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Structure of Undeca(tetrathiafulvalene)* Tris(hexacyanoferrate) Pentahydrate

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Abstract. $11C_6H_4S_4.3[Fe(CN)_6].5H_2O$, $M_r = 2973.84$, triclinic, $P\bar{1}$, $a = 10.795\,(5)$, $b = 10.889\,(6)$, $c = 25.212\,(2)$ Å, $\alpha = 85.21\,(4)$, $\beta = 89.59\,(3)$, $\gamma = 80.54\,(4)°$, $V = 2913.2$ Å^3, $Z = 1$, $D_x = 1.695$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 11.83$ cm^{-1}, $F(000) = 1506$, $T = 293$ K, $R = 0.035$ for 4554 observed reflections. Eight fully oxidized tetrathiafulvalene (TTF) molecules form dimerized stacks, parallel to the |011| direction with the three other molecules perpendicular to this. Four types of overlap are observed in the stack [shortest inter-TTF S···S contact 3.270 (3) Å]. Strong interactions between $[Fe(CN)_6]^3$ anions and the TTF stack are also observed: N···S = 3.099 (7). $[Fe(CN)_6]^{3-}$ units and water molecules are associated via hydrogen bonding [N···O = 2.76 (1) Å]. The compound is a semiconductor ($\sigma_{300K} = 8.5 \times 10^{-4} \Omega^{-1} cm^{-1}$).

Introduction. In the course of our investigation of organo-mineral materials (Ouahab, 1985; Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986), we have prepared new compounds made of organic donors [such as tetrathia(selena)fulvalene and its derivatives] and octahedral hexacyanometalates $\{[M(CN)_6]; M = Fe, Co, Cr, Mn\}$. Some of the anions are magnetic $\{[Fe(CN)_6]^{3-}: S = 3/2; [Mn(CN)_6]^{3-}: S = 5/2\}$ and offer the possibility of access to compounds where electron delocalization on the organic systems coexists with paramagnetic centers localized on the inorganic anion. Similar materials have been reported (Lacroix, Kahn, Gleizes, Valade & Cassoux, 1984; Batail, Ouahab, Torrance, Pylman & Parkin, 1985). We report here the preparation and the structure of the 3:11 $[Fe(CN)_6]$: TTF.5H$_2$O.

Experimental. Black crystals of the title compound were prepared by electrocrystallization from the neutral donor (5 mM) in rigorously dried acetonitrile, using the tetraethylammonium salts of the anion (15 mM). The latter was prepared according to the literature (Masharak, 1986). The electrocrystallization was carried out under constant low current (0.95 µA) in a 50 ml cell. The working electrode was a platinum wire. Crystal 0.15 × 0.2 × 0.2 mm. Enraf–Nonius CAD-4

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* Alternative nomenclature. Tetrathiafulvalene ≡ 2,2'-bi-1,3-dithiolylidene.

