

increase of 26 Å<sup>3</sup> when going from the Se—Cl to the S—Br systems. For KRe<sub>6</sub>S<sub>5</sub>Br<sub>3</sub>, this would lead to a hypothetical cubic cell of about 13.25 Å (*i.e.* a cell volume of 2326.2 Å<sup>3</sup>), a value above those we have observed for any cubic material in this family. The passage to the monoclinic symmetry is in fact accompanied by a reduction in the cell volume to the actual value of 2261.5 Å<sup>3</sup> at the expense of a distortion of the K<sup>+</sup> site. The latter results in a clear reduction of one pair of Re—Br—K angles (107° instead of 123° for the other), while in KRe<sub>6</sub>Se<sub>5</sub>Cl<sub>9</sub>, all the Re—Cl—K angles are equal (125.35°).

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## Structures of Some Quasi-Two-Dimensional Molecular Conductors. I. Structure of $\kappa$ -Tetrakis(3,4-methylenedithio-2,2',5,5'-tetrathiafulvalen)ium Tetracyanoplatinate Dihydrate: $\kappa$ -(MDTTTF)<sub>4</sub>Pt(CN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>

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**Abstract.** Tetrakis[2-(1,3-dithiol-2-ylidene)-[1,3]dithiolo[4,5-*d*][1,3]dithiol]ium tetracyanoplatinate dihydrate, [C<sub>7</sub>H<sub>4</sub>S<sub>6</sub>]<sub>4</sub>[Pt(CN)<sub>4</sub>].2H<sub>2</sub>O, *M<sub>r</sub>* = 1457.2, triclinic, *P*1, *a* = 8.569 (9), *b* = 9.991 (5), *c* = 14.811 (5) Å,  $\alpha$  = 108.84 (3),  $\beta$  = 95.10 (4),  $\gamma$  = 90.37 (7)°, *V* = 1194.5 Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 2.03 g cm<sup>-3</sup>, *Mo K*α,  $\lambda$  = 0.71073 Å,  $\mu$  = 40.16 cm<sup>-1</sup>, *F*(000) = 718, *T* = 293 K, *R* = 0.054 for 3234 reflections with *I* ≥ 3σ(*I*). The crystal structure contains alternating layers of MDTTTF molecules and Pt(CN)<sub>4</sub><sup>2-</sup> anions. The MDTTTF packing presents a  $\kappa$  mode characterized by face-to-face dimers of MDTTTF molecules which are orthogonal to adjacent dimers. The anionic sheet contains water molecules located at cavities generated by the organic dimers and the Pt(CN)<sub>4</sub> units. The latter form a one-dimensional polymer through hydrogen bonding as indicated by

C—N···O1*W* of 2.848 (14) and 3.121 (14) Å. Strong intra- and interdimer S···S interactions (3.38–3.58 Å) are observed.

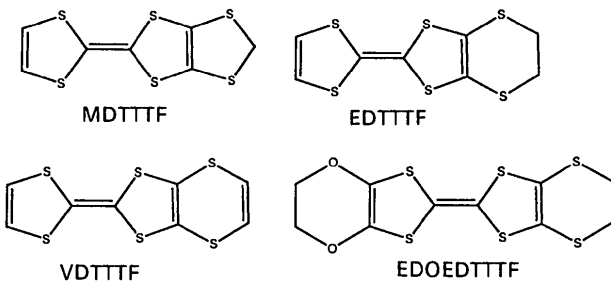
**Introduction.** In previous papers (Ouahab, Padiou, Grandjean, Garrigou-Lagrange, Delhaes & Bencharif, 1989; Garrigou-Lagrange, Ouahab, Grandjean & Delhaes, 1990; Ouahab, Triki, Grandjean, Bencharif, Garrigou-Lagrange & Delhaes, 1991; Garrigou-Lagrange, Amiéll, Dupart, Delhaes, Ouahab, Fettouhi, Triki & Grandjean 1991) we reported the synthesis and X-ray and physical characterizations of conducting salts based on symmetrical TTF (tetrathiafulvalene) derivatives and tetracyanometalate dianions, which are, in our opinion, of great interest, especially as a recent investigation revealed the first example of superconductivity in this kind of polyanion material (Mori, Hirabayashi, Tanaka, Mori, Maruyama & Inokuchi, 1991). We report here,

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and in future communications, the X-ray crystal structures of a new series of conducting radical ion salts based on unsymmetrical donors: MDTTTF (methylenedithiotetrathiafulvalene); EDTTTF (ethylenedithiotetrathiafulvalene); VDTTTF (vinylenedithiotetrathiafulvalene) and EDOEDTTTF (ethylenedioxyethylenedithiotetrathiafulvalene); and tetracyanometalate dianions:  $M(\text{CN})_4^{2-}$ ,  $M = \text{Pt, Ni}$  and  $\text{Pd}$ . We report here the first  $\kappa$  phase observed in such materials:  $\kappa\text{-(MDTTTF)}_4\text{Pt}(\text{CN})_4(\text{H}_2\text{O})_2$ .



