0.0027 (4)	0.0047 (7)	0.0003 (9)	-0.002 (1)	0.002 (1)
C4	0.007 (1)	0.0030 (4)	0.0047 (7)	0.0022 (9)	-0.003 (1)	0.001 (1)
C5	0.009 (1)	0.0036 (5)	0.0039 (7)	0.0006 (9)	-0.001 (1)	0.000 (1)
C6	0.0064 (9)	0.0024 (4)	0.0045 (7)	0.0002 (8)	0.000 (1)	0.0018 (9)
C7	0.0045 (7)	0.0020 (3)	0.0041 (6)	-0.0000 (7)	-0.003 (1)	0.0001 (8)
C8	0.0048 (7)	0.0028 (4)	0.0025 (5)	0.0007 (7)	-0.001 (1)	0.0018 (8)
C9	0.0034 (6)	0.0029 (4)	0.0039 (6)	0.0003 (8)	-0.002 (1)	0.0007 (8)
C10	0.0048 (8)	0.0030 (4)	0.0033 (6)	0.0001 (8)	-0.004 (1)	0.0014 (9)
C11	0.0063 (9)	0.0028 (4)	0.0048 (7)	0.0011 (9)	-0.002 (1)	0.0022 (9)
C12	0.006 (1)	0.0032 (5)	0.008 (1)	0.001 (1)	-0.002 (2)	0.003 (1)
C13	0.011 (1)	0.0028 (4)	0.007 (1)	0.000 (1)	-0.008 (2)	0.003 (1)
C14	0.011 (1)	0.0029 (5)	0.0066 (9)	0.003 (1)	-0.005 (2)	-0.003 (1)
C15	0.008 (1)	0.0028 (4)	0.0051 (7)	0.0015 (9)	-0.002 (1)	-0.001 (1)
C16	0.0047 (7)	0.0022 (3)	0.0029 (5)	0.0003 (7)	-0.001 (1)	0.0009 (8)
C17	0.0071 (9)	0.0027 (4)	0.0037 (6)	0.0000 (8)	0.001 (1)	-0.000 (1)
C18	0.008 (1)	0.0029 (4)	0.0044 (7)	0.0031 (9)	-0.000 (1)	0.000 (1)
C19	0.0063 (9)	0.0028 (4)	0.0046 (6)	0.0023 (8)	-0.001 (1)	0.0017 (9)
C20	0.0055 (8)	0.0034 (5)	0.0037 (6)	0.0014 (8)	0.002 (1)	0.001 (1)
C21	0.0051 (8)	0.0026 (4)	0.0034 (5)	0.0010 (7)	0.000 (1)	0.0020 (8)
C22	0.0043 (7)	0.0027 (4)	0.0027 (5)	0.0006 (7)	-0.0020 (9)	-0.0002 (8)
C23	0.0031 (6)	0.0027 (4)	0.0028 (5)	0.0016 (7)	-0.0003 (9)	0.0011 (7)
C24	0.0040 (7)	0.0034 (4)	0.0026 (5)	0.0001 (8)	-0.0011 (9)	0.0014 (8)
C25	0.0039 (7)	0.0024 (3)	0.0027 (5)	0.0003 (7)	-0.0001 (9)	-0.0001 (8)
C26	0.009 (1)	0.0022 (4)	0.0037 (6)	0.0020 (8)	-0.000 (1)	-0.000 (1)
C27	0.009 (1)	0.0033 (5)	0.0049 (8)	0.000 (1)	0.001 (1)	0.001 (1)
C28	0.0048 (8)	0.0029 (4)	0.0058 (8)	0.0028 (9)	-0.000 (1)	-0.0001 (9)
C29	0.008 (1)	0.0038 (5)	0.0035 (6)	0.0014 (9)	0.001 (1)	0.004 (1)
C30	0.0065 (9)	0.0035 (5)	0.0038 (6)	0.0014 (9)	0.002 (1)	0.002 (1)
C31	0.0045 (7)	0.0022 (3)	0.0023 (5)	0.0017 (7)	0.0009 (9)	0.0016 (7)
C32	0.0043 (7)	0.0027 (4)	0.0039 (6)	0.0002 (8)	-0.001 (1)	0.0007 (8)
C33	0.0066 (9)	0.0022 (3)	0.0036 (6)	0.0014 (7)	0.002 (1)	0.0015 (9)
C34	0.0051 (8)	0.0019 (3)	0.0046 (6)	0.0011 (7)	0.004 (1)	-0.0003 (8)
C35	0.0036 (7)	0.0028 (4)	0.0054 (7)	0.0031 (9)	0.000 (1)	0.0004 (8)
C36	0.0053 (7)	0.0018 (3)	0.0031 (6)	0.0009 (7)	-0.002 (1)	-0.0004 (7)
C37	0.0038 (6)	0.0020 (3)	0.0029 (5)	0.0011 (6)	0.0009 (9)	0.0017 (7)
C38	0.0033 (6)	0.0020 (3)	0.0025 (5)	-0.0007 (6)	-0.0009 (8)	0.0016 (7)
C39	0.0045 (7)	0.0015 (3)	0.0033 (5)	-0.0007 (6)	0.0001 (9)	0.0009 (7)
C40	0.0034 (6)	0.0022 (3)	0.0025 (5)	0.0009 (6)	-0.0001 (8)	0.0013 (7)
C41	0.0039 (7)	0.0023 (3)	0.0041 (6)	0.0022 (7)	0.000 (1)	0.0021 (7)
C42	0.0042 (7)	0.0032 (4)	0.0034 (6)	0.0008 (8)	-0.000 (1)	0.0023 (8)
C43	0.0049 (7)	0.0024 (3)	0.0032 (5)	0.0020 (7)	0.002 (1)	0.0020 (8)
C44	0.0057 (8)	0.0021 (4)	0.0041 (6)	0.0011 (8)	0.001 (1)	0.0003 (8)
C45	0.0039 (7)	0.0021 (3)	0.0042 (6)	0.0007 (7)	0.000 (1)	0.0001 (7)
C46	0.0033 (6)	0.0017 (3)	0.0043 (6)	0.0001 (7)	-0.001 (1)	-0.0004 (7)
C47	0.0066 (9)	0.0028 (4)	0.0043 (7)	0.0018 (8)	-0.003 (1)	-0.000 (1)
C48	0.0065 (9)	0.0028 (4)	0.0051 (7)	0.0022 (9)	-0.005 (1)	-0.0006 (9)
C49	0.0043 (7)	0.0031 (4)	0.0059 (8)	0.0028 (9)	-0.000 (1)	0.0021 (9)
C50	0.0049 (8)	0.0025 (4)	0.0055 (8)	-0.0010 (9)	0.001 (1)	0.0003 (9)
C51	0.0044 (7)	0.0014 (3)	0.0060 (7)	0.0011 (8)	0.002 (1)	0.0006 (7)
C52	0.0036 (6)	0.0025 (3)	0.0031 (5)	-0.0003 (7)	-0.0000 (9)	0.0021 (7)
C53	0.0034 (6)	0.0022 (3)	0.0038 (6)	-0.0008 (7)	-0.0021 (9)	0.0010 (7)
C54	0.0039 (6)	0.0015 (3)	0.0033 (6)	-0.0008 (6)	-0.0006 (9)	0.0008 (7)
C55	0.0035 (6)	0.0017 (3)	0.0049 (6)	0.0002 (7)	-0.002 (1)	0.0009 (7)
C56	0.0045 (7)	0.0026 (4)	0.0040 (6)	-0.0000 (8)	-0.001 (1)	-0.0000 (8)
C57	0.0065 (9)	0.0038 (5)	0.0039 (7)	0.0012 (9)	-0.002 (1)	0.001 (1)
C58	0.0062 (9)	0.0031 (4)	0.0041 (6)	0.0029 (8)	0.000 (1)	0.001 (1)
C59	0.0042 (8)	0.0031 (4)	0.0057 (8)	0.0013 (9)	0.000 (1)	0.0003 (9)
C60	0.0060 (8)	0.0025 (4)	0.0034 (6)	0.0014 (8)	-0.000 (1)	0.0027 (9)

