We wish to thank Dr E. R. Clark of the Pharmacology Department of Leeds University for valuable discussions, Mr D. Akrigg for technical assistance and the Leeds University Computing Laboratory for the provision of computing facilities.

Note added in proof:– The structure of TM1 has been congrmed as TTTT. The structure of ome TM1 has recently been determined as TTGT (manuscripts in preparntion).

References

Chothia, C. & Pauling, P. (1969). *J. Chem. Soc.* (*D*), **12**, 626–627.

Clark, E. R., Dawes, P. M. & Williams, S. G. (1968). *Brit. J. Pharmacol.* **32**, 113–126.

Clark, E. R. & Jana, M. de L. S. A. (1966). *Brit. J. Pharmacol.* **27**, 135–144.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). *Symposium on Computer Methods*. Oxford: Pergamon Press.

Hey, P. (1952). *Brit. J. Pharmacol.* **7**, 117–129.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Karle, I. L., Dragonette, K. S. & Brenner, S. A. (1965). *Acta Cryst.* **19**, 713–716.

Liquori, A. M., Damiani, A. & De Coen, J. L. (1968). *J. Mol. Biol.* **33**, 445–450.

Mills, O. S. & Rollett, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 107. Oxford: Pergamon Press.

Sundaralingam, M. (1968). *Nature, Lond.* **217**, 35–37.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1974). B30, 886

The Structure of Bis-(3,5-dimethyl-1,2-dithiolium) Tetrachloroferrate(II): a Comparison of Structural Details Derived from Two Independent Diffractometer Analyses

By H. C. Freeman, G. H. W. Milburn* and C. E. Nockolds†
School of Chemistry, University of Sydney, Sydney 2006, *Australia*

and R. Mason,‡ G. B. Robertson§ and G. A. Rusholme
*Department of Chemistry, University of Sheffield, Sheffield S*3 *7HF, England*

(*Received* 17 *September* 1973; *accepted* 25 *November* 1973)

Results from two independent X-ray diffraction studies are discussed. Both analyses are based on three-dimensional diffractometer data with least-squares refinement of the scattering model. In other details the experimental and refinement techniques employed are substantially different. The mean difference between corresponding parameters derived from the two analyses is *ca.* 1·2σ. Terminal R values are 0·039 (MRR) and 0·061 (FMN), respectively. Similar agreement is observed between the two sets of $F_{\text{obs}}\,[R(F_o)=0{\cdot}069]$ and the two sets of $F_{\text{calc}}\,[R(F_c)=0{\cdot}054]$. The crystals are monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), with $a=17{\cdot}68\,(1)$, $b=7{\cdot}65\,(1)$, $c=15{\cdot}80\,(1)$ Å, $\beta=122{\cdot}0\,(1)^\circ$ (mean values) and $Z=4$. The structure comprises discrete 3,5-dimethyl-1,2-dithiolium $[=(\text{SacSac})^+=(C_5H_7S_2)^+]$ cations and $[\text{FeCl}_4]^{2-}$ anions. The tetrachloroferrate(II) ions lie on the twofold rotation axes and therefore have exact C_2 symmetry, but deviate markedly from the free ion (T_d) symmetry. Charge transfer, associated with close contacts between each $\text{Fe}^{\text{II}}\text{Cl}_4^{2-}$ ion and two pairs of dithiolium cations, results in the intense broad absorption band (centred at *ca.* 20 000 cm^{-1}) in the reflectance spectrum.

Introduction

At the time when the present work was initiated independently in Sheffield and Sydney, there was much interest in 'model' transition metal complexes for non-haem iron–sulphur proteins such as rubredoxin and the ferredoxins. In this context our preliminary results (Mason, McKenzie, Robertson & Rusholme, 1968; Freeman, Milburn, Nockolds, Hemmerich & Knauer, 1969) and related spectroscopic data (Heath, Martin & Stewart, 1969) were negative. They showed that there were no Fe–S bonds at all in a class of complexes which had been thought to contain thioacetylacetonato ligands bound to iron and to be related to the redox site in rubredoxin. Subsequently the structures of rubredoxin (*Peptococcus aerogenes*) and ferredoxin (*P. aerogenes*) were solved by Jensen and coworkers (Herriot, Sieker, Jensen & Lovenberg, 1970; Sieker, Adman & Jensen, 1972). The structural chemistry of these and related systems has recently been reviewed (Mason & Zubieta, 1973), and the present work turns out to be related in an unexpected way to the mechanisms of

---

* Present address: Department of Chemistry, Sheffield Polytechnic, Sheffield, England.

† Present address: Electron Microscope Unit, University of Sydney, Sydney 2006, Australia.

‡ Present address: School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, England.

§ Present address: Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia.

electron-transfer in haem and non-haem proteins. It is also of wider interest in connexion with the mechanisms of charge transfer in crystals of transition metal complexes. But here we emphasize the crystallographic results obtained under very different experimental conditions by the two structural groups.

Experimental

Except for the use of common hydrogen-atom parameters in the final stages of refinement, the separate and more or less concurrent analyses by Freeman *et al.* (henceforth FMN) and by Mason *et al.* (henceforth MRR) were carried out quite independently. Characteristics common to the two analyses are restricted essentially to the fact that both are based on three-dimensional data collected on fully automated equi-inclination type X-ray diffractometers. In each case the scattering model has been refined by a least-squares procedure but, like the experimental procedures, data reduction and refinement techniques differ substantially in detail. Specific parameters relating to data collection, to data reduction, and to refinement procedures employed in both analyses are summarized in Table 1.