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diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation. Cell dimensions: least-squares refinement from setting angles of 25 accurately centered reflections ($\theta \le 13°$). Intensities collected by $\theta/2\theta$ scans. Three standard reflections measured every hour: no fluctuations in intensity. One set of reflections collected up to $2\theta = 50°$. 10 165 independent reflections measured ($0 \le h \le 12$, $-12 \le k \le 12$, $-30 \le l \le 30$), 4554 with $I > 3\sigma(I)$. Lorentz and polarization corrections, no absorption correction ($\mu_R < 1$). Direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). H atoms placed at geometrically reasonable positions, C–H $= 1$ Å (H atoms of water molecules not observed). Full-matrix least-squares anisotropic (β_{ij}) refinement [H atoms isotropic ($B = 4$ Å²), not refined], secondary-extinction refined, $g = 9.65 \times 10^{-8}$, $R = 0.035$, $wR = 0.050$. $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + (0.06F_o)^2]^{-1}$, $S = 1.25$, $(\Delta/\sigma)_{max} = 0.05$, $\Delta\rho_{max} = 0.038$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computer programs from Enraf–Nonius *SDP* described by Frenz (1978).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å²)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Fe1	0·000	0·000	0·000	3·24 (3)
Fe2	−0·02065 (8)	0·37029 (8)	0·33049 (4)	3·29 (2)
S1	0·2655 (2)	−0·0874 (2)	0·30764 (7)	3·81 (4)
S2	0·3828 (2)	−0·3259 (2)	0·36012 (7)	4·15 (4)
S3	0·5413 (2)	−0·0369 (2)	0·26773 (7)	3·57 (4)
S4	0·6551 (2)	−0·2684 (2)	0·32611 (7)	3·77 (4)
S5	0·4393 (2)	0·5524 (2)	0·22548 (7)	3·99 (4)
S6	0·3233 (2)	0·7929 (1)	0·17528 (7)	3·73 (4)
S7	0·7131 (2)	0·6055 (2)	0·18698 (7)	3·84 (4)
S8	0·5977 (2)	0·8470 (1)	0·13621 (7)	3·81 (4)
S9	0·3019 (2)	0·6994 (2)	0·05401 (8)	5·43 (5)
S10	0·3019 (2)	0·4503 (2)	0·09937 (8)	5·05 (5)
S11	0·5824 (2)	0·7418 (2)	0·09190 (8)	5·72 (5)
S12	0·6827 (2)	0·4897 (2)	0·06303 (8)	5·46 (5)
S13	0·6527 (2)	0·1534 (2)	0·11596 (8)	4·53 (4)
S14	0·6158 (2)	0·2526 (2)	0·22092 (7)	4·47 (4)
S15	0·3605 (2)	0·1197 (2)	0·11309 (7)	4·54 (4)
S16	0·3213 (2)	0·2255 (2)	0·21672 (8)	4·89 (5)
S17	0·3972 (2)	−0·1605 (2)	0·41763 (7)	4·31 (4)
S18	0·2661 (2)	0·0678 (2)	0·41621 (8)	4·64 (4)
S19	0·6637 (2)	−0·0851 (2)	0·43071 (7)	3·91 (4)
S20	0·5275 (2)	0·1386 (2)	0·37283 (8)	4·48 (4)
S21	0·3308 (2)	0·1386 (2)	0·54755 (8)	5·59 (5)
S22	0·3863 (2)	0·4169 (2)	0·44632 (7)	4·33 (4)
O1	0·9805 (5)	0·9099 (4)	0·2281 (2)	5·3 (1)
O2	0·0659 (5)	0·1834 (4)	0·5516 (2)	6·0 (1)
O3	0·9826 (9)	0·4500 (8)	0·1028 (4)	5·2 (2)
N1	0·0388 (6)	−0·2688 (5)	−0·0349 (3)	5·8 (2)
N2	0·0376 (6)	−0·1000 (5)	0·1174 (2)	4·7 (1)
N3	0·2833 (5)	0·0121 (6)	−0·0064 (3)	5·6 (2)
N4	−0·0008 (6)	0·4690 (6)	0·2130 (2)	5·9 (2)
N5	0·2659 (5)	0·3657 (6)	0·3413 (3)	5·7 (2)
N6	−0·0299 (6)	0·2587 (6)	0·4468 (2)	5·7 (2)
N7	−0·3094 (5)	0·4038 (6)	0·3167 (3)	6·0 (2)
N8	−0·0583 (6)	0·6317 (5)	0·3717 (2)	4·7 (1)
N9	0·0110 (6)	0·1010 (5)	0·2978 (3)	5·6 (2)
C1	0·0258 (6)	−0·1700 (6)	−0·0218 (3)	3·7 (1)
C2	0·0232 (5)	−0·0645 (5)	0·0734 (2)	3·4 (1)
C3	0·1799 (6)	0·0064 (5)	−0·0043 (3)	3·8 (2)
C4	−0·0091 (6)	0·4347 (6)	0·2567 (3)	3·8 (2)
C5	0·1588 (6)	0·3640 (6)	0·3371 (3)	4·0 (2)
C6	−0·0288 (6)	0·2995 (6)	0·4036 (3)	3·9 (2)
C7	−0·2019 (6)	0·3900 (5)	0·3217 (3)	3·8 (1)
C8	−0·0441 (6)	0·5360 (6)	0·3553 (3)	3·6 (1)