Terminal atomic coordinates are listed in Table 1 and anisotropic thermal parameters in Table 2. Bond lengths and bond angles are listed in Tables 3 and 4. Certain distances and angles involved in important anion–cation non-valence interactions are given in Table 5, and equations of the cation ring planes in Table 6. Observed and calculated structure amplitudes

Table 3. (SbzSbz)$_2$[FeCl$_4$] *and* (SbzSbz)$_2$[MgCl$_4$]: *bond lengths and estimated standard deviations* (Å)

	Iron isomorph	Mercury isomorph
M(1)–Cl(1)	2·301 (3)	2·462 (4)
M(1)–Cl(2)	2·337 (3)	2·523 (4)
M(1)–Cl(3)	2·275 (3)	2·441 (5)
M(1)–Cl(4)	2·305 (3)	2·476 (4)
M(2)–Cl(5)	2·303 (3)	2·465 (4)
M(2)–Cl(6)	2·314 (2)	2·474 (4)
M(3)–Cl(7)	2·337 (3)	2·535 (4)
M(4)–Cl(8)	2·287 (3)	2·448 (4)
S(1)—S(2)	2·002 (3)	2·000 (6)
S(3)—S(4)	2·008 (3)	2·011 (6)
S(5)—S(6)	2·010 (3)	2·020 (5)
S(7)—S(8)	2·012 (3)	2·007 (5)
S(1)—C(7)	1·704 (8)	1·67 (1)
S(2)—C(9)	1·700 (8)	1·71 (1)
S(3)—C(22)	1·703 (8)	1·66 (1)
S(4)—C(24)	1·705 (8)	1·72 (1)
S(5)—C(37)	1·706 (7)	1·70 (1)
S(6)—C(39)	1·702 (8)	1·69 (1)
S(7)—C(52)	1·701 (7)	1·68 (1)
S(8)—C(54)	1·695 (8)	1·70 (1)
C(1)—C(2)	1·39 (1)	1·36 (2)
C(1)—C(6)	1·39 (1)	1·38 (2)
C(1)—C(7)	1·45 (1)	1·44 (2)
C(2)—C(3)	1·39 (1)	1·38 (2)
C(3)—C(4)	1·35 (1)	1·37 (2)
C(4)—C(5)	1·37 (1)	1·35 (2)
C(5)—C(6)	1·38 (1)	1·41 (2)
C(7)—C(8)	1·37 (1)	1·39 (2)
C(8)—C(9)	1·39 (1)	1·37 (2)
C(9)—C(10)	1·46 (1)	1·48 (2)
C(10)-C(11)	1·39 (1)	1·41 (2)
C(10)-C(15)	1·40 (1)	1·41 (2)
C(11)-C(12)	1·39 (1)	1·37 (2)
C(12)-C(13)	1·38 (1)	1·38 (3)
C(13)-C(14)	1·36 (2)	1·40 (3)
C(14)-C(15)	1·39 (1)	1·38 (3)
C(16)-C(17)	1·40 (1)	1·41 (2)
C(16)-C(21)	1·38 (1)	1·36 (2)
C(16)-C(22)	1·46 (1)	1·47 (2)
C(17)-C(18)	1·37 (1)	1·40 (2)
C(18)-C(19)	1·37 (1)	1·36 (2)
C(19)-C(20)	1·38 (1)	1·36 (2)
C(20)-C(21)	1·38 (1)	1·40 (2)
C(22)-C(23)	1·38 (1)	1·39 (2)
C(23)-C(24)	1·38 (1)	1·38 (2)
C(24)-C(25)	1·46 (1)	1·46 (2)
C(25)-C(26)	1·38 (1)	1·35 (2)
C(25)-C(30)	1·39 (1)	1·39 (2)
C(26)-C(27)	1·37 (1)	1·41 (2)
C(27)-C(28)	1·38 (1)	1·38 (2)
C(28)-C(29)	1·36 (1)	1·37 (2)
C(29)-C(30)	1·37 (1)	1·35 (2)
C(31)-C(32)	1·38 (1)	1·44 (2)
C(31)-C(36)	1·40 (1)	1·36 (2)
C(31)-C(37)	1·45 (1)	1·45 (2)
C(32)-C(33)	1·40 (1)	1·37 (2)
C(33)-C(34)	1·38 (1)	1·40 (2)
C(34)-C(35)	1·38 (1)	1·38 (2)
C(35)-C(36)	1·39 (1)	1·35 (2)
C(37)-C(38)	1·38 (1)	1·39 (2)
C(38)-C(39)	1·37 (1)	1·38 (2)
C(39)-C(40)	1·45 (1)	1·46 (2)
C(40)-C(41)	1·39 (1)	1·41 (2)
C(40)-C(45)	1·40 (1)	1·39 (2)
C(41)-C(42)	1·37 (1)	1·37 (2)
C(42)-C(43)	1·39 (1)	1·40 (2)
C(43)-C(44)	1·37 (1)	1·39 (2)
C(44)-C(45)	1·37 (1)	1·37 (2)
C(46)-C(47)	1·39 (1)	1·39 (2)
C(46)-C(51)	1·41 (1)	1·40 (2)
C(46)-C(52)	1·47 (1)	1·46 (2)
C(47)-C(48)	1·38 (1)	1·38 (2)
(C48)-C(49)	1·38 (1)	1·40 (2)
C(49)-C(50)	1·37 (1)	1·37 (2)
C(50)-C(51)	1·38 (1)	1·40 (2)
C(52)-C(53)	1·37 (1)	1·41 (2)
C(53)-C(54)	1·39 (1)	1·34 (2)
C(54)-C(55)	1·46 (1)	1·46 (2)
C(55)-C(56)	1·40 (1)	1·42 (2)
C(55)-C(60)	1·40 (1)	1·38 (2)
C(56)-C(57)	1·36 (1)	1·37 (2)
C(57)-C(58)	1·37 (1)	1·37 (2)
C(58)-C(59)	1·38 (1)	1·36 (2)
C(59)-C(60)	1·37 (1)	1·41 (2)
Mean C–H	1·08	1·08

Table 4. (SbzSbz)$_2$[FeCl$_4$] *and* (SbzSbz)$_2$[HgCl$_4$]: *interbond angles and estimated standard deviations* (°)