**Experimental.** The preparation of the title compound has been reported elsewhere (Mousdis, Ducasse, Fettouhi, Ouahab, Dupart, Garrigou-Lagrange, Amiell, Canet & Delhaes, 1992). A crystal of approximate dimensions  $0.4 \times 0.15 \times 0.1$  mm was selected for the intensity data collection which was carried out on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated  $\text{Mo K}\alpha$  radiation. Three standard reflections monitored throughout data collection showed very small changes in intensity (less than 5%). Cell dimensions were obtained and refined by least squares from setting angles of 25 centered reflections ( $2\theta \leq 26^\circ$ ). 4502 reflections were recorded by a  $\theta$ - $2\theta$  scan in the range  $2 \leq 2\theta \leq 50^\circ$  and  $0 \leq h \leq 10$ ,  $-11 \leq k \leq 11$ ,  $-17 \leq l \leq 17$ . The intensities were corrected for Lorentz-polarization and absorption phenomena. The latter correction was performed using the *DIFABS* (Walker & Stuart, 1983) procedure (correction factors 0.664–1.576). The structure was solved by direct methods (*MULTAN84*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and successive difference Fourier syntheses. 3234 independent reflections with  $I \geq 3\sigma(I)$ , after averaging the symmetry related reflections ( $R_{\text{int}} = 0.061$ ), were used for full-matrix least-squares anisotropic ( $\beta_{ij}$ ) refinements (on  $F$ ); secondary extinction refined,  $g = 1.32 \times 10^{-7}$ ;  $R = 0.054$ ,  $wR = 0.068$  [ $w = 4F_o^2/[\sigma(I)^2 + (0.07F_o^2)^2]$ ],  $S = 1.556$ ;  $(\Delta/\sigma)_{\text{max}} = 0.01$ ,  $(\Delta\rho)_{\text{max}} = 3.45 \text{ e } \text{\AA}^{-3}$ . H atoms were placed at computed positions ( $\text{C-H} = 1.09 \text{ \AA}$ ,  $B_{\text{eq}} = 5. \text{\AA}^2$ ) and not refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a

Table 1. Atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}$
Pt	0	0	0	2.24 (1)
Cl	0.049 (1)	-0.167 (1)	0.0408 (7)	2.8 (2)
C2	0.215 (1)	0.088 (1)	0.0498 (7)	3.0 (2)
N1	0.077 (1)	-0.264 (1)	0.0628 (7)	4.6 (2)
N2	0.335 (1)	0.139 (1)	0.0794 (7)	5.2 (3)
S1	0.3826 (3)	0.1555 (2)	0.3879 (2)	2.61 (5)
S2	0.1994 (3)	-0.0772 (3)	0.4098 (2)	2.77 (5)
S3	0.2924 (3)	0.0377 (2)	0.6376 (2)	2.32 (4)
S4	0.4713 (3)	0.2770 (2)	0.6176 (2)	2.52 (5)
S5	0.3596 (3)	0.1547 (3)	0.8562 (2)	3.39 (6)
S6	0.5406 (4)	0.3992 (3)	0.8363 (2)	4.23 (7)
C3	0.316 (1)	0.0734 (9)	0.4642 (6)	2.2 (2)
C4	0.356 (1)	0.1254 (9)	0.5623 (6)	2.2 (2)
C5	0.285 (1)	0.040 (1)	0.2854 (7)	3.4 (2)
C6	0.201 (1)	-0.067 (1)	0.2954 (7)	3.3 (2)
C7	0.458 (1)	0.2718 (9)	0.7319 (7)	2.7 (2)
C8	0.377 (1)	0.1611 (9)	0.7412 (6)	2.5 (2)
C9	0.521 (1)	0.285 (1)	0.9090 (7)	3.7 (2)
S7	0.0625 (3)	0.3652 (3)	0.6736 (2)	3.18 (5)
S8	-0.2118 (3)	0.5460 (3)	0.6953 (2)	3.14 (5)
S9	-0.2961 (3)	0.4443 (2)	0.4674 (2)	2.70 (5)
S10	-0.0139 (3)	0.2668 (2)	0.4400 (2)	2.35 (5)
S11	-0.1261 (3)	0.1322 (3)	0.2261 (2)	2.86 (5)
S12	-0.4140 (3)	0.3036 (3)	0.2549 (2)	2.97 (5)
C10	-0.098 (1)	0.4250 (8)	0.6171 (6)	2.1 (2)
C11	0.026 (1)	0.469 (1)	0.7886 (7)	3.9 (3)
C12	-0.097 (1)	0.551 (1)	0.7990 (7)	4.1 (3)
C13	-0.132 (1)	0.3812 (8)	0.5206 (6)	2.1 (2)
C14	-0.271 (1)	0.3335 (9)	0.3522 (6)	2.3 (2)
C15	-0.143 (1)	0.2541 (9)	0.3403 (6)	2.0 (2)
C16	-0.278 (1)	0.212 (1)	0.1688 (7)	3.1 (2)
O1W	0.218 (1)	0.470 (1)	-0.0097 (7)	7.0 (3)