Table 1 *(cont.)*

	x	y	z	B_{eq}
C9	−0·0006 (6)	0·2006 (6)	0·3092 (3)	4·0 (2)
C10	0·2221 (6)	−0·2928 (6)	0·3614 (3)	4·5 (2)
C11	0·1672 (6)	−0·1825 (7)	0·3372 (3)	4·6 (2)
C12	0·4008 (6)	−0·1893 (5)	0·3237 (2)	3·3 (1)
C13	0·5211 (5)	−0·1662 (5)	0·3073 (2)	2·8 (1)
C14	0·7537 (6)	−0·1855 (6)	0·2896 (3)	3·9 (2)
C15	0·7024 (6)	−0·0785 (6)	0·2637 (3)	4·1 (2)
C16	0·2810 (6)	0·5913 (6)	0·2301 (3)	4·2 (2)
C17	0·2269 (6)	0·7017 (6)	0·2078 (3)	4·2 (2)
C18	0·4596 (5)	0·6885 (5)	0·1900 (3)	3·2 (1)
C19	0·5754 (6)	0·7117 (5)	0·1725 (3)	3·3 (1)
C20	0·8109 (6)	0·6997 (6)	0·1574 (3)	4·2 (2)
C21	0·7578 (6)	0·8101 (6)	0·1343 (3)	4·1 (2)
C22	0·1986 (7)	0·6096 (7)	0·0808 (3)	5·6 (2)
C23	0·2466 (7)	0·4955 (6)	0·1015 (3)	5·6 (2)
C24	0·4354 (7)	0·5873 (6)	0·0667 (3)	4·5 (2)
C25	0·5517 (7)	0·6041 (6)	0·0511 (3)	4·1 (2)
C26	0·7408 (8)	0·6915 (7)	0·0213 (3)	6·4 (2)
C27	0·7852 (8)	0·5756 (8)	0·0319 (3)	6·1 (2)
C28	0·7799 (6)	0·1968 (7)	0·1469 (3)	5·8 (2)
C29	0·7630 (7)	0·2400 (7)	0·1944 (4)	6·0 (2)
C30	0·5499 (6)	0·1909 (5)	0·1681 (3)	3·2 (1)
C31	0·4278 (6)	0·1786 (5)	0·1666 (2)	3·2 (1)
C32	0·2097 (7)	0·1363 (7)	0·1387 (4)	5·9 (2)
C33	0·1935 (7)	0·1826 (7)	0·1854 (4)	6·3 (2)
C34	0·2378 (7)	0·1311 (7)	0·4771 (3)	5·1 (2)
C35	0·1773 (6)	−0·0261 (7)	0·4523 (3)	5·4 (2)
C36	0·4081 (6)	−0·0255 (6)	0·4231 (2)	3·5 (1)
C37	0·5210 (6)	0·0035 (5)	0·4138 (2)	3·4 (1)
C38	0·7519 (6)	0·0154 (7)	0·3964 (3)	5·0 (2)
C39	0·6863 (7)	0·1778 (6)	0·3706 (3)	5·3 (2)
C40	0·4399 (6)	0·4870 (5)	0·4989 (3)	3·8 (2)
C41	0·2108 (7)	0·4677 (8)	0·5171 (3)	6·3 (2)
C42	0·2375 (7)	0·4181 (7)	0·4708 (3)	5·4 (2)

Discussion. Final atomic parameters are in Table 1.* The atomic numbering is shown in Fig. 1. The crystal structure, represented in Fig. 2, is built from three [Fe(CN)₆]³⁻ units located at 000, 0$\frac{1}{3}\frac{1}{3}$ and 0$\frac{2}{3}\frac{2}{3}$ and eleven TTF units: eight form a stack parallel to the [011] direction and three are perpendicular to this stack.

The geometrical parameters of the [Fe(CN)₆]³⁻ unit [Fe–C $= 1.943$ (6), C–N $= 1.143$ (9) Å] are in good agreement with those found in 3[(C₂H₅)₄N][Fe(CN)₆].5H₂O (Ouahab, in preparation).

The charge on each TTF molecule has been determined by comparing the geometrical parameters with those found in the neutral TTF (Philips, Kistenmacher, Ferraris & Cowan, 1973) and the fully oxidized TTF in (TTF)I₃ (Teitelbaum, Marks & Johnson, 1980). These structural features (Table 2), suggest that the TTF molecules 1, 2, 3, 4 (forming the stack) and 5 are fully oxidized, while 6 is neutral. This is consistent with the number of positive charges which must be found on the organic system and also with the low conductivity of this salt.