Crystal data

Crystals of bis-(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate(II) [(SacSac)$_2$FeCl$_4$], $C_{10}H_{14}Cl_4FeS_4$, F.W. 460·2, of suitable size and quality for X-ray diffraction

Table 1. *Comparison of experimental and refinement details*

Detail	MRR	FMN
Instrument	PAILRED	Automated Buerger–Supper Diffractometer[a]
Geometry	Equi-inclination	Equi-inclination
Radiation used to measure unit-cell parameters	Cu $K\alpha$, Ni filter	Cu $K\alpha$, Ni filter
Determination of unit-cell parameters	Least-squares analysis of high-θ reflexions. Weissenberg photographs calibrated with Al powder lines ($t=20\pm2$°C)	Direct calculation from high-θ reflexions. Counter measurements on diffractometer. ($t=20\pm2$°C)
Radiation used to record intensities	Mo $K\alpha$ ($\lambda\alpha=0{\cdot}7107$ Å)	Cu $K\alpha$ ($\lambda\alpha_1=1{\cdot}5405$, $\lambda\alpha_2=1{\cdot}5443$ Å)
Monochromatization	Si crystal monochromator	Ni, β filter
Type of scan	ω scan	ω scan
Angular range	$6° \le 2\theta \le 60°$	$10° \le r \le 140°$
Scan range, $\Delta\varphi$	2–4°, constant for layer	Computed for each reflexion[a]
Scan rate, φ'	Constant: 0·04° s^{-1}	Variable, optimized:[a] $0{\cdot}03 \le \varphi' \le 0{\cdot}333°$ s^{-1}
Background count, time	2 × 20 s	$2\times(\Delta\varphi/2\varphi')$
Effect of background imbalance	If $\lvert B_1-B_2\rvert > 3\sigma(B)$, reject	If $\lvert B_1-B_2\rvert > 10\sigma(B)+0{\cdot}01\ (P-B)$, increment $\Delta\varphi$, repeat measurement
Crystal size	0·18 × 0·52 × 0·22 mm	0·04 × 0·17 × 0·05 mm [dimensions ⊥ (100), (010) and (101) faces, respectively]
Axes of rotation	*b*	*b*, *c*
Layers recorded	*h*0*l* to *h*9*l*	*h*0*l* to *h*7*l*, *hk*0 to *hk*5
Criterion for observability	$I_{obs} \ge 3\sigma(I_{obs})$	$I_{obs} \ge 2\sigma(I_{obs})$, $I_{min}=2\sigma(I_{obs})$
Treatment of unobservably weak reflexions	If $I<3\sigma(I)$, put $I_{unobs}=0$	If $I<2\sigma(I)$, put $I_{unobs}=0{\cdot}33I_{min}$ (Hamilton,1955)
Number of reflexions above threshold	1452	1099
Number of I_{unobs} recorded	–	438
Criterion of data quality	$\sum\sigma(F)/\sum F=0{\cdot}024$	Agreement between *b*- and *c*-axis data, $R_1=0{\cdot}031$, $R_2=0{\cdot}017$[b]
Absorption corrections	Levy & Busing (1957)	Coppens, Leiserowitz & Rabinovich (1965)
Grid for absn. corrn.	6 × 6 × 6	4 × 8 × 4
Least-squares refinement	Block-diagonal[c]	Full-matrix[c]
Function minimized	$\sum w\lvert\lvert F_o\rvert - s\lvert F_c\rvert\rvert^2$	$\sum w\lvert\lvert F_o\rvert - s\lvert F_c\rvert\rvert^2$
Atomic scattering factors	Fe, Cl, S, C (*International Tables for X-ray Crystallography*, 1962), H (Stewart, Davidson & Simpson, 1965)	Fe^{2+}, Cl^-, S, C (Cromer & Waber, 1965) H (Stewart, Davidson & Simpson, 1965)
Atoms treated as anomalous scatterers	–	Fe, Cl, S (Cromer, 1965)
Correction for extinction	$F_c^2=F_o^2(K'+K'cI_{obs})$, (Zachariasen, 1963)[d]	–
Initial weights for refinement	$w=1$	$w=1/\sigma^2(F)$ from counting statistics
Final weights for refinement	From plot of $(\Delta F)^2$ *vs.* $\lvert F_o\rvert$[e]	From plots of $\lvert\Delta F\rvert$/*vs.* $\lvert F_o\rvert$ and $\sin\theta/\lambda$[f]
Inclusion of H atoms	Located in (F_o-F_c) synthesis. Included at calculated positions[g]	Included at positions calculated from MRR
Largest parameter change in final cycle	$0{\cdot}04\sigma$	$0{\cdot}15\sigma$
Residual *R*		
– at end of isotropic refinement	0·103	0·101
– before inclusion of H atoms	0·048	0·061 (F_{obs}), 0·089 (all *F*'s)
– after inclusion of H atoms	0·042	0·061 (F_{obs})
– final	0·039	0·061 (F_{obs})

Table 1 (*cont.*)

[a] The instrumentation and procedure have been described by Freeman, Guss, Nockolds, Page & Webster (1970). The control parameters and instrumental constants were as follows: $\Delta\lambda=0\cdot007$ Å; $X=0\cdot6°$; $\varphi_m=1\cdot0°$; $p=0\cdot001$; $\delta\mu=0\cdot05°$; φ'_{FAST} (maximum scan rate) $=0\cdot333°\ \text{s}^{-1}$; φ'_{MIN} (minimum scan rate) $=0\cdot03°\ \text{s}^{-1}$ for *b*-axis data, $0\cdot04°\ \text{s}^{-1}$ for *c*-axis data; R_ε (expectation value of residual) $=0\cdot03$; c_1, c_2 (constants for background imbalance test) $=10\cdot0$, $0\cdot1$; source-to-crystal distance $=145$ mm; crystal-to-counter distance $=75$ mm; angle subtended at crystal by counter aperture (adjusted for each layer) $=3°$ to $3°45'$. Attenuation of the X-ray beam was not necessary, as the maximum count rate did not exceed the limits of linear counter response.

[b] The relative scale factors between the *b*-axis and *c*-axis data were found by the method of Rae (Rae, 1965; Rae & Blake, 1966), using 359 reflexions common to both sets. After application of these scale factors, the unweighted and weighted agreement indices between the two original sets of data are defined as

$$R_1=\{[\sum_h\sum_i k_i^{-2}(F_h-k_iF_{hi})^2]/[\sum_h\sum_i F_{hi}^2]\}^{1/2}$$

$$R_2=\{[\sum_h\sum_i w_{hi}k_i^{-2}(F_h-k_iF_{hi})^2]/[\sum_h\sum_i w_{hi}F_{hi}^2]\}^{1/2}$$

where k_i represents the calculated scale-factor applied to the observation F_{hi} of the *h*th reflexion on the *i*th layer;
$w_{hi}=1/\sigma_{hi}^2$, σ_{hi} being the standard deviation of F_{hi} from counting statistics;
$F_h=\sum_i [F_{hi}/k_i\sigma_{hi}^2]/\sum_i (k_i\sigma_{hi})^{-2}$ is the weighted mean value of the *h*th structure amplitude.
Then $\sigma(F)$, the standard deviation of F_h, is given by (EOF) $[\sum_i (k_i\sigma_{hi})^{-2}]^{-1/2}$
where $\text{EOF}=\sum_i \sigma_{hi}^{-2}(|F_h|-|F_{hi}|)^2$ / (number of common reflexions – number of scale-factors).