	Iron isomorph	Mercury isomorph
Cl(1)–M(1)–Cl(2)	102·82 (9)	100·9 (1)
Cl(1)–M(1)–Cl(3)	108·2 (1)	110·1 (2)
Cl(1)–M(1)–Cl(4)	118·1 (1)	118·4 (1)
Cl(2)–M(1)–Cl(3)	120·6 (1)	122·1 (2)
Cl(2)–M(1)–Cl(4)	103·18 (9)	101·9 (1)
Cl(3)–M(1)–Cl(4)	104·7 (1)	104·2 (2)
Cl(5)–M(2)–Cl(6)	109·76 (9)	109·6 (1)
Cl(5)–M(2)–Cl(7)	103·71 (9)	102·5 (1)
Cl(5)–M(2)–Cl(8)	114·8 (1)	115·8 (1)
Cl(6)–M(2)–Cl(7)	112·22 (9)	111·4 (1)
Cl(6)–M(2)–Cl(8)	107·99 (9)	109·8 (1)
Cl(7)–M(2)–Cl(8)	108·39 (9)	107·6 (1)
C(2)—C(1)—C(7)	120·8 (7)	121 (1)
C(6)—C(1)—C(7)	120·4 (8)	121 (1)
S1——C(7)—C(1)	117·8 (6)	119 (1)
C(1)—C(7)—C(8)	126·5 (7)	125 (1)
S(2)—C(9)—C(10)	117·9 (6)	118 (1)
C(8)—C(9)—C(10)	126·3 (7)	127 (1)
C(9)—C(10)-C(11)	120·3 (8)	120 (1)
C(9)—C(10)-C(15)	121·1 (8)	121 (1)
C(17)-C(16)-C(22)	121·0 (7)	118 (1)
C(21)-C(16)-C(22)	120·8 (7)	123 (1)
S(3)—C(22)-C(16)	117·1 (6)	119 (1)
C(16)-C(22)-C(23)	126·9 (7)	124 (1)
S(4)—C(24)-C(25)	118·6 (6)	119 (1)
C(23)-C(24)-C(25)	126·5 (7)	127 (1)
C(24)-C(25)-C(26)	120·8 (7)	120 (1)
C(24)-C(25)-C(30)	120·9 (7)	121 (1)
C(32)-C(31)-C(37)	121·8 (7)	119 (1)
C(36)-C(31)-C(37)	119·4 (7)	123 (1)
S(5)—C(37)-C(31)	118·5 (5)	121 (1)
C(31)-C(37)-C(38)	126·9 (7)	125 (1)
S(6)—C(39)-C(40)	118·1 (5)	118·4 (9)
C(38)-C(39)-C(40)	126·7 (7)	127 (1)
C(39)-C(40)-C(41)	119·1 (7)	118 (1)
C(39)-C(40)-C(45)	122·2 (7)	122 (1)
C(47)-C(46)-C(52)	121·1 (7)	120 (1)
C(51)-C(46)-C(52)	120·3 (7)	121 (1)
S(7)—C(52)-C(46)	116·1 (5)	118 (1)
C(46)-C(52)-C(53)	127·7 (7)	127 (1)
S(8)—C(54)-C(55)	118·8 (6)	118 (1)
C(53)-C(54)-C(55)	126·3 (7)	127 (1)
C(54)-C(55)-C(56)	121·3 (7)	120 (1)
C(54)-C(55)-C(60)	120·6 (7)	121 (1)

Table 4 (*cont.*)

Internal angles of the phenyl and five-membered dithiolium rings at the atom specified.

S(1)	96·0 (3)	96·3 (5)	C(27)	120·4 (9)	119 (2)
S(2)	95·7 (3)	95·6 (5)	C(28)	119·3 (9)	120 (2)
S(3)	95·4 (3)	95·9 (5)	C(29)	120·7 (9)	120 (2)
S(4)	96·4 (3)	96·2 (5)	C(30)	120·8 (9)	121 (1)
S(5)	96·1 (3)	96·0 (5)	C(31)	118·8 (7)	118 (1)
S(6)	95·9 (3)	96·2 (5)	C(32)	120·5 (8)	120 (1)
S(7)	95·2 (3)	95·8 (5)	C(33)	120·0 (8)	120 (1)
S(8)	96·4 (3)	96·4 (5)	C(34)	119·7 (8)	119 (1)
C(1)	118·8 (8)	119 (1)	C(35)	120·6 (8)	122 (1)
C(2)	120·2 (8)	122 (1)	C(36)	120·4 (8)	121 (1)
C(3)	120·5 (9)	120 (2)	C(37)	114·6 (6)	114 (1)
C(4)	120·1 (9)	119 (2)	C(38)	118·3 (7)	118 (1)
C(5)	121 (1)	122 (2)	C(39)	115·1 (6)	115 (1)
C(6)	119·6 (9)	118 (1)	C(40)	118·7 (7)	120 (1)
C(7)	115·7 (6)	116 (1)	C(41)	120·1 (7)	119 (1)
C(8)	116·8 (7)	117 (1)	C(42)	120·7 (8)	121 (1)
C(9)	115·8 (6)	115 (1)	C(43)	119·5 (7)	120 (1)
C(10)	118·6 (8)	119 (1)	C(44)	120·6 (7)	120 (1)
C(11)	119·8 (9)	120 (1)	C(45)	120·4 (7)	121 (1)
C(12)	121 (1)	121 (2)	C(46)	118·6 (7)	119 (1)
C(13)	118 (1)	119 (2)	C(47)	121·1 (8)	121 (1)
C(14)	122 (1)	121 (2)	C(48)	119·6 (9)	120 (1)
C(15)	119·7 (9)	119 (2)	C(49)	120·4 (8)	119 (1)
C(16)	118·1 (7)	119 (1)	C(50)	120·7 (8)	122 (1)
C(17)	121·3 (9)	119 (1)	C(51)	119·7 (7)	119 (1)
C(18)	119·5 (9)	121 (1)	C(52)	116·2 (6)	115 (1)
C(19)	120·7 (9)	121 (1)	C(53)	117·3 (7)	118 (1)
C(20)	119·6 (8)	120 (1)	C(54)	114·9 (6)	115 (1)
C(21)	120·9 (8)	120 (1)	C(55)	118·0 (7)	119 (1)
C(22)	116·0 (6)	117 (1)	C(56)	120·2 (8)	119 (1)
C(23)	117·3 (7)	117 (1)	C(57)	121·6 (8)	122 (1)
C(24)	114·9 (6)	114 (1)	C(58)	119·0 (8)	119 (1)
C(25)	118·2 (8)	119 (1)	C(59)	120·6 (8)	122 (1)
C(26)	120·6 (9)	120 (1)	C(60)	120·6 (8)	119 (1)

Table 5. *Interionic distances and angles*

(SbzSbz)$_2$[FeCl$_4$] and (SbzSbz)$_2$[HgCl$_4$]:
interionic S···Cl contacts (Å).

Cl(1)···S(1)	3·907 (3)	3·904 (6)
Cl(1)···S(2)	3·939 (3)	3·912 (6)
Cl(2)···S(3)	3·168 (3)	3·153 (6)
Cl(2)···S(4)	3·378 (3)	3·369 (6)
Cl(2)···S(7)	3·151 (3)	3·146 (6)
Cl(2)···S(8)	3·393 (3)	3·404 (6)
Cl(3)···S(1)	3·951 (3)	3·948 (6)
Cl(3)···S(5)	3·920 (3)	3·767 (6)
Cl(4)···S(6)	3·816 (3)	3·779 (5)
Cl(5)···S(3)	3·899 (3)	3·910 (6)
Cl(6)···S(7)	3·896 (3)	3·809 (5)
Cl(6)···S(8)	3·844 (3)	3·857 (5)
Cl(7)···S(1)	3·358 (3)	3·303 (6)
Cl(7)···S(2)	3·245 (3)	3·196 (6)
Cl(7)···S(5)	3·276 (3)	3·269 (6)
Cl(7)···S(6)	3·208 (3)	3·179 (6)
Cl(8)···S(4)	3·887 (3)	3·875 (6)
Cl(8)···S(8)	3·601 (3)	3·609 (6)