MicroVAX 3100 using the *SDP* programs (B. A. Frenz & Associates, Inc. 1985). The atomic coordinates are given in Table 1, bond distances and bond angles in Table 2.\*

**Discussion.** The crystal structure is built of alternating layers of orthogonal MDTTTF dimers and of mixed layers containing anions and water molecules.

There are two independent MDTTTF molecules denoted *A* and *B* (see Figs. 1 and 2). The geometrical parameters of each molecule are in the range of those observed for such a molecule with a formal valence state averaged to +0.5, as in the superconducting salt  $\kappa\text{-(MDTTTF)}_2\text{AuI}_2$  (Hountas, Terzis, Papavasillou, Hilti, Burkle, Meyer & Zambounis, 1990). Moreover, on the basis of the slight difference between the central C—C bond distances [1.39 (1) and 1.36 (1)  $\text{\AA}$  for molecules *A* and *B*, respectively], we can reasonably expect a slight difference (*i.e.*  $0.5 \pm \epsilon$ ) in the charge borne by the MDTTTF molecules. Each MDTTTF molecule forms a dimer with its centrosymmetrically related one. The adjacent dimers are orthogonal and present a  $\kappa$  mode of packing (see Fig. 1). This constitutes the first

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55274 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0278]

Table 2. Bond distances (Å) and bond angles (°)

Pt—C1	1.99 (1)	C5—C6	1.34 (2)
Pt—C2	2.005 (9)	C7—C8	1.35 (1)
C1—N1	1.14 (2)	S7—C10	1.752 (9)
C2—N2	1.13 (1)	S7—C11	1.74 (1)
S1—C3	1.73 (1)	S8—C10	1.752 (8)
S1—C5	1.723 (9)	S8—C12	1.73 (1)
S2—C3	1.723 (8)	S9—C13	1.769 (9)
S2—C6	1.73 (1)	S9—C14	1.740 (8)
S3—C4	1.74 (1)	S10—C13	1.762 (8)
S3—C8	1.723 (8)	S10—C15	1.733 (9)
S4—C4	1.726 (8)	S11—C15	1.756 (8)
S4—C7	1.72 (1)	S11—C16	1.82 (1)
S5—C8	1.74 (1)	S12—C14	1.752 (9)
S5—C9	1.83 (1)	S12—C16	1.83 (1)
S6—C7	1.744 (8)	C10—C13	1.36 (1)
S6—C9	1.82 (1)	C11—C12	1.33 (2)
C3—C4	1.39 (1)	C14—C15	1.35 (1)
C1—Pt—C2	91.8 (4)	S5—C9—S6	110.2 (6)
Pt—C1—N1	179.0 (8)	C10—S7—C11	94.4 (5)
Pt—C2—N2	178.5 (8)	C10—S8—C12	95.4 (5)
C3—S1—C5	95.3 (5)	C13—S9—C14	93.7 (4)
C3—S2—C6	94.9 (5)	C13—S10—C15	93.8 (4)
C4—S3—C8	94.6 (4)	C15—S11—C16	93.3 (4)
C4—S4—C7	94.6 (5)	C14—S12—C16	92.5 (4)
C8—S5—C9	92.6 (5)	S7—C10—S8	114.7 (5)
C7—S6—C9	93.4 (5)	S7—C10—C13	123.1 (7)
S1—C3—S2	115.4 (5)	S8—C10—C13	122.3 (7)
S1—C3—C4	121.9 (7)	S7—C11—C12	118.5 (9)
S2—C3—C4	122.7 (8)	S8—C12—C11	116.9 (8)
S3—C4—S4	115.9 (5)	S9—C13—S10	115.5 (5)
S3—C4—C3	121.1 (7)	S9—C13—C10	121.2 (6)
S4—C4—C3	123.1 (8)	S10—C13—C10	123.2 (7)
S1—C5—C6	116.9 (8)	S9—C14—S12	123.4 (5)
S2—C6—C5	117.4 (7)	S9—C14—C15	117.8 (6)
S4—C7—S6	124.7 (6)	S12—C14—C15	118.3 (6)
S4—C7—C8	117.7 (6)	S10—C15—S11	123.7 (5)
S6—C7—C8	117.6 (8)	S10—C15—C14	118.5 (6)
S3—C8—S5	124.3 (6)	S11—C15—C14	117.6 (6)
S3—C8—C7	117.1 (7)	S11—C16—S12	110.4 (5)
S5—C8—C7	118.5 (6)		