[c] MRR: block-diagonal least-squares program for ATLAS (R. S. Diamand, personal communication).
FMN: Program *ORFLS* (Busing, Martin & Levy, 1962) with anomalous dispersion option (J. A. Ibers, personal communication).

[d] $K'=0\cdot92$, $c=2\cdot31\times10^{-6}$.

[e] 8 Reflexions were given $w=0$ because the extinction corrections applied to them appeared to be inadequate. Otherwise $w=1/\overline{(\Delta F)^2}$, with $\overline{(\Delta F)^2}$ plotted as a smooth monotonic function of $|F_o|$

[f] After each refinement cycle with anisotropic thermal parameters, the constants in the weighting function $w=[1-\exp\{a(b+\sin\theta/\lambda)^2\}]/[c+d|F_o|+e|F_o|^2]$ were adjusted. The final values were $a=-35\cdot0$, $b=-0\cdot16$, $c=13\cdot0$, $d=-0\cdot35$, $e=0\cdot0025$; w (unobs) $=0$.

[g] The peak densities of the hydrogen atoms in the difference synthesis ranged from 0·33 to 0·42 e Å^{-3}. The positions were modified slightly to give good bond lengths and angles, and the atoms were given the isotropic Debye factors shown in Table 3. The listed hydrogen-atom coordinates imply an average C–H distance of 1·00 Å (r.m.s. $\Delta=0\cdot05$ Å) and mean C–C–H and H–C–H angles of 107·5° (r.m.s. $\Delta=3\cdot1°$) and 111·2° (r.m.s. $\Delta=3\cdot6°$), respectively. Inclusion of H atoms led to a reduction of R from 0·048 to 0·042, without causing a significant change in any atomic positional or thermal parameter.

Table 2. $(\text{SacSac})_2\text{FeCl}_4$: *atom coordinates** ($\times10^4$) *and isotropic thermal parameters†*

	x/a		*y/b*		*z/c*		B(Å)^2
	MRR	FMN	MRR	FMN	MRR	FMN	
Fe	0	0	10974 (1)	10971 (2)	7500	7500	
Cl(1)	789 (1)	788 (1)	12642 (2)	12647 (4)	7023 (1)	7028 (1)	
Cl(2)	1015 (1)	1014 (1)	9351 (2)	9356 (3)	8905 (1)	8905 (1)	
S(1)	906 (1)	906 (1)	7429 (2)	7421 (4)	6924 (1)	6921 (1)	
S(2)	474 (1)	476 (1)	7335 (2)	7341 (4)	5458 (1)	5460 (1)	
C(1)	1893 (3)	1892 (5)	6466 (6)	6487 (10)	7327 (3)	7324 (6)	
C(2)	2054 (3)	2059 (5)	5989 (6)	5999 (13)	6593 (3)	6613 (5)	
C(3)	1395 (3)	1395 (5)	6322 (6)	6335 (10)	5619 (3)	5622 (6)	
C(4)	2508 (3)	2509 (6)	6144 (8)	6154 (17)	8429 (3)	8426 (6)	
C(5)	1452 (3)	1455 (6)	5850 (8)	5858 (17)	4736 (3)	4727 (6)	
C(4)H(1)	2292		5075		8585		8·0
C(4)H(2)	3187		6050		8600		8·0
C(4)H(3)	2500		7100		8850		8·0
C(2)H(1)	2687		5450		6767		4·8
C(5)H(1)	840		5500		4200		8·0
C(5)H(2)	1660		6905		4560		8·0
C(5)H(3)	1900		5000		4950		8·0

* Common idealized hydrogen coordinates employed in both refinements (see Table 1, footnote *g*).
† $B_{\text{H}}\simeq B_{\text{C}}+1\cdot0$ Å^2 assumed.

studies, are conveniently obtained either by slow crystallization from the reaction mixture or by recrystallization from aqueous solution (Knauer, Hemmerich & van Voorst, 1967). Crystals are deep red, prismatic in habit, and generally elongated along **b** (see below). Weissenberg and precession photographs confirm the crystal class as monoclinic (diffraction symmetry C_{2h}) with systematic absences hkl ($h+k=2n+1$) and $h0l$ ($l=2n+1$) only. Possible space groups are therefore Cc (C_s^4, No. 9) and $C2/c$ (C_{2h}^5, No. 15). The refined

Table 3. $(SacSac)_2FeCl_4$: *anisotropic thermal parameters* ($\times 10^4$)

The temperature factors have the form $\exp[-\{h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23}\}]$.

	β_{11}		β_{22}		β_{33}		β_{12}		β_{13}		β_{23}	
	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN
Fe	24 (1)	27 (1)	122 (2)	118 (3)	29 (1)	33 (1)	0	0	13 (1)	16 (1)	0	0
Cl(1)	35 (1)	36 (1)	194 (1)	209 (5)	54 (1)	60 (1)	−10 (2)	−15 (2)	25 (1)	26 (1)	18 (2)	18 (2)
Cl(2)	34 (1)	36 (1)	171 (2)	170 (4)	33 (1)	39 (1)	10 (2)	11 (2)	10 (1)	12 (1)	15 (2)	18 (2)
S(1)	35 (1)	35 (1)	172 (2)	177 (5)	41 (1)	40 (1)	12 (2)	12 (2)	20 (1)	20 (1)	−8 (2)	−9 (2)
S(2)	31 (1)	30 (1)	188 (3)	189 (5)	37 (1)	36 (1)	20 (2)	20 (2)	13 (1)	13 (1)	−4 (2)	−8 (2)
C(1)	28 (2)	28 (3)	122 (8)	102 (14)	41 (2)	46 (4)	−3 (6)	3 (5)	16 (3)	16 (3)	2 (7)	−6 (7)
C(2)	30 (2)	27 (3)	130 (8)	153 (16)	43 (2)	39 (4)	2 (6)	3 (6)	19 (3)	14 (3)	5 (7)	1 (7)
C(3)	32 (2)	40 (4)	123 (8)	85 (14)	43 (2)	47 (4)	2 (6)	0 (6)	19 (3)	26 (4)	−5 (7)	−6 (7)
C(4)	46 (2)	48 (4)	234 (12)	304 (26)	36 (2)	34 (4)	19 (9)	35 (10)	18 (4)	18 (4)	24 (9)	11 (9)
C(5)	44 (2)	47 (4)	257 (13)	333 (27)	45 (3)	52 (5)	19 (9)	27 (10)	27 (4)	35 (4)	−5 (10)	−17 (11)