(SbzSbz)$_2$[FeCl$_4$]:
interionic angles associated with short S···Cl contacts

Fe(1)–Cl(2)–S(3)	129·8 (1)	128·9 (2)
Fe(1)–Cl(2)–S(4)	112·2 (1)	110·0 (2)
Fe(1)–Cl(2)–S(7)	116·9 (1)	115·8 (2)
Fe(1)–Cl(2)–S(8)	117·8 (1)	115·6 (2)
Fe(2)–Cl(7)–S(1)	111·8 (1)	109·0 (2)
Fe(2)–Cl(7)–S(2)	122·5 (1)	119·1 (2)
Fe(2)–Cl(7)–S(5)	114·6 (1)	113·2 (2)
Fe(2)–Cl(7)–S(6)	113·8 (1)	113·6 (2)

Table 6. *The dithiolium cations*

(*a*) (SbzSbz)$_2$[FeCl$_4$]: least-squares best planes in the dithiolium cations and maximum atom deviations from the ring planes (Å).*

Ring	Equation of normal		Maximum deviation from plane (Å)
1	$0{\cdot}9598X+0{\cdot}0180Y+0{\cdot}2801Z=$	8·339	0·025
2	$0{\cdot}8518X+0{\cdot}1053Y+0{\cdot}5132Z=$	9·906	0·006
3	$0{\cdot}8061X+0{\cdot}1503Y+0{\cdot}5723Z=$	10·313	0·012
4	$0{\cdot}9062X+0{\cdot}0613Y+0{\cdot}4183Z=$	16·567	0·006
5	$0{\cdot}8457X+0{\cdot}1612Y+0{\cdot}5088Z=$	16·900	0·003
6	$0{\cdot}9456X+0{\cdot}0506Y+0{\cdot}3214Z=$	16·445	0·011
7	$0{\cdot}8912X-0{\cdot}1474Y-0{\cdot}4289Z=$	5·391	0·006
8	$0{\cdot}8474X-0{\cdot}1876Y-0{\cdot}4968Z=$	5·077	0·001
9	$-0{\cdot}5223X+0{\cdot}4425Y+0{\cdot}7290Z=$	−2·566	0·015
10	$0{\cdot}9561X-0{\cdot}0457Y-0{\cdot}2893Z=$	13·972	0·009
11	$-0{\cdot}8675X+0{\cdot}0807Y+0{\cdot}2893Z=$	−12·323	0·011
12	$-0{\cdot}9192X+0{\cdot}0611Y+0{\cdot}3889Z=$	−13·052	0·004

(*b*) (SbzSbz)$_2$[FeCl$_4$]: ring–ring dihedral angles in the dithiolium cations.

Rings involved	Angle	Rings involved	Angle
1–2	15°	7–8	5°
2–3	5	9–9	27
4–5	8	10–11	13
5–6	14	11–12	7

* The ring-numbering scheme is defined in Fig. 2(*c*). The direction cosines refer to *a*, *b** and *c′* respectively.

for the terminal refinement cycles are available.* The atom labelling scheme is defined in Fig. 2.

Discussion

Like the analogous SacSac complexes (Freeman *et al.*, 1974), crystals of (SbzSbz)$_2$MCl$_4$ [M = Fe, Hg] consist of essentially discrete dithiolium cations and tetrachlorometallate(II) anions, with contributions to the binding energy both from dispersion and from strong charge-transfer interactions. In both series of complexes† the charge-transfer interactions involve close contacts from each of the cation sulphur atoms to the chlorine atoms of neighbouring tetrachlorometallate ions. The contact distances are similar in each series (*ca.* 3·2–3·4 Å) but the overall pattern is dissimilar. In (SacSac)$_2$FeCl$_4$ and its isomers all four chlorines of each anion are involved in short S···Cl contacts. Moreover each cation effectively 'bridges' two anions in such a way as to form continuous charge-transfer pathways directed along the crystallographic *c*-axis

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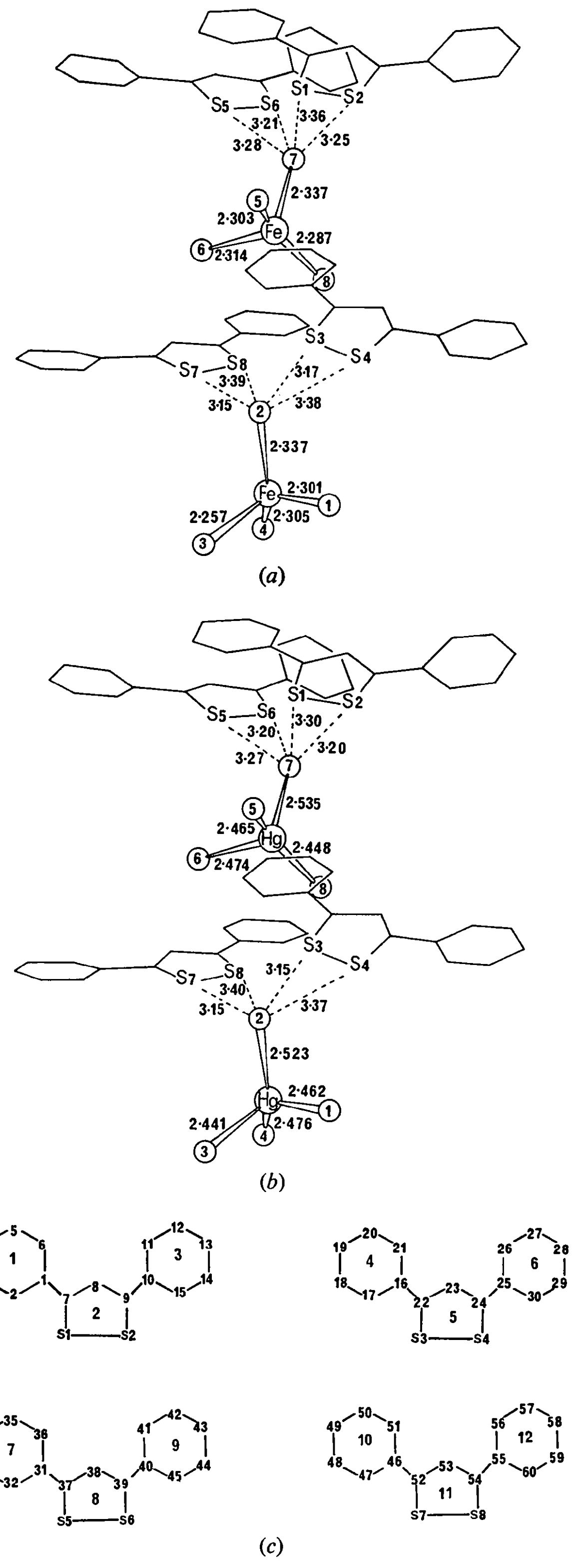
* The list has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30310 (53 pp. 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† Crystals of (SacSac)$_2$MCl$_4$ [M = Mn, Fe, Co, Zn, Cd] are isomorphous (Freeman *et al.*, 1974). The complexes (SbzSbz)$_2$MCl$_4$ [M = Mn, Fe, Zn, Cd, Hg] also form an isomorphous series (α structures). (SbzSbz)$_2$CoCl$_4$ is representative of a third isomorphous series (γ structures) which includes polymorphs of (SbzSbz)$_2$MnCl$_4$ and (SbzSbz)$_2$ZnCl$_4$ (Mason *et al.*, 1974).