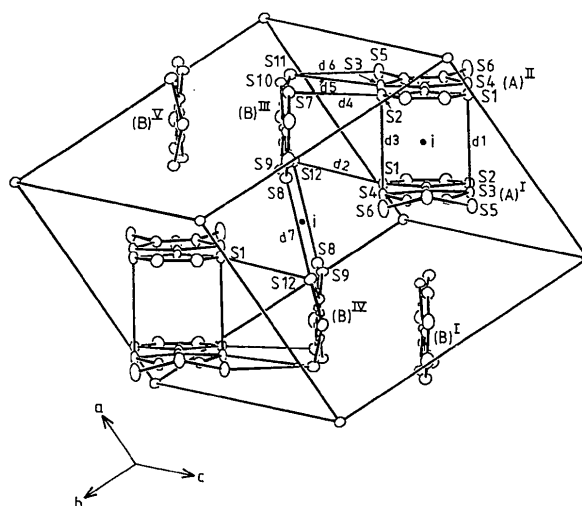


Fig. 1.  $\kappa$ -Packing mode of the MDTTF molecules with intra- and interdimer S...S contacts lower than 3.6 Å:  $d1 = 3.378$  (3);  $d2 = 3.401$  (4);  $d3 = 3.445$  (3);  $d4 = 3.460$  (3);  $d5 = 3.418$  (4);  $d6 = 3.308$  (3);  $d7 = 3.585$  (3) Å. Symmetry code: (I)  $x, y, z$ ; (II)  $1-x, -y, 1-z$ ; (III)  $1+x, y, z$ ; (IV)  $-x, 1-y, 1-z$ ; (V)  $-1-x, 1-y, 1-z$ .

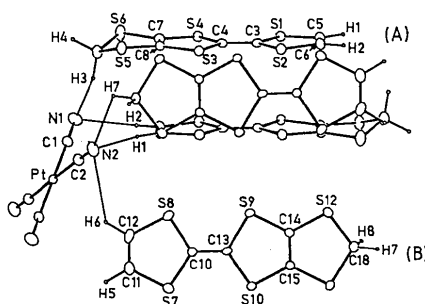


Fig. 2. Atomic numbering scheme and anion-cation contacts:  $N1 \cdots H2 = 2.442$ ;  $N1 \cdots H3 = 2.513$ ;  $N2 \cdots H1 = 2.499$ ;  $N2 \cdots H6 = 2.970$ ;  $N2 \cdots H7 = 2.771$  Å

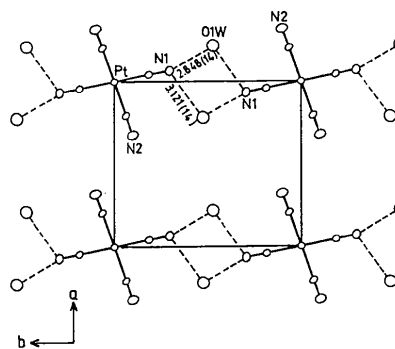


Fig. 3. Arrangement of anions and water molecules in the anionic layer.

example of a  $\kappa$ -packing mode obtained with such a dianion. Strong intra- and interdimer interactions are observed, as indicated by the S...S contacts given in Fig. 1. Nevertheless, we note that the *A* dimer gives rise to more S...S interactions  $\leq 3.6$  Å than the *B* dimer (see Fig. 1).

