Fig. 2. Crystallographic atomic numbering scheme.

makes an angle of 77·7 (3)° with that bond line. The Ni—N bond distances [2·158 (2) and 2·107 (2) Å] and the N—Ni—N angle of 82·2 (1)° for the diamine agree reasonably well with the values of 2·095 (4) Å and 83·0 (2)° for *trans*-diaquabis(ethylenediamine)-nickel(II) bis(trichloroacetate) (Garcia-Granda & Gómez-Beltran, 1984). The influence of the N-substitution is clearly shown by the difference in Ni—N(diamine) coordination distances. The distance of 2·079 (2) Å found for the Ni—N(isothiocyanate) matches with the value of 2·062 (1) Å reported for the *trans* complex, bis(3-aminopropanol-*O,N*)bis(isothiocyanato)nickel(II) (Sanni, Lenstra & Patel, 1985). The OH distance is 0·81 (3) Å, while the average NH distance is 0·87 (3) Å. The CH distances in the complex lie in the range 0·93 (3) to 1·02 (3) Å [average 0·97 (4) Å]. There is an internal hydrogen bond OH···S with an O···S distance of 3·332 (3) Å, an

H···S distance of 2·530 (4) Å and an O—H···S angle of 171· (2)°.

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Tetra(methylthio)tetrathiafulvalenium Tetrachloroferrate(III)

BY HELMUT ENDRES

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany

Abstract. $C_{10}H_{12}S_8^{+}.FeCl_4^{-}$, $M_r = 586·39$, monoclinic, $P2_1/c$, $a = 12·271$ (4), $b = 14·725$ (5), $c = 13·973$ (3) Å, $\beta = 115·35$ (2)°, $V = 2286$ Å^3, $Z = 4$, $D_x = 1·70$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 18·3$ cm^{-1}, $F(000) = 1176$, room temperature, final $R = 0·056$ for 2044 observed $[I/\sigma(I) \geq 2·5]$ independent reflections and 208 variables. The structure consists of isolated π-dimers of the organic radical cations and of tetrahedral $[FeCl_4]^-$ anions. The methyl groups are forced out of the molecular planes and the TTF skeleton is slightly bent. The arrangement of the radical cations makes electrical conductivity unlikely.

Introduction. We are investigating the possibility of oxidizing the donor tetra(methylthio)tetrathiafulvalene (TTM-TTF) by metal cations in order to obtain cation

radical salts with electrical conductivity. This work has been encouraged by the fact that the related donor bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF or ET), having the same skeleton of S atoms, forms superconducting salts with polyhalide and AuI_2^- counterions (Williams, 1985; Williams & Carneiro, 1985). TTM-TTF, the molecular shape of which is more flexible than that of BEDT-TTF, has been described by several groups (Moses & Chambers, 1974; Mizuno, Garito & Cava, 1978; Wu, Mori, Enoki, Imaeda, Saito & Inokuchi, 1986). The structure of phase I of the neutral donor (Katayama, Honda, Kumagai, Tanaka, Saito & Inokuchi, 1985) forms charge-transfer compounds with several organic acceptors (Mizuno et al., 1978; Katayama et al., 1985); a metallic non-stoichiometric triiodide salt (Wu et al., 1986) has also been reported. We have recently described two tribromide salts containing the donor in oxidation states +1 and +2 (Endres, 1986a), a second phase of the neutral donor and its complex with HgI_2 (Endres, 1986b), and two phases of $[(TTM-TTF)^+]_2[Cu_2Cl_6]^{2-}$ (Endres, 1987). The product of the redox reaction of the donor with $FeCl_3$ is described below.

The structural information accumulated so far allows a correlation of the charge of the donor and the lengths of the central C=C and C—S bonds (Katayama et al., 1985; Endres, 1986a). This is important in cases where the composition does not allow the degree of ionicity to be determined, e.g. in organic charge-transfer compounds.

Experimental. Dark-green plates obtained by evaporating at 313 K a mixed solution in acetonitrile (Uvasol; Merck, Darmstadt) of TTM-TTF (purchased from Tokyo Kasai Kogyo Co., Tokyo) and anhydrous $FeCl_3$. Crystal $0.05 \times 0.14 \times 0.23$ mm mounted on a glass capillary. Lattice parameters derived from setting angles of 25 reflections ($3.7 < 2\theta < 23.8°$) centered on diffractometer (Syntex $R3$, Mo $K\alpha$ radiation, graphite monochromator). $\theta/2\theta$ data collection background–peak–background, $2\theta \le 60°$, hkl range $-17,0,0$ to $17,20,20$. 2044 unique reflections observed $[I \ge 2.5\sigma(I)]$ out of 6656 possible observations. Two check reflections measured at intervals of 100 reflections, intensity variation $\pm 3.8\%$. Empirical absorption correction: ψ scans of four reflections with $7.5 < 2\theta < 31.2°$, min. transmission $= 0.73$, max. $= 1$. Equivalent reflections merged, $R_{int} = 0.021$.