direction (Freeman *et al.*, 1974). In the present complexes no analogous cation bridging is observed, and only one chlorine of each of the two independent tetrachlorometallate ions is involved in short S···Cl contacts. The contact pattern around each anion is remarkably similar. The relevant chlorines [Cl(2) and Cl(7)] are each involved in a roughly pyramidal array of short contacts to the four sulphur atoms of neighbouring, and similarly oriented, pairs of cations (Figs. 2, 3). In turn, the independent $(SbzSbz)_2MCl_4$ moieties are related, approximately, by a pseudo-twofold screw axis passing through the metal atoms and directed parallel to the arbitarily assigned crystallographic *a* axis. As shown in Fig. 5, cation pairs related by the pseudo-screw operation (and separated by *a*/2) are interleaved by oppositely directed (but parallel) inversion related pairs forming part of the $(SbzSbz)_2MCl_4$ stack generated by a second pseudo-2_1 axis. There are a number of relatively short C(phenyl)–C(phenyl) contacts (*ca.* 3·3–3·5 Å) in each cation stack, and occasional contacts of similar magnitude between neighbouring stacks (Table 8). Close contacts between carbon atoms and those chlorines not involved in Cl···S bonding are also observed. Typically the C···Cl con-



(*a*)

(*b*)

(*c*)

Fig. 2. (*a*) Iron, chlorine and sulphur atom labelling in $(SbzSbz)_2[FeCl_4]$ and some important bond-lengths. (*b*) Mercury, chlorine and sulphur atom labelling in $(SbzSbz)_2[HgCl_4]$ and some important bond-lengths. (*c*) Carbon, sulphur and ring labels in the diphenyldithiolium cations.

Table 7. $(SbzSbz)_2[FeCl_4]$: *representative short* C···Cl *contacts* (*to the* $Fe(1)Cl_4^{2-}$ *moiety*)

Contact	Distance (Å)	Contact	Distance (Å)
Cl(1)···C(6)	3·63	Cl(3)···C(19)	3·75
Cl(1)···C(7)	3·68	Cl(4)···C(38)	3·60
Cl(1)···C(8)	3·64	Cl(4)···C(39)	3·51
Cl(1)···C(9)	3·72	Cl(4)···C(49)	3·65
Cl(1)···C(48)	3·68	Cl(4)···C(51)	3·61
Cl(3)···C(2)	3·75	Cl(4)···C(52)	3·65
Cl(3)···C(18)	3·45		

Table 8. $(SbzSbz)_2[FeCl_4]$ *and* $(SbzSbz)_2[HgCl_4]$: *interionic* C···C *contacts less than* 3·8 Å

	Symmetry relationship*	Iron isomorph	Mercury isomorph
C(1)····C(11)	4/001	3·77 (1)	–
C(1)····C(25)	4/101	3·75 (1)	3·76 (2)
C(2)····C(12)	4/001	3·68 (1)	3·65 (2)
C(2)····C(27)	$3/\bar{1}\bar{1}0$	3·62 (1)	3·67 (2)
C(3)····C(12)	4/001	3·56 (1)	3·55 (2)
C(3)····C(17)	2/101	3·76 (1)	–
C(3)····C(18)	2/101	3·64 (1)	3·70 (2)
C(3)····C(27)	$3/\bar{1}\bar{1}0$	3·77 (1)	3·78 (2)
C(3)····C(27)	4/101	–	3·77 (2)
C(4)····C(12)	4/001	3·60 (1)	3·63 (2)
C(4)····C(13)	4/001	3·75 (1)	3·77 (3)
C(4)····C(28)	4/101	3·75 (1)	3·73 (2)
C(4)····C(29)	4/101	3·75 (1)	–
C(5)····C(12)	4/001	3·74 (2)	–
C(5)····C(29)	4/101	3·74 (1)	3·72 (2)
C(5)····C(30)	4/101	3·69 (1)	3·72 (2)
C(5)····C(42)	1/001	3·75 (1)	–
C(6)····C(11)	4/001	3·65 (1)	3·78 (2)
C(6)····C(25)	4/101	3·75 (1)	3·64 (2)
C(6)····C(30)	4/101	3·77 (1)	3·77 (2)
C(7)····C(24)	4/101	3·72 (1)	3·79 (2)
C(9)····C(22)	4/101	3·60 (1)	3·61 (2)

Table 8 (*cont.*)

	Symmetry relationship*	Iron isomorph	Mercury isomorph
C(12)···C(13)	2/111	3·42 (1)	3·51 (2)
C(13)···C(13)	2/111	3·27 (1)	3·27 (3)
C(14)···C(47)	3/$\bar{1}$00	3·80 (1)	–
C(15)···C(17)	4/101	3·57 (1)	3·59 (2)
C(15)···C(47)	3/$\bar{1}$00	3·67 (1)	3·70 (2)
C(15)···C(48)	3/$\bar{1}$00	3·68 (1)	3·70 (2)
C(18)···C(26)	4/101	3·78 (1)	–
C(19)···C(25)	4/101	3·63 (1)	3·64 (2)
C(19)···C(26)	4/101	3·61 (1)	3·68 (2)
C(19)···C(33)	2/101	3·64 (1)	3·68 (2)
C(19)···C(57)	1/001	3·67 (1)	3·70 (2)
C(19)···C(58)	1/001	3·76 (1)	3·77 (2)
C(20)···C(23)	4/101	3·78 (1)	3·80 (2)
C(20)···C(24)	4/101	3·67 (1)	3·66 (2)
C(20)···C(25)	4/101	3·65 (1)	3·71 (2)
C(20)···C(33)	2/101	3·75 (1)	–
C(21)···C(23)	4/101	3·54 (1)	3·57 (2)
C(27)···C(27)	2/211	3·66 (1)	3·78 (3)
C(29)···C(32)	3/000	3·64 (1)	3·62 (2)
C(29)···C(41)	4/100	3·74 (1)	3·72 (2)
C(30)···C(42)	4/100	3·65 (1)	3·68 (2)
C(30)···C(43)	4/100	3·69 (1)	3·73 (2)
C(31)···C(39)	2/100	3·79 (1)	–
C(31)···C(56)	2/100	3·73 (1)	3·71 (2)
C(32)···C(39)	2/100	3·65 (1)	3·66 (2)
C(32)···C(57)	2/100	3·77 (1)	3·73 (2)
C(33)···C(40)	2/100	3·80 (1)	–
C(33)···C(45)	2/100	3·36 (1)	3·42 (2)
C(33)···C(57)	2/100	3·77 (1)	3·71 (2)
C(33)···C(58)	2/100	3·69 (1)	3·70 (2)
C(34)···C(45)	2/100	3·60 (1)	3·67 (2)
C(34)···C(58)	2/100	3·44 (1)	3·49 (2)
C(34)···C(59)	2/100	3·59 (1)	3·61 (2)
C(35)···C(55)	2/100	3·75 (1)	3·73 (2)
C(35)···C(58)	2/100	3·72 (1)	3·79 (2)
C(35)···C(59)	2/100	3·55 (1)	3·61 (2)
C(35)···C(60)	2/100	3·55 (1)	3·58 (2)
C(36)···C(55)	2/100	3·62 (1)	3·66 (2)
C(36)···C(56)	2/100	3·59 (1)	3·62 (2)
C(37)···C(37)	2/100	3·60 (1)	3·61 (2)
C(40)···C(50)	3/$\bar{1}$00	3·72 (1)	3·76 (2)
C(41)···C(46)	2/100	3·69 (1)	3·70 (2)
C(41)···C(50)	2/100	3·75 (1)	3·77 (2)
C(41)···C(51)	2/100	3·46 (1)	3·47 (2)
C(42)···C(46)	2/100	3·66 (1)	3·70 (2)
C(42)···C(47)	2/100	3·74 (1)	3·72 (2)
C(42)···C(48)	2/100	3·62 (1)	3·58 (2)
C(42)···C(49)	2/100	3·41 (1)	3·40 (2)
C(42)···C(50)	2/100	3·31 (1)	3·35 (2)
C(42)···C(51)	2/100	3·46 (1)	3·49 (2)
C(44)···C(50)	3/$\bar{1}$00	3·50 (1)	3·56 (2)
C(44)···C(51)	3/$\bar{1}$00	3·78 (1)	–
C(45)···C(50)	3/$\bar{1}$00	3·39 (1)	3·41 (2)
C(46)···C(55)	2/200	3·60 (1)	3·61 (2)
C(46)···C(60)	2/200	3·58 (1)	3·55 (2)
C(47)···C(59)	2/200	3·76 (1)	3·78 (2)
C(48)···C(59)	2/200	3·70 (1)	3·72 (2)
C(51)···C(60)	2/200	3·57 (1)	3·53 (2)
C(51)···C(54)	2/200	3·52 (1)	3·56 (2)
C(52)···C(55)	2/200	3·62 (1)	3·59 (2)
C(53)···C(53)	2/200	3·73 (1)	3·72 (2)
C(52)···C(54)	2/200	3·62 (1)	3·61 (2)