Table 4. $(SacSac)_2FeCl_4$: *thermal ellipsoid principal axes and direction cosines referred to abc**

	$(u^2)_{min}$		D.C's		$(u^2)_{med}$		D.C's		$(u^2)_{max}$		D.C's	
	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN	MRR	FMN
			−0·461	−0·468			0	0			−0·887	−0·884
Fe	0·148	0·159	0	0	0·190	0·187	−1·000	−1·000	0·207	0·217	0	0
			−0·887	−0·884			0	0			0·461	0·468
			−0·632	−0·679			0·346	0·280			0·693	0·679
Cl(1)	0·191	0·195	−0·018	−0·086	0·231	0·239	0·888	0·888	0·269	0·283	−0·460	−0·452
			−0·775	−0·730			−0·304	−0·365			−0·554	−0·578
			0·355	0·398			0·092	0·141			0·930	0·906
Cl(2)	0·156	0·167	−0·151	−0·200	0·226	0·226	0·988	0·978	0·251	0·262	−0·040	−0·064
			0·923	0·895			0·126	0·156			−0·364	−0·417
			0·443	0·422			−0·370	−0·444			0·817	0·791
S(1)	0·178	0·177	−0·028	−0·011	0·219	0·221	0·905	0·869	0·251	0·251	0·425	0·494
			0·896	0·907			0·211	0·217			−0·390	−0·362
			0·474	0·476			−0·511	−0·578			0·717	0·663
S(2)	0·163	0·161	−0·091	−0·069	0·224	0·220	0·781	0·727	0·255	0·254	0·617	0·683
			0·876	0·877			0·358	0·371			−0·324	−0·306
			0·579	0·633			0·031	−0·039			−0·814	−0·824
C(1)	0·166	0·168	0·042	−0·034	0·190	0·173	0·997	0·996	0·238	0·250	0·068	−0·079
			0·814	0·773			−0·074	0·076			0·576	0·629
			0·568	0·566			0·102	−0·025			−0·817	−0·824
C(2)	0·173	0·161	−0·114	−0·036	0·196	0·213	0·992	0·998	0·240	0·236	0·044	−0·055
			0·815	0·824			0·068	0·061			0·575	0·564
			−0·527	0			0·100	−0·435			−0·844	−0·900
C(3)	0·176	0·158	−0·056	−0·996	0·190	0·194	−0·995	0·079	0·245	0·257	−0·083	−0·038
			−0·848	−0·088			0·004	−0·897			0·530	0·434
			−0·227	−0·200			0·211	−0·869			−0·951	−0·452
C(4)	0·171	0·170	0·165	0·079	0·265	0·267	−0·954	0·455	0·273	0·308	−0·251	−0·891
			−0·960	−0·869			−0·214	0·214			0·182	0·020
			−0·328	−0·355			−0·801	−0·873			−0·501	−0·334
C(5)	0·194	0·210	0·031	0·003	0·253	0·255	0·521	0·356	0·284	0·321	−0·853	−0·935
			−0·944	−0·935			0·295	0·333			0·146	0·124

Table 5. $(SacSac)_2FeCl_4$: *intraionic bond lengths* (Å) *and bond angles** (°)

	MRR	FMN		MRR	FMN
Fe—Cl(1)	2·290 (1)	2·293 (2)	C(1)–C(2)	1·382 (6)	1·36 (1_5)
Fe—Cl(2)	2·336 (1)	2·337 (2)	C(1)–C(4)	1·504 (7)	1·51 (1_5)
S(1)–S(2)	2·019 (2)	2·015 (3)	C(3)–C(2)	1·374 (7)	1·40 (1_3)
S(1)–C(1)	1·667 (5)	1·67 (1)	C(3)–C(5)	1·494 (7)	1·52 (1_5)
S(2)–C(3)	1·696 (5)	1·69 (1)	Mean C–H	1·01	
Cl(1)–Fe—Cl(1′)	112·34 (6)	111·8 (2)	S(1)–C(1)–C(4)	118·7 (4)	118·9 (8)
Cl(1)–Fe—Cl(2)	108·22 (5)	108·3 (2)	C(2)–C(1)–C(4)	125·7 (4)	124·6 (9)
Cl(1)–Fe—Cl(2′)	106·15 (5)	106·3 (2)	C(1)–C(2)–C(3)	117·5 (4)	117·1 (8)
Cl(2)–Fe—Cl(2′)	115·91 (6)	116·0 (2)	S(2)–C(3)–C(5)	115·4 (4)	115·0 (7)
			S(2)–C(3)–C(5)	120·3 (4)	120·4 (8)
S(2)—S(2)–C(1)	96·0 (2)	96·2 (4)	C(2)–C(3)–C(5)	124·4 (4)	124·7 (9)
S(1)—S(2)–C(3)	95·5 (2)	95·3 (4)	Mean C–C (Me)–H	107·5	
S(1)—C(1)–C(2)	115·6 (4)	116·4 (7)	Mean H–C(Me)–H	111·2	

* Idealized hydrogen coordinates (see Table 1, footnote *g*).

structure is consistent with the centrosymmetric space group. Unit-cell dimensions, determined by the procedures outlined in Table 1, are:

	MRR	FMN
a	17·67 (2) Å	17·69 (2) Å
b	7·64 (1)	7·67 (1)
c	15·79 (2)	15·82 (2)
β	122·0 (1)°	122·0 (1)°.