Structure solved by direct methods and Fourier syntheses. Non-H atoms refined anisotropically, methyl H inserted at calculated positions and refined riding on their C atoms with isotropic temperature factors tied to C, 208 variables. Cascaded least squares based on F with $w = 1/\sigma^2(F)$, σ from counting statistics. Max. shift/e.s.d. $= 0.05$, largest values in final difference Fourier map 0.42 and -0.43 e $Å^{-3}$, $R = 0.056$, $wR = 0.044$, $S = 1.52$. SHELXTL program system (Shel-

drick, 1983) on Nova 3 computer, scattering factors, including anomalous dispersion, from International Tables for X-ray Crystallography (1974).

Discussion. Atom coordinates are listed in Table 1, bond distances and angles in Table 2.* The numbering scheme of the $(TTM-TTF)^+$ radical cation is shown in Fig. 1. The large vibrational ellipsoids of the methyl C atoms indicate high mobility or disorder. The assignment of a charge of $+1$ for the cation is based on the lengths of the charge-sensitive bonds $C(1)-C(2)$, $C(1)-S$ and $C(2)-S$ (Endres, 1986a) and on the formulation of the tetrahedral anion as $[Fe^{III}Cl_4]^-$. The latter assumption is justified by the mean Fe—Cl distance of 2.17 Å, which compares well with the distances in other $[FeCl_4]^-$ salts, e.g. 2.19 Å (Kistenmacher & Stucky, 1968) and 2.16 Å (Bennett, Cotton & Weaver, 1967). From the difference in the ionic radii of Fe^{2+} and Fe^{3+} (Shannon, 1976), the bond length in $[Fe^{II}Cl_4]^{2-}$ would be 0.14 Å larger.

As shown in Fig. 2 the donor cations form π-dimers with crystallographic inversion centers relating the two molecules of a dimer. These dimers are isolated from each other. Short intermolecular $S \cdots S$ contacts occur within a dimer, 3.356 (5) and 3.386 (5) Å. The mode of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43457 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(Å^2 \times 10^3)$

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S(1)	1560 (2)	3782 (1)	−423 (2)	50 (1)
S(2)	64 (2)	3104 (1)	559 (2)	54 (1)
S(3)	−751 (2)	5001 (1)	−2029 (2)	52 (1)
S(4)	−2147 (2)	4264 (1)	−981 (2)	59 (1)
S(5)	3656 (2)	2568 (2)	887 (2)	66 (1)
S(6)	1892 (2)	1744 (2)	1904 (2)	76 (1)
S(7)	−2858 (2)	5982 (2)	−3685 (2)	79 (1)
S(8)	−4430 (2)	5186 (2)	−2444 (2)	96 (2)
C(1)	−788 (7)	4293 (5)	−1065 (5)	44 (4)
C(2)	166 (7)	3778 (4)	−379 (5)	45 (4)
C(3)	−2280 (7)	5281 (5)	−2576 (6)	57 (4)
C(4)	−2928 (6)	4934 (5)	−2076 (5)	55 (4)
C(5)	2185 (6)	2947 (4)	533 (5)	48 (4)
C(6)	1484 (7)	2620 (5)	974 (5)	49 (4)
C(7)	4094 (7)	3166 (5)	−10 (6)	78 (5)
C(8)	753 (9)	959 (6)	1277 (8)	144 (7)
C(9)	−2959 (12)	5255 (7)	−4677 (7)	200 (11)
C(10)	−4898 (8)	4279 (6)	−1888 (8)	115 (7)
Fe	2200 (1)	8250 (1)	2582 (1)	59 (1)
Cl(1)	2805 (2)	9452 (2)	3611 (2)	82 (1)
Cl(2)	2903 (3)	7046 (2)	3524 (2)	134 (2)
Cl(3)	242 (2)	8215 (2)	1850 (2)	118 (2)
Cl(4)	2829 (3)	8329 (2)	1362 (2)	123 (2)

Table 2. *Bond lengths* (Å) *and angles* (°)

S(1)—C(2)	1·737 (9)	S(1)—C(5)	1·735 (7)
S(2)—C(2)	1·692 (8)	S(2)—C(6)	1·737 (8)
S(3)—C(1)	1·720 (8)	S(3)—C(3)	1·746 (8)
S(4)—C(1)	1·722 (9)	S(4)—C(4)	1·726 (7)
S(5)—C(5)	1·747 (8)	S(5)—C(7)	1·792 (10)
S(6)—C(6)	1·747 (7)	S(6)—C(8)	1·736 (9)
S(7)—C(3)	1·741 (7)	S(7)—C(9)	1·715 (11)
S(8)—C(4)	1·729 (8)	S(8)—C(10)	1·762 (11)
C(1)—C(2)	1·380 (9)	C(3)—C(4)	1·364 (13)
C(5)—C(6)	1·344 (13)	Fe—Cl(1)	2·201 (2)
Fe—Cl(2)	2·158 (3)	Fe—Cl(3)	2·173 (3)
Fe—Cl(4)	2·154 (4)		