* Figures preceding the solidus denote the equipoint number

$$1=X,\ Y,\ Z;\quad 3=\tfrac{1}{2}+X,\ \tfrac{1}{2}+Y,\ Z$$
$$2=\bar{X},\ \bar{Y},\ \bar{Z};\quad 4=\tfrac{1}{2}-X,\ \tfrac{1}{2}-Y,\ \bar{Z}$$

Figures following the solidus denote translations in the **a**, **b** and **c** directions respectively.

tacts range down to *ca.* 3·5 Å, involve both phenyl and heterocycle carbon atoms, and probably complete a more or less continuous charge transfer path analogous to that observed for $(SacSac)_2FeCl_4$. Representative values are listed in Table 7.

The crystal packing arrangement provides a fairly obvious rationale for the observed temperature dependence of the $(SbzSbz)_2FeCl_4$ Mössbauer spectrum. At room temperature, distinct signals are observed for each of the (two) inequivalent tetrachloroferrate(II) ions. However, the low-temperature spectrum indicates a common environment (*i.e.* crystallographic equivalence) for each ion. As is clear from the diagram (Fig. 5), relatively small changes in atom coordinates would be required either to cause exact halving of the crystallographic *a* axis or, alternatively, to relate the two

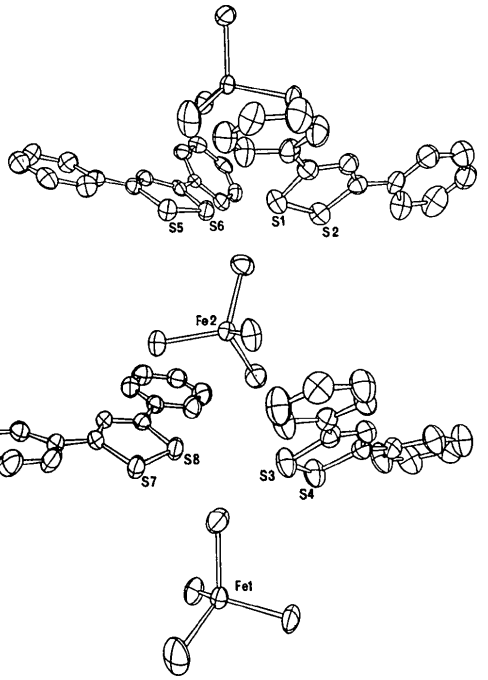


Fig. 3. $(SbzSbz)_2[FeCl_4]$: Anion–cation packing and atomic thermal ellipsoids (50% probability).

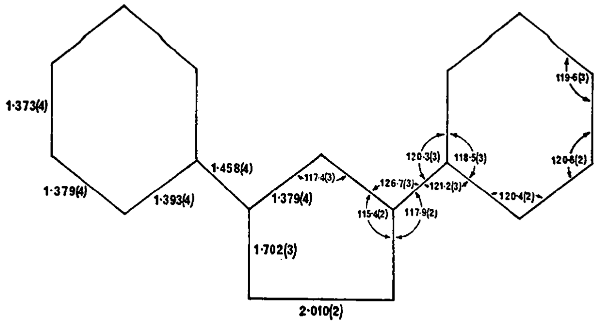


Fig. 4. $(SbzSbz)_2[FeCl_4]$: mean bond lengths and bond angles in the diphenyldithiolium cations.

(SbzSbz)$_2$FeCl$_4$ moieties by an exact twofold screw operation. Either situation would result in the metal ions having crystallographically equivalent environments.

Geometry of the tetrachlorometallate ions

The tetrachlorometallate ions each exhibit less than T_d ($\bar{4}3m$) symmetry, the deviations from T_d being manifest both by small but significant inequivalences in metal–ligand distances and by appreciable angular distortions (ligand–metal–ligand) from the regular tetrahedral value (109·47°). Deviations of the metal–ligand bond-distances from their mean values are summarized in Table 9(*a*) and the angular deviations are summarized in Table 9(*b*). These data clearly illustrate the marked environmental dependence of the anion geometry. In particular, the virtual identity of the environments experienced by isomorphous tetrachloromercurate–tetrachloroferrate pairs results in a near one-to-one correspondence of both bond-length and bond-angle deformations in the separate anions. In contrast, the effects of relatively minor environmental differences are clearly manifest in the appreciably smaller angular deformations observed in the case of the metal(2) tetrachloro-anions (*ca.* 4° r.m.s.) as compared with their metal(1) tetrachloro-anion counterparts (*ca.* 8° r.m.s.). The slightly larger angular deformations observed for the tetrachloromercurate (*cf.* tetrachloroferrate) anions most probably result from the increased polarizability of the heavier metal ion. The close correspondence between bond lengths and bond-angle deformations in related tetrachloromercurate–tetrachloroferrate pairs conclusively rules out any appreciable Jahn–Teller contribution to distortion of the [FeCl$_4$]$^{2-}$ ions. Deformations of comparable magnitude reported for the anions in bis-(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate(II) (Freeman *et al.*, 1974) and in {[Fe(h^5–C$_5$H$_5$)(CO)$_2$]$_3$SbCl}$_2$[FeCl$_4$].CH$_2$Cl$_2$ (Trinh-Toan & Dahl, 1971) [Table 9] are also attributable to asymmetric anion–cation and anion–solvent dipolar interactions. Despite the environmental (hence bond-length deformation) differences, average Fe–Cl distances in the above-mentioned complexes (2·313 and 2·310 Å respectively) and in (SbzSbz)$_2$[FeCl$_4$] [Fe(1)–Cl = 2·305; Fe(2)–Cl = 2·310 Å] are in close agreement. The average Hg–Cl distance (2·479 Å) is identical, within experimental error, to the sum of standard covalent radii (2·48 Å) (Pauling, 1960).