In the stack, the TTF molecules are dimerized (Fig. 3) (intradimer separation 3·42 Å) and four types of overlap coexist. All the intradimer TTF are eclipsed

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* Lists of bond distances and bond angles, structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51483 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
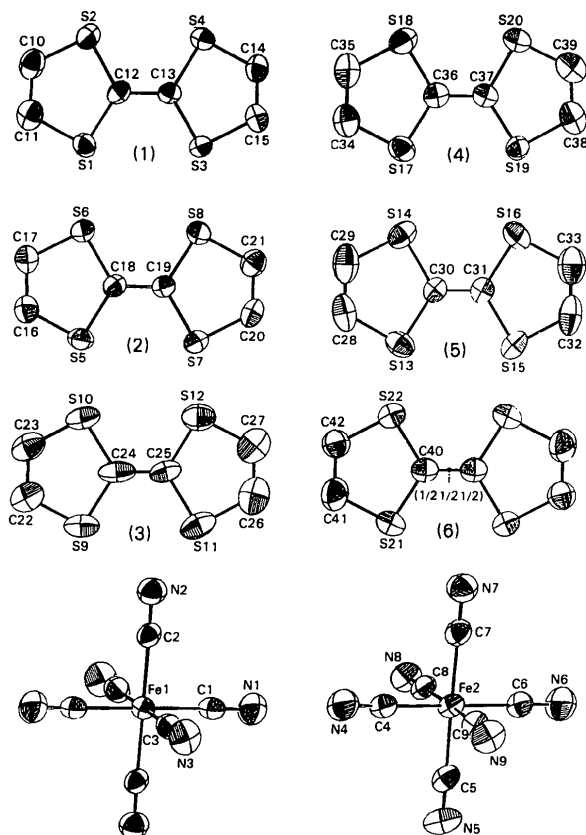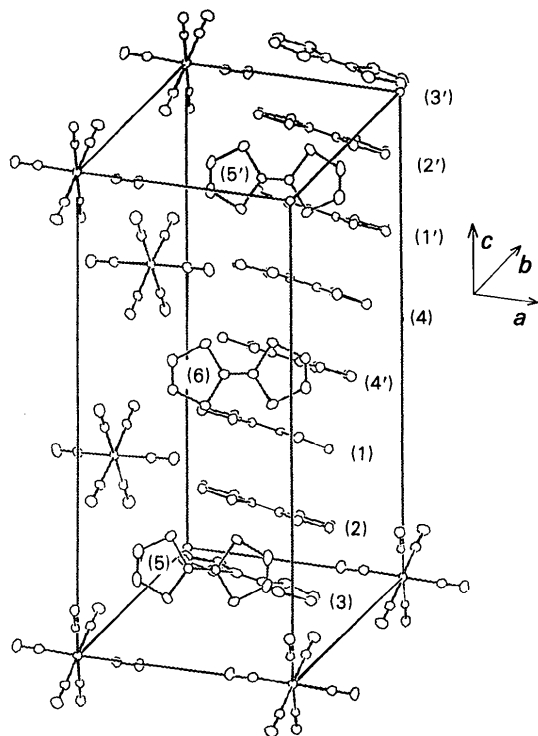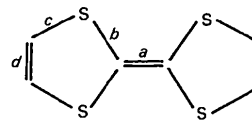
Fig. 1. Atom numbering.

Table 2. *Comparison of the TTF structural features of molecules 1–6 with those of TTF⁰ and TTF⁺ (mmm symmetry imposed)*

	1	2	3	4	5	6	TTF⁰	TTF⁺
a (Å)	1·415	1·378	1·349	1·376	1·347	1·376	1·349	1·382
b (Å)	1·712	1·725	1·730	1·725	1·749	1·727	1·757	1·719
c (Å)	1·721	1·708	1·706	1·713	1·729	1·726	1·726	1·728
d (Å)	1·336	1·330	1·329	1·33	1·321	1·336	1·314	1·322

Table 3. *Selected intermolecular contacts* (Å)

Intradimer contacts

S1···S18	3·335 (3)	S5···S10	3·498 (3)
S2···S17	3·480 (3)	S6···S9	3·324 (3)
S3···S20	3·382 (3)	S7···S12	3·503 (3)
S4···S19	3·448 (3)	S8···S11	3·270 (3)

Interdimer contacts

S1···S6	3·695 (2)	S3···S8	3·658 (2)

Other TTF contacts

S2···S22	3·394 (2)	S5···S14	3·510 (2)
S3···S14	3·498 (2)	S8···S13	3·480 (2)

|Fe(CN)₆| and TTF contacts

S1···N9	3·145 (6)	S11···N3	3·242 (7)
S4···N8	3·289 (6)	S14···N7	3·213 (7)
S7···N4	3·245 (6)	S22···N5	3·090 (7)