With $Z=4$ and a formula weight of 460·2, the calculated density $D_c=1{\cdot}68$ g cm^{-3} is in excellent agreement with the value $D_m=1{\cdot}68$ (1) g cm^{-3} determined by flotation in CCl_4/1,2-dibromomethane (FMM) or C_6H_6/tetrabromoethane (MRR) solutions. Standard errors, given throughout in parentheses, correspond to the least significant digit of the preceding number.

Solution and refinement

Coordinates of all non-hydrogen atoms were determined in a straightforward way from conventional Patterson and Fourier syntheses. Hydrogen atoms were subsequently located (MRR) in a difference synthesis as relatively diffuse peaks of maximum density *ca.* 0·4 e A^{-3}. Attempts to improve the definition by omission of all coefficients with $\sin\theta/\lambda \geq 0{\cdot}40$ were unsuccessful. Coordinates were therefore idealized and hydrogen atoms included as fixed contributions to the scattering models in both analyses. For the MRR analysis, inclusion of hydrogens reduced $R=\sum||F_o|-|F_c||/\sum|F_o|$ from 0·048 to 0·042. In the FMN analysis there was no significant improvement in R when hydrogens were included. Additional details of the refinement calculations are included in Table 1. Atom coordinates from the separate analyses are listed in Table 2, and anisotropic thermal parameters in Table 3. Magnitudes and directions of the vibration-ellipsoid principal axes are given in Table 4. Bond-length and bond-angle data are presented in Table 5 and information relating to

Table 6. $(SacSac)_2FeCl_4$: *close interionic contacts between non-hydrogen atoms*

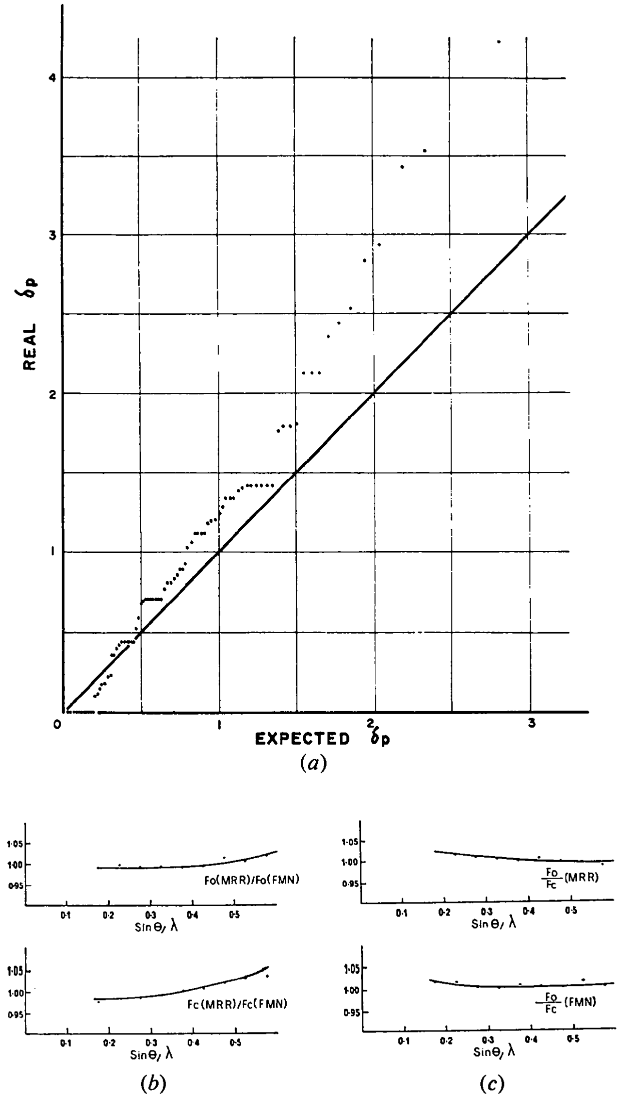
Contacts are derived from Table 1 coordinates using the symmetry transformations:

i	$-x$	y	$1\frac{1}{2}-z$	iv	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$1\frac{1}{2}-z$
ii	$-x$	$2-y$	$1-z$	v	x	$1+y$	z
ii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1\frac{1}{2}-z$	vi	x	$-1+y$	z.

Distances are from MRR coordinates, angles from FMN.

Fe·····S(1)		3·502 (1) Å
Cl(1)···S(2^{ii})	S(2)···Cl(1^{ii})	3·326 (2)
Cl(1)···C(1^{v})	C(1)···Cl(1^{vi})	3·403 (5)
Cl(1)···C(2^{iii})	C(2)···Cl(2^{iv})	3·475 (5)
Cl(2)···S(1)		3·377 (2)
Cl(2)···S(1^{i})	S(1)···Cl(2^{i})	3·268 (2)

Fe———Cl(2)···S(1)	73·3°
Fe———Cl(2)···S(1^{i})	75·6
S(1)·····Cl(2)···S(1^{i})	84·0
Fe———Cl(1)···S(2^{ii})	104·0
Fe———Cl(1)···C(2^{iii})	104·5
Fe———Cl(1)···C(1^{v})	147·0
S(2^{ii})····Cl(1)···C(2^{iii})	124·0
S(2^{ii})····Cl(1)···C(1^{v})	97·8
C(2^{iii})···Cl(1)···C(1^{v})	82·5
Cl(1)——S(1)···Cl(2)	107·5
C(1)——S(1)···Cl(2^{i})	178·2
Cl(2)···S(1)···Cl(2^{i})	73·0
C(3)——S(2)···Cl(1^{ii})	99·7
C(3)——C(2)···Cl(1^{iv})	128·4
C(1)——C(2)···Cl(1^{iv})	92·1
S(1)——C(1)···Cl(1^{vi})	85·0
C(2)——C(1)···Cl(1^{vi})	90·5
C(4)——C(1)···Cl(1^{vi})	91·3



(*b*) (*c*)