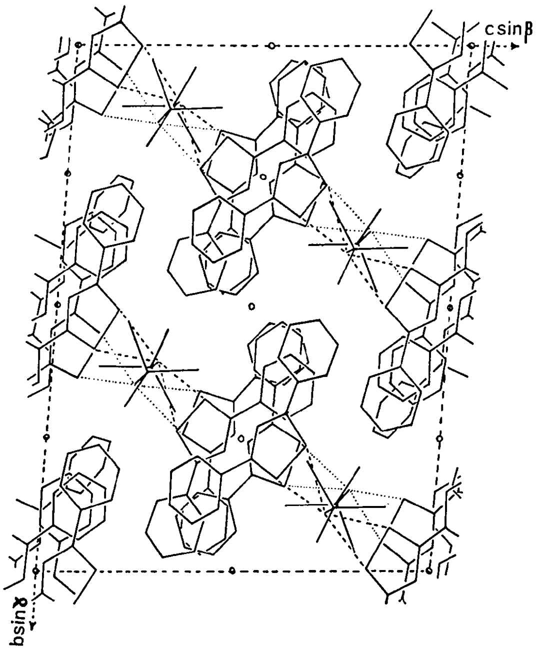
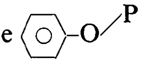


Fig. 5. (SbzSbz)$_2$[FeCl$_4$]: the crystal structure viewed down **a** showing interleaving of cations and schematic electron-transfer pathways (------) corresponding to close S···Cl contacts.

Geometry of the dithiolium cations

The dithiolium cations exhibit little asymmetry. The ring systems, both five- and six-membered, are each planar within experimental error, with the five-membered (heterocyclic) rings possessing experimental C_{2v} symmetry. Equations to the ring normals, together with maximum atom deviations from the corresponding (least-squares) ring planes (iron isomer only) are detailed in Table 6. Mean bond-length and bond-angle data, averaged over chemically equivalent parameters in the four crystallographically independent cations of the tetrachloroferrate isomer, are summarized in Fig. 4. With one exception [angle S(7)–C(52)–C(46): $\Delta/\sigma \simeq$ 3·6], individual bond lengths and bond angles are each within experimental error of their appropriate mean values.

The heterocycle dimensions differ only marginally from those in the 3,5-dimethyl substituted cations in (SacSac)$_2$[FeCl$_4$] (Freeman *et al.*, 1974). The S–S, S–C and C–C distances, each intermediate between the accepted single- and double-bond values, are indicative of appreciable cyclic delocalization over the ring system. In the SacSac complex, however, the heterocycle skeleton shows slight but significant departures from C_{2v} symmetry. The S–S and S–C distances [2·019 (2) and 1·681 (4) Å] also differ marginally from the present values [2·010 (2) Å, $\Delta/\sigma \simeq 3$ and 1·702 (3) Å, $\Delta/\sigma \simeq 4$]. At 2·023 (5) Å, the S–S distance in (SbzSbz)$_2$[FeCl$_4$]Cl (Mason *et al.*, 1974) is marginally longer again, the differences probably reflecting the effects of increasingly energetic interactions with the counter ions.

Both the ring–ring bond-distance in the (SbzSbz)$^+$ ion [1·458 (5) Å] and the ring–methyl distance in (SacSac)$^+$ [1·499 (5) Å] are consistent with a C(sp^2) σ-orbital radius of 0·73 Å. In turn, this value is consistent with that deriving from spectroscopic data for butadiene (0·73 Å; Cole, Mohay & Osborne, 1967) but is rather smaller (*ca.* 0·02 Å) than values deriving from X-ray diffraction studies of diphenyl (Robertson, 1961) and 2,2′-dipyridyl (Mason & Robertson, 1967). In any case, the present result needs to be treated with some caution since the 3- and 5-carbon atoms of the heterocycle are not strictly sp^2-hybridized. The altered hybridization at these atoms results, in part, from steric constraints imposed by formation of the 5-membered ring. However, the gross inequivalence of the external (C–C–C and S–C–C) angles (126·7 and 117·9° respectively) can only be attributed to an appreciable charge drift to the (effectively) highly electronegative hetero-atoms. The latter effect closely parallels that recently observed in the  moieties in chlorobis-[2-(diphenoxyphosphinooxy)phenyl](triphenylphosphite)iridium(III) (Guss & Mason, 1972).

Bond-lengths and bond-angles in the phenyl rings (Fig. 4), notably the progressive shortening of the C–C distances towards the ring extremities, are indicative of fairly substantial torsional vibrations. Torsional modes are also manifest, qualitatively, in the relative dimensions of the vibration ellipsoids (50% probability) depicted in Fig. 3. No detailed analysis of the rigid-body modes has been attempted. It seems likely, however, that the deformation of the internal angle at the 2-carbon (1·5°) is appreciably greater than can be accounted for in terms of libration effects and, like the deformations at the 3-heterocycle carbon, results largely from rehybridization induced by charge drift.

Though less precise, bond lengths and bond angles deriving from the bis-(3,5-diphenyl-1,2-dithiolium) tetrachloromercurate(II) analysis are all within experimental error of the corresponding values for the tetrachloroferrate isomer.

Table 9. *Metal–ligand bond-length and angle deviations from mean values*

(*a*) Metal–ligand bond-length deviations from their mean values in tetrachloroferrate(II) and tetrachloromercurate(II) anions.*

		Deviation from mean (Å)		R.m.s.d. (Å)		Mean distance (Å)	
Complex	Bond	Hg isomer	Fe isomer	Hg isomer	Fe isomer	Hg isomer	Feisomer
$(SbzSbz)_2MCl_4$	M(1)–Cl(2)	+0·048 (4)	+0·033 (3)	0·030	0·022	2·476†	2·305†
	M(1)–Cl(4)	+0·001 (4)	+0·001 (3)				
	M(1)–Cl(1)	−0·013 (4)	−0·003 (3)				
	M(1)–Cl(3)	−0·034 (4)	−0·029 (3)				
	M(2)–Cl(7)	+0·055 (4)	+0·027 (3)	0·033	0·018	2·481†	2·310†
	M(2)–Cl(6)	−0·006 (4)	+0·004 (3)				
	M(2)–Cl(5)	−0·015 (4)	−0·007 (3)				
	M(2)–Cl(8)	−0·032 (4)	−0·023 (3)				
$(SacSac)_2FeCl_4$	Fe—Cl(2)		+0·023 (1)		0·023		2·313‡
	Fe—Cl(1)		−0·023 (1)				
$\{[Fe(h^5\text{-}C_5H_5)(CO)_2]_3SbCl\}_2$ $[FeCl_4].CH_2Cl_2$	Fe—Cl(3)		+0·024 (5)		0·024		2·314§
	Fe—Cl(2)		−0·024 (5)				

* Values in parentheses are estimated bond-length standard errors.
References: † Present work. ‡ Freeman *et al.* (1973). § Trinh-Toan *et al.* (1971).