Water-molecule contacts

O2···S19	2·963		
O1···N2	2·859 (7)	O2···N8	2·897 (8)
O1···N9	2·894 (8)	O3···N1	2·757 (11)
O2···N6	2·848 (8)	O3···N4	2·810 (11)

Fig. 2. Contents of the unit cell. Four [Fe(CN)₆] units and the water molecules are omitted for clarity.
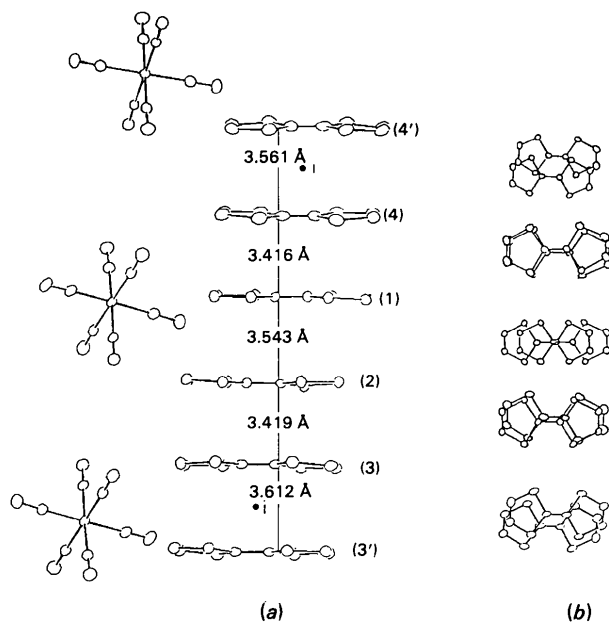

(a)   (b)

Fig. 3. Stacking deformation evidence. (a) Intra- and interdimer separations; (b) intra- and interdimer overlap.

(interdimer separation 3·54, 3·56 and 3·61 Å). This configuration maximizes the S···S bonding (Lowe, 1980) [the intradimer S···S distances range from 3·27 to 3·50 Å (Table 3)]. On the other hand, three interdimer types of overlaps are observed showing the irregularity of the packing. The intermolecular contacts (Table 3) reveal strong interactions between the $[Fe(CN)_6]^{3-}$ anions and the organic molecules. $[Fe(CN)_6]^{3-}$ units and H_2O molecules are associated through hydrogen bonding. Magnetic measurements of this material are in progress and will be reported elsewhere.

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Copper Disodium Tetrahydroxide

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Abstract. $CuNa_2(OH)_4$, $M_r = 177·55$, orthorhombic, $Pna2_1$, $a = 6·750$ (3), $b = 6·726$ (5), $c = 8·993$ (5) Å, $V = 408·3$ (7) Å^3, $Z = 4$, $D_x = 2·888$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 5·442$ mm^{-1}, $F(000) = 348$, room temperature, $R = 0·030$ for 549 reflections. The structure contains $[NaO_6]$ octahedra and $[CuO_4]$ square planes. It can be described as deriving from the NaCl type. 3/4 of the octahedral sites formed by O atoms are occupied by Na or Cu atoms, 1/4 by H atoms. A study of the hydrogen bonds shows that they are very weak.

Introduction. In 1933, Scholder described several new compounds belonging to the ternary system Na_2O, MO, H_2O (M: divalent metal). Since then, several papers have been published; the synthesis was published in 1966 (Scholder & Schwochow, 1966). In all the previous studies, the syntheses gave rise to powders and no crystallographic study has ever been mentioned. The chemical formula of these compounds, mostly $Na_2M(OH)_4$, was deduced only from chemical analysis.

These compounds, which are unstable in air, have never been obtained for other alkali metals.

In a recent paper (Cudennec, Lecerf, Riou & Gerault, 1988), we proposed a new method of synthesis for one compound belonging to these systems: $Na_2Cu(OH)_4$. This method made possible the growth of crystals; therefore a complete crystallographic study became possible. This paper reports the results of the structure determination and discusses peculiar properties.

Experimental. As stated in our previous publication, crystals of $Na_2Cu(OH)_4$ were prepared from a system containing 1 mol of CuO, 10 mol of NaOH and 40 mol of H_2O. The mixture was placed in a dry box using KOH at room temperature for several weeks to be slowly dehydrated and protected from CO_2. Well formed blue octahedral-shaped crystals appeared, of average size about 0·1 mm. Crystals could not be isolated and washed because of their instability;