The  $Pt(CN)_4^{2-}$  units are located at the origin of the lattice. The Pt—C bond distances and bond angles compare well with those found, for instance, in the  $(BEDTTTF)_4Pt(CN)_4$  [BEDTTTF = bis(ethylenedithio)tetrathiafulvalene] salt (Fettouhi, Ouahab, Grandjean & Toupet, 1992). The water molecules act as bridges between the  $Pt(CN)_4^{2-}$  units in the anionic layers (Fig. 3). The interactions between the CN groups of the anions and the O atom of the water molecules are  $C1-N1 \cdots OW1 = 2.848$  (14) and  $C1-N1 \cdots OW1 = 3.121$  (14) Å. These contacts are shorter than the value [3.415 (7) Å] observed in the superconducting salt  $(BEDTTTF)_4Pt(CN)_4 \cdot H_2O$  (Mori *et al.*, 1991). The anionic layers could be considered as comprising one-dimensional polymers through hydrogen bonds.

The organic-inorganic (C—H...N) interactions established *via* hydrogen bonding are represented in Fig. 2. These interactions (2.45–2.98 Å) are similar to those found in superconducting BEDTTTF salts (Williams, Schults, Geiser, Carlson, Kini, Wang,

Kwok, Whangbo & Schriber, 1991). The physical properties are currently under investigation in order to check the possible occurrence of a superconducting state.

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## Structure of Bis[ $\mu$ -4-amino-3,5-bis(aminomethyl)-1,2,4-triazole- $N'$ , $N^1$ , $N^2$ , $N''$ ]-bis[diaquacopper(II)] Bis(sulfate) Tetrahydrate

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**Abstract.**  $[\text{Cu}(\text{C}_4\text{H}_{10}\text{N}_6)(\text{H}_2\text{O})_2]_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $M_r = 747.6$ , monoclinic,  $C2/c$ ,  $a = 19.009$  (8),  $b = 11.273$  (4),  $c = 13.144$  (7) Å,  $\beta = 103.50$  (4)°,  $Z = 4$  (dinuclear units),  $D_x = 1.81$  g cm<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu = 17.88$  cm<sup>-1</sup>,  $F(000) = 1544$ ,  $T = 293$  K, final  $R = 0.0583$ ,  $wR = 0.0619$  for 1019 reflections [ $I > 2\sigma(I)$ ]. The title compound represents the first doubly  $N1, N2$  triazole-bridged copper(II) compound in which the anion is not involved in coordination. The symmetry-dependent copper(II) ions are in a distorted octahedral environment, with four N-donor atoms of the triazole ligand in the equatorial positions of which the Cu—N(triazole) distances [1.954 (9) and 1.96 (1) Å] are shorter than the Cu—N(amino) distances [2.04 (1) and 2.052 (9) Å]. Two water molecules are coordinated axially at 2.60 (1) and 2.63 (1) Å. The sulfate anions are not coordinated and are fixed in the lattice by an extended hydrogen-bonding network with the amino group of the triazole and the water molecules.

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**Introduction.** One of the strategies in obtaining polynuclear transition-metal(II) coordination compounds is the use of polyfunctional ligands that contain  $N_2$  diazine moieties such as 1,2,4-triazole. The most extensively studied are the dinuclear metal(II) compounds where the metal ions are linked by an  $N1, N2$  triazole bridge (Prins, Birker, Haasnoot, Verschoor & Reedijk, 1985; Koomen–van Oudenniel, de Graaff, Haasnoot, Prins & Reedijk, 1989; Keij, de Graaff, Haasnoot & Reedijk, 1984). For this group of compounds the structures have been studied in relation to their magnetic properties and magneto–structural correlations have been made. Recently, a class of compounds of the general formula  $[\text{Cu}(\text{aamt})A(\text{H}_2\text{O})_2A_2(\text{H}_2\text{O})_x(\text{CH}_3\text{OH})_y]$  [aamt = 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole ( $\text{C}_4\text{H}_{10}\text{N}_6$ );  $A = \text{Br}^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ] has been reported (Koomen–van Oudenniel, de Graaff, Haasnoot, Prins & Reedijk, 1989). Here the equatorial positions of copper(II) are occupied by four ligand N-donor atoms. The axial positions are occupied by a bromine anion and a water molecule. In analogy