(*b*) Ligand–metal–ligand angular deviations from 109·47° in tetrachloroferrate(II) and tetrachloromercurate(II) anions.*

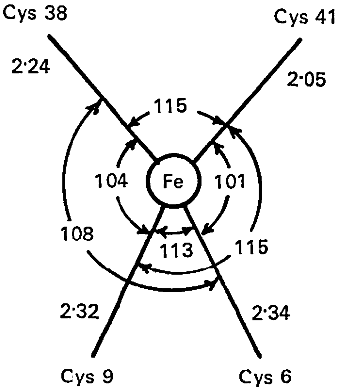
		Deviation (°)		R.m.s.d. (°)	
Complex	Angle	Hg isomer	Feisomer	Hg isomer	Fe isomer
$(SbzSbz)_2MCl_4$	Cl(2)–M–Cl(3)	+12·6 (2)	+11·1 (1)	8·2†	7·2†
	Cl(1)–M–Cl(4)	+8·9 (1)	+8·6 (1)		
	Cl(1)–M–Cl(3)	+0·6 (2)	−1·3 (1)		
	Cl(3)–M–Cl(4)	−5·3 (2)	−4·8 (1)		
	Cl(2)–M–Cl(4)	−7·6 (1)	−6·3 (1)		
	Cl(1)–M–Cl(2)	−8·6 (1)	−6·7 (1)		
	Cl(5)–M–Cl(8)	+6·3 (1)	+5·3 (1)	4·0†	3·5†
	Cl(6)–M–Cl(7)	+1·9 (1)	+2·7 (1)		
	Cl(6)–M–Cl(8)	+0·3 (1)	−1·5 (1)		
	Cl(5)–M–Cl(6)	+0·1 (1)	+0·3 (1)		
	Cl(7)–M–Cl(8)	−1·9 (1)	−1·1 (1)		
	Cl(5)–M–Cl(7)	−7·0 (1)	−5·8 (1)		
$(SacSac)_2FeCl_4$	Cl(2)–Fe–Cl(2′)		+6·44 (6)		3·9‡
	Cl(1)–Fe–Cl(1′)		+2·87 (6)		
	Cl(1)–Fe–Cl(2)		−1·25 (5)		
	Cl(1)–Fe–Cl(2′)		−3·32 (5)		
$\{[Fe(h^5\text{-}C_5H_5)(CO)_2]_3SbCl\}_2$ $[FeCl_4].CH_2Cl_2$	Cl(2)–Fe–Cl(3′)		+5·5 (2)		4·1§
	Cl(2)–Fe–Cl(2′)		−1·0 (2)		
	Cl(2)–Fe–Cl(3)		−2·3 (2)		
	Cl(3)–Fe–Cl(3′)		−5·3 (2)		

* Values in parentheses are estimated bond-angle standard errors.
† Present work. ‡ Freeman *et al.* (1973). § Trinh-Toan *et al.* (1971).

Electron-transfer metalloenzymes

The present results appear to bear some relevance to electron-transfer processes in metalloenzymes (Mason & Zubieta, 1973). Structural data for cytochrome-C (Dickerson, Takano & Kallan, 1972), for ferredoxin (*P. aerogenes*) (Sieker, Adman & Jensen, 1972, 1973), and for rubredoxin (Herriot, Sieker, Jensen & Lovenberg, 1970) are identical in showing an aromatic amino-acid residue in close proximity to the respective transition-metal chromophores. However, in the reduced form of cytochrome-C this residue (tyrosine 67) rotates away from a facial interaction with the iron-haem grouping, suggesting that the aromatic residues may act as one-electron 'trap-doors'. In general, the inorganic chromophores are located in hydrophobic pockets, whereas the aromatic residues are positioned on the protein surface. They may readily form radical anions, transfer the electron to the metal centre and then, through a general conformational change, move away from 'contact' with the chromophore so that further transfer is prevented. Similar interactions, between aromatic residues and the metal chromophore, are evident in the structure of flavodoxin (Watenpaugh, Sieker, Jensen, Legall & Dubourdieu, 1972) and have been inferred (from ^{13}C n.m.r. data) in a second ferredoxin (*C. acidi urici*) (Packer, Sternlicht & Rabinowitz, 1972). The packing arrangement in the present complexes would also appear to implicate the phenyl substituents in the charge-transfer process. In particular, the more or less parallel arrangement of the phenyl rings in the cation stacks might be expected to result in facile charge-transfer, both parallel to the crystallographic *a* axis and, more generally, in directions parallel to the $\{0\bar{2}1\}$ planes.

The present results also have implications for the stereochemistry of the chromophore in rubredoxin. The redox centre in oxidized rubredoxin consists of a (formal) ferric ion coordinated by four cysteine ligands in a pseudo-tetrahedral arrangement. Metal–ligand distances (Å) and ligand–metal–ligand angles (°) are shown below (Jensen, 1972).



The angular deformations (from regular tetrahedral) are of similar magnitude to those observed in the present complexes, and probably reflect simple steric constraints imposed by the protein chain. The significant shortening of the Fe–S(Cys 41) bond also has a parallel in the present results. In the bis(dithiolium)-[MCl$_4$] complexes the metal–chlorine bond-length differences are clearly a consequence of strong, local charge-transfer interactions with the cations. The short Fe–S(Cys 41) bond in rubredoxin results, in all probability, from an analogous interaction with an electronegative group (*e.g.* O–H of water or tyrosine).

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References

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.

Busing, W. R. & Levy, H. A. (1967). *Acta Cryst.* **14**, 598–602.

Cole, A. R. H., Mohay, G. M. & Osborne, G. A. (1967). *Spectrochim. Acta*, A**23**, 909–920.

Dickerson, R. E., Takano, T. & Kallan, O. B. (1972). *Abstr. Metalloenzymes Conf. Oxford*, p. 19.

Freeman, H. C., Milburn, G. H. W., Nockolds, C. E., Hemmerich, P. & Knauer, K. H. (1969). *Chem. Commun.* pp. 55–56.

Freeman, H. C., Milburn, G. H. W., Nockolds, C. E., Mason, R., Robertson, G. B. & Rusholme, G. A. (1974). *Acta Cryst.* B**30**, 886–894.

Guss, J. M. & Mason, R. (1972). *J. Chem. Soc. Dalton*, pp. 2193–2196.

Heath, G. A., Martin, R. L. & Stewart, I. M. (1969). *Chem. Commun.* pp. 54–55.

Herriot, J. R., Sieker, L. C., Jensen, L. H. & Lovenberg, W. (1970). *J. Mol. Biol.* **50**, 391–406.

International Tables for X-ray Crystallography (1972). Vol. III, p. 202. Birmingham: Kynoch Press.

Jensen, L. H. (1972). *Proc. Int. Conf. Metalloenzymes*, *Oxford.*

Mason, R. & Robertson, G. B. (1967). Unpublished results.

Mason, R., McKenzie, E. D., Robertson, G. B. & Rusholme, G. A. (1968). *Chem. Commun.* pp. 1673–1674.

Mason, R., Robertson, G. B. & Rusholme, G. A. (1974). *Acta Cryst.* B**30**, 906–910.

Mason, R. & Zubieta, J. A. (1973). *Angew. Chem. Int. Ed.* **12**, 390–399.

Packer, E. L., Sternlicht, H. & Rabinowitz, J. C. (1972). *Proc. Natl. Acad. Sci. U. S.* **69**, 3278–3282.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 2nd ed., p. 260. Ithaca: Cornell Univ. Press.

Robertson, G. B. (1961). *Nature, Lond.* **191**, 593–595.

Rusholme, G. A. (1970). Ph. D. Thesis, Univ. of Sheffield.

Sieker, L. C., Adman, E. & Jensen, L. H. (1972). *Nature Lond.* **235**, 40–41.

Sieker, L. C., Adman, E. & Jensen, L. H. (1973). *J. Biol. Chem.* **248**, 3987–3996.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Trinh-Toan & Dahl, L. F. (1971). *J. Amer. Chem. Soc.* **93**, 2754–2666.

Watenpaugh, K. D., Sieker, L. C., Jensen, L. H., Legall, J. & Dubourdieu, M. (1972). *Proc. Natl. Acad. Sci. U. S.* **69**, 3185–3188.