Fig. 1. $(SacSac)_2FeCl_4$: comparison of MRR and FMN results and data. In (*b*) and (*c*), only those values corresponding to reflexions observed as non-zero in both analyses are included in the mean ratios. (*a*) Half-normal probability plot of the differences between the two sets of refined parameters. (*b*) $\sin\theta/\lambda$ dependence of $\overline{F_o(\mathrm{MRR})/F_o(\mathrm{FMN})}$ and $\overline{F_c(\mathrm{MRR})/F_c(\mathrm{FMN})}$. (*c*) $\sin\theta/\lambda$ dependence of $\overline{F_o(\mathrm{MRR})/F_c(\mathrm{MRR})}$ and $\overline{F_o(\mathrm{FMN})/F_c(\mathrm{FMN})}$.

short inter-ion non-bonding contacts in Table 6. Observed and calculated (terminal model) structure-factor amplitudes for both analyses are available.*

Comparison of MRR and FMN results

The independently determined cell dimensions do not differ significantly within the stated error limits. Comparison of the two terminal parameter sets (Tables 2 and 3) shows the over-all agreement to be generally satisfactory. The mean deviation between the 86 parameter pairs which were refined in both analyses is *ca.* 1·2σ (σ is the estimated standard error of the appropriate parameter difference). However, five pairs exhibit differences which are equal to or greater than 3σ, with a maximum of *ca.* 5σ. All of the affected parameters [the z coordinates of Cl(1) and C(2), and the β_{33} parameters of Fe, Cl(1) and Cl(2)] are l-dependent, but the origin of the discrepancy is unclear. Despite the coordinate differences noted here, the differences between bond lengths and bond angles from the two analyses are uniformly less than 3σ. Not unexpectedly, the maximum difference (*ca.* 2·6σ) is observed for the angle Cl(1)–Fe–Cl(1′).

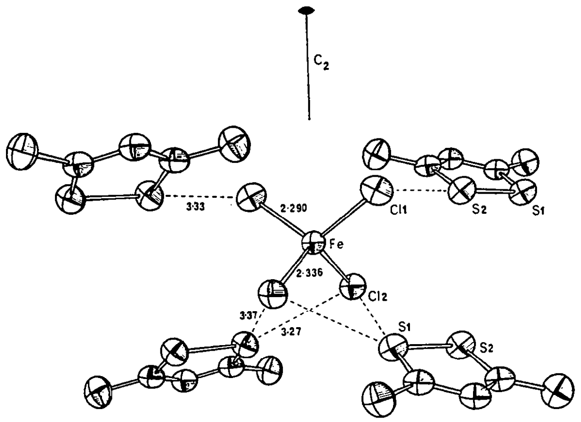


Fig. 2. (SacSac)$_2$FeCl$_4$: atom nomenclature and interatomic distances in the tetrachloroferrate anion and its environment.

The existence of parameter differences in excess of 3σ has caused us to test the hypothesis that the parameter standard deviations derived from the least-squares refinements do not – as is often the case – adequately reflect the errors in the data. A halfnormal probability plot of all the parameter differences (Abrahams & Keve, 1971) is shown in Fig. 1(*a*). The plot is approximately linear but its slope is 1·4 instead of 1·0. This indicates that the estimated standard deviations *of the parameter differences* are about 40% too low.

The half-normal probability plot does not allow us to state whether only one set of parameter e.s.d.'s has been underestimated, or both. There is no evidence that the e.s.d.'s derived by MRR from the block-diagonal matrix are substantially more optimistic than those derived by FMN from the full least-squares matrix (or *vice versa*). The mean ratio between the MRR and FMN e.s.d.'s (0·5) is consistent with the corresponding $\{\sum\Delta^2/(n-s)\}^{1/2}$ ratio (0·55). The factor by which the MRR parameter e.s.d.'s would have to be multiplied if they alone had been underestimated is about 2·2. The corresponding factor for the FMN e.s.d.'s is 1·5. The preceding argument suggests that the truth lies between these two extremes.

Two attempts to identify sources of systematic errors in the data are illustrated in Fig. 1(*b*) and (*c*). The curves in Fig. 1(*b*) show that the mean ratio of the observed structure amplitudes $\overline{F_o(\mathrm{MRR})/F_o(\mathrm{FMN})}$ increases smoothly with increasing sin θ/λ, and that the least-square fitting procedure has reproduced this behaviour in the $\overline{F_c/F_c}$ ratio. Two types of discrepancies are observed in these curves. The large deviation of the low-angle $\overline{F_o/F_o}$ point and the slight difference (*ca.* 1%) in absolute scale are thought to be attributable to residual extinction effects in the MRR data. The observed sin θ/λ dependence probably results from a number of factors. In equ-inclination geometry the reflexion backgrounds are liable to be underestimated (and the reflexion intensities overestimated) at low sin θ/λ val-

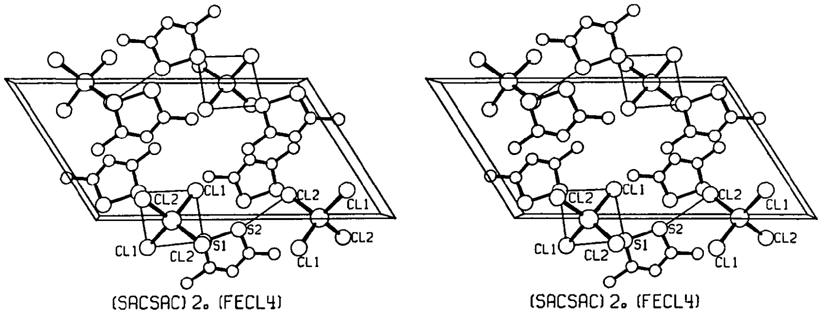


Fig. 3. (SacSac)$_2$FeCl$_4$: stereoscopic packing diagram, showing part of a schematic electron-transfer pathway (—). x axis left to right, y axis towards reader, z axis upwards.

---

* These tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30307 (1 microfiche). Copies can be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ues. The problem is more serious when polychromatic radiation is used (FMN) than when monochromated radiation is used (MRR). On the other hand, the application of an appropriate inter-layer scaling procedure to data-sets recorded about two axes (FMN) is likely to minimize systematic errors which may be incurred by assuming a constant scale factor for all reciprocal-lattice layers recorded about one axis (MRR). The use of a single-crystal monochromator (MRR) also introduces unavoidable uncertainties since the correct form of the polarization correction depends on the degree of perfection of the monochromator crystal (which is generally unknown). Finally, sin θ/λ-dependent differences may have been caused by the approximations inherent in either one or both of the absorption correction procedures employed.