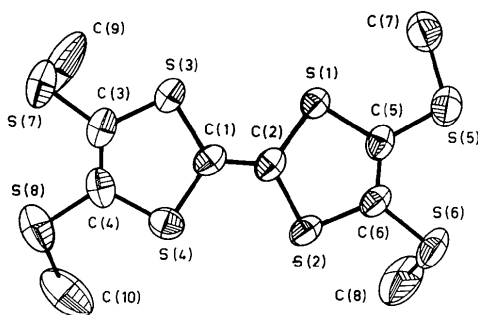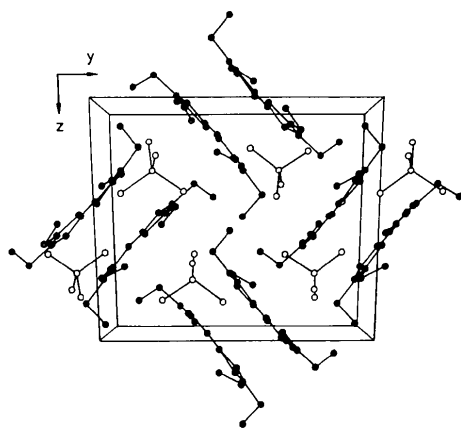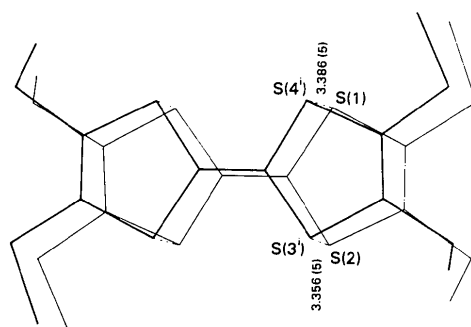|			
C(2)—S(1)—C(5)	95·1 (4)	C(2)—S(2)—C(6)	95·9 (4)
C(1)—S(3)—C(3)	95·9 (4)	C(1)—S(4)—C(4)	96·4 (4)
C(5)—S(5)—C(7)	103·2 (4)	C(6)—S(6)—C(8)	101·8 (4)
C(3)—S(7)—C(9)	102·1 (4)	C(4)—S(8)—C(10)	102·2 (4)
S(3)—C(1)—S(4)	114·8 (4)	S(3)—C(1)—C(2)	125·4 (7)
S(4)—C(1)—C(2)	119·8 (6)	S(1)—C(2)—S(2)	115·5 (4)
S(1)—C(2)—C(1)	121·9 (7)	S(2)—C(2)—C(1)	122·6 (7)
S(3)—C(3)—S(7)	118·9 (6)	S(3)—C(3)—C(4)	116·1 (5)
S(7)—C(3)—C(4)	125·1 (6)	S(4)—C(4)—S(8)	120·2 (5)
S(4)—C(4)—C(3)	116·4 (5)	S(8)—C(4)—C(3)	123·2 (5)
S(1)—C(5)—S(5)	120·5 (5)	S(1)—C(5)—C(6)	116·7 (5)
S(5)—C(5)—C(6)	122·8 (5)	S(2)—C(6)—S(6)	118·7 (5)
S(2)—C(6)—C(5)	116·5 (5)	S(6)—C(6)—C(5)	124·8 (6)
Cl(1)—Fe—Cl(2)	109·2 (1)	Cl(1)—Fe—Cl(3)	108·8 (1)
Cl(2)—Fe—Cl(3)	109·9 (1)	Cl(1)—Fe—Cl(4)	109·8 (1)
Cl(2)—Fe—Cl(4)	110·0 (1)	Cl(3)—Fe—Cl(4)	109·1 (1)

Fig. 3. Two cations of a π-dimer, viewed perpendicular to the mean plane.

Fig. 1. The numbering scheme in the (TTM-TTF)⁺ radical cation. Thermal ellipsoids are drawn at 50% probability.

overlap is shown in Fig. 3. The close dimer formation forces the methyl groups out of the molecular planes, and the TTF skeleton itself is slightly bent: the dihedral angle between the two five-membered rings of a cation is 8·5 (5)°. The arrangement of the radical cations means that electrical conductivity cannot be expected.

The cations result, of course, from a redox reaction between neutral TTM-TTF and Fe^{III}. But the reduced Fe species does not enter the crystals, which are composed of the oxidized donor and a complex of the unreduced metal ion. This has also been observed for the oxidation of the donor with $CuCl_2$ (Endres, 1987).

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Fig. 2. Perspective view of the structure along **a**.