A sin θ/λ dependence is also apparent in the $\overline{F_o}/\overline{F_c}$ plots of Fig. 1(*b*). The dependence is marked in the MRR data, where the depression of both scale and thermal parameters is strongly indicative of the combined effects of residual extinction and inadequate allowance for scale-thermal parameter correlations in the block-diagonal least-squares procedures. For the FMN data the sin θ/λ dependence is marginal, but for this data set the $\overline{F_o}/\overline{F_c}$ ratio is uniformly greater than unity. Inclusion of 'unobserved' terms, used in the refinement scheme but consistently underestimated by FMN (Table 1 and structure-factor list), removes the apparent scaling anomaly but increases the sin θ/λ dependence.

Description of the structure

The structure is made up from discrete 3,5-dimethyl-1,2-dithiolium [=(SacSac)$^+$ =($C_5H_7S_2$)$^+$] cations and ($FeCl_4$)$^{2-}$ anions. The stereochemical arrangement of (SacSac)$^+$ ions around a single tetrachloroferrate(II) anion is shown, along with the atom labelling, in Fig. 2. Bounding surfaces of the vibration ellipsoids shown in the figure correspond to the 50% probability level. For clarity, hydrogen atoms have been omitted. The packing of ions within one complete unit cell is shown in Fig. 3 and the orientation of the methyl groups in Fig. 4. All figures have been produced using the program *ORTEP* (Johnson, 1965).

Each (FeCl)$_4^{2-}$ is surrounded by four dithiolium cations, related to one another in pairs by the crystallographic twofold axis passing through the iron atom. There are several counter-ion contacts less than the van der Waals radii sums (Pauling, 1960). The iron atom makes two (equivalent) Fe···S(1) contacts of 3·502 (1) Å. The next shortest Fe···S contacts are 4·5 Å. The closest counter-ion approaches, however, involve the Cl atoms. Altogether, each (FeCl)$_4^{2-}$ ion makes six (three pairs of) very short Cl···S contacts, *viz.* Cl(1)···S(2) [3·326 (2) Å], and Cl(2)···S(1) [3·367 (2) and 3·268 (2) Å], respectively. In addition, there are two pairs of Cl···C contacts (both approximately equal to the sum of the van der Waals radii) lying along the normals to yet four more (SacSac)$^+$ ions. The anion–cation packing is such as to establish a continuous pathway for electron transfer parallel to **c** (Fig. 3).

Geometry of the ($FeCl_4$)$^{2-}$ *ions*

In the presence of symmetrical cations such as $As(C_6H_5)_4^+$ and $P(C_6H_5)_4^+$, the symmetry of ($FeCl_4$)$^{2-}$ is T_d (Pauling, 1966). In the present structure, the ($FeCl_4$)$^{2-}$ ions are severely distorted from T_d symmetry, though they do exhibit the C_2 symmetry required by the space-group. Each of the Cl–Fe–Cl angles deviates significantly from the tetrahedral value (Table 5), the angular distortion being best described in terms of a compression or 'flattening' of the tetrahedron along the direction of the crystallographic C_2 axis together with a 3° twist about this axis, resulting in a 93° dihedral angle between the planes Cl(1)–Fe–Cl(1′) and Cl(2)–Fe–Cl(2′). Distortions of similar magnitude have been observed in ($CoCl_4$)$^{2-}$ and ($ZnCl_4$)$^{2-}$ (Figgis, Gerloch & Mason, 1964; Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter, 1967), both of which have orbitally non-degenerate ground states, and more recently in the ($FeCl_4$)$^{2-}$ ion in [Fe(h^5-C_5H_5)(CO)$_2$]$_3$SbCl$_2$(FeCl$_4$).CH$_2$Cl$_2$ (Trinh-Toan & Dahl, 1971). In the latter structure, however, the distortion results from an elongation, rather than compression, along the crystallographic C_2 axis. Largely because of the ($CoCl_4$)$^{2-}$ and ($ZnCl_4$)$^{2-}$ results, the variability of the (MCl_4)$^{2-}$ geometry (M = Mn, Fe, Co, Ni, Zn) has been widely attributed to differences in crystal packing. The recent observation of virtually identical distortions of the (MCl_4)$^{2-}$ ions in both bis (3,5-diphenyl-1,2-dithiolium)tetrachloroferrate(II) and in its tetrachloromercurate(II) isomer (Mason, Robertson & Rusholme, 1974) puts the validity of this rationale beyond any reasonable doubt.

The two crystallographically inequivalent Fe–Cl bond distances are significantly different [Δ/σ(MRR) ≈ 33, Δ/σ(FMN) ≈ 16, Table 5]. The longer distance is that involving Cl(2), this atom being involved in two short Cl···S contacts compared with only one such contact for Cl(1). Similar bond-length differences, also attributable to ground-state dipolar interactions, have been observed in bis(3,5-diphenyl-1,2-dithiolium) tet-

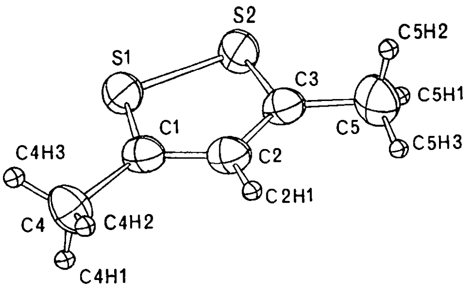


Fig. 4. Orientation of methyl groups and atom labelling in the 3,5-dimehyl-1,2-dithiolium cations.

rachloroferrate(II). In $\{[Fe(h^5\text{-}C_5H_5)(CO)_2]_3SbCl\}_2[FeCl_4].CH_2Cl_2$ the discrepancy between the Fe–Cl distances [C_2 symmetry, distances uncorrected for libration = 2·284 (5) and 2·320 (5) Å, respectively] is slightly smaller ($\Delta = 0{\cdot}036$ Å) and has been attributed in part to weak C–H···Cl bonding (Trinh-Toan & Dahl, 1971).

Geometry of the dithiolium cations

The dimensions of the dithiolium ions do not differ significantly from the corresponding values in the iodide salts of 3-phenyl-, 4-phenyl- and 3,5-diamino-1,2-dithiolium cations (Hordvik & Kjøge, 1965; Hordvik & Sletten, 1966; Hordvik, 1965). Nor do they differ significantly from corresponding values observed in the tetrachloroferrate and tetrachloromercurate salts of the 3,5-diphenyl-1,2-dithiolium cation (Mason, Robertson & Rusholme, 1974). We note, also, that the S–C and C–C distances in the free cation do not differ significantly from those reported for the chelated SacSac⁻ anions in $Co(SacSac)_2$ (Beckett & Hoskins, 1967) and $Fe(SacSac)_3$ (Beckett & Hoskins, 1970); the bond angles and S–S distances necessarily differ. The two chemically equivalent bond lengths, S(1)–C(1) and S(2)–(3), are significantly different in the MRR analysis ($\Delta/\sigma = 3{\cdot}8$); the difference is as expected, since S(1) has stronger non-bonded interactions with adjacent chlorines than does S(2). The bond lengths in the dithiolium cation clearly indicate substantial cyclic delocalization. The maximum deviations from a plane fitted to the atoms of the dithiolium cation are significant. The MRR and FMN values of the deviations are: S(1) 0·005 (4σ), 0·01 Å; S(2) −0·0015 (1σ), −0·005 Å; C(1) −0·005(1σ), −0·004 Å; C(2) −0·025(5σ), −0·024 Å; C(3) −0·013 (3σ), −0·023 Å; C(4) 0·020 (3σ), 0·024 Å; and C(5) 0·019 (3σ), 0·021 Å. The groups S(1)C(3)C(2)C(4) and S(2)C(1)C(2)C(5) are both planar within the limits of precision, and make angles of 0·7 and 1·6° with the plane of S(1)C(2)S(2), respectively.

Discussion

The structure analysis clearly indicates that the intense colour of $(SacSac)_2FeCl_4$ must have a cause other than the types of Fe–SS coordination originally suggested by Knauer, Hemmerich & van Voorst (1967). Since the highly coloured crystals may grow from colourless solutions (Heath, Martin & Stewart, 1969), one concludes that the absorption is connected with the crystalline arrangement of the complexes. The outstanding feature of the crystalline structure is the existence of six Cl···S contacts per $(FeCl_4)^{2-}$ ion, which are significantly shorter (3·3–3·4 Å) than the sum of the conventional van der Waals radii of S and Cl, 3·65 Å (Pauling, 1960). These short contacts imply that the absorption by the crystals is caused by charge transfer (CT) between the $(FeCl_4)^{2-}$ and $(SacSac)^+$ ions. The same conclusion was reached by Heath, Martin & Stewart (1969) on the basis of spectroscopic data alone. Analogous σ–π CT absorption occurs in the intensely coloured crystalline $FeCl_4^{2-}$ salt of the planar 'paraquat' ion ($pq^{2+} = H_3C\text{–}N^+C_5H_4\text{–}C_5H_4N^+\text{–}CH_3$) (Prout & Wright, 1968; Macfarlane & Williams, 1969). The structure of $pqFeCl_4$ has not been reported, but it is isomorphous with $pqCoCl_4$ (Prout & Wright, 1968). In both $pqCoCl_4$ and $pqCuCl_4$ there are short Cl···N contacts along the perpendiculars to the planes of the pq^{2+} ions at the N atoms (Prout & Murray-Rust, 1969). The analogy with $(SacSac)_2FeCl_4$ is perhaps not complete, since the short Cl···S contacts do not lie along normals to the $(SacSac)^+$ ions. Short contacts with dithiolium ions are, however, already known. In the structure of 4-phenyl-1,2-dithiolium iodide there are abnormally short S···I⁻ distances which have been attributed to CT interactions (Hordvik & Sletten, 1966).

Finally we note the observation of Mason *et al.* (1968) that the salts $(SacSac)_2MCl_4$ (where M = Fe, Co, Mn, Zn) are isomorphous (as is the case in the same series for $pqMCl_4$, above). The isomorphism confirms the conclusion drawn by Heath *et al.* (1969) from the infrared spectra that the salts with M = Fe, Co, Ni, Mn form an isostructural series.

This work was supported by grants from the Science Research Council (to MRR), and from the Australian Research Grants Committee (65/15552) and the Institute of General Medical Sciences, U.S. Public Health Service (GM 10867-08) (to FMN). The crystals used by FMN were supplied by Professor P. Hemmerich and Dr K. Knauer, University of Basel.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 159–165

BECKETT, R. & HOSKINS, B. F. (1967). *Chem. Commun.* pp. 909–910

BECKETT, R. & HOSKINS, B. F. (1970). *Inorg. Nucl. Chem. Lett.* **6**, 257–260.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

BUSING, W. R., MARTIN, K. O. & LEVY, R. A. (1962). Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

FIGGIS, B. N., GERLOCH, M. & MASON, R. (1964). *Acta Cryst.* **17**, 506–508.

FREEMAN, H. C., GUSS, J. M., NOCKOLDS, C. E., PAGE, R. & WEBSTER, A. (1970). *Acta Cryst.* A**26**, 149–152.

FREEMAN, H. C., MILBURN, G. H. W., NOCKOLDS, C. E., HEMMERICH, P. & KNAUER, K. H. (1969). *Chem. Commun.* pp. 55–56.

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 105.

HEATH, G. A., MARTIN, R. L. & STEWART, I. M. (1969). *Chem. Commun.* 54–55.

HERRIOT, J. R., SIEKER, L. C., JENSEN, L. H. & LOVENBERG, W. (1970). *J. Mol. Biol.* **50**, 391–406.

HORDVIK, A. (1965). *Acta Chem. Scand.* **19**, 1039–1044.

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)

BY R. MASON,* G. B. ROBERTSON† AND G. A. RUSHOLME
Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England

(*Received* 14 *September* 1973; *accepted* 25 *November* 1973)

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.

---

* Present address: School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, England.

† Present address: Research School of Chemistry, The Australian National University, Canberra, A.C.T. 2600, Australia.