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Structure of Two Tetrakis(3,4-ethylenedithio-2,2′,5,5′-tetrathiafulvalene) Tetracyanometallate Dihydrate Salts: β-[EDTTTF]$_4$[M(CN)$_4$].2H$_2$O, M = Pt$^{\rm II}$, Pd$^{\rm II}$

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Abstract. (I) Tetrakis{5,6-dihydro-2-(1,3-dithiol-2-ylidene)[1,3]dithiolo[4,5-*b*][1,4]dithiin}ium tetracyanoplatinate(II) dihydrate, $[C_8H_6S_6]_4[Pt(CN)_4].2H_2O$, $M_r = 1513.3$, monoclinic, $C2/m$, $a = 27.217\,(12)$, $b = 11.708\,(2)$, $c = 8.416\,(6)$ Å, $\beta = 104.82\,(2)°$, $V = 2592.5$ Å^3, $Z = 2$, $D_x = 1.938$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 37.04$ cm^{-1}, $F(000) = 1500$, $T = 293$ K, $R = 0.056$, $wR = 0.076$ for 2068 reflections with $I \geq 3\sigma(I)$. (II) Tetrakis{5,6-dihydro-2-(1,3-dithiol-2-ylidene)[1,3]dithiolo[4,5-*b*][1,4]dithiin}ium tetracyanopalladate(II) dihydrate, $[C_8H_6S_6]_4[Pd(CN)_4].2H_2O$, $M_r = 1424.59$, monoclinic, $C2/m$, $a = 26.790\,(16)$, $b = 11.736\,(4)$, $c = 8.467\,(4)$ Å, $\beta = 104.19\,(5)°$, $V = 2580.7$ Å^3, $Z = 2$, $D_x = 1.833$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 13.29$ cm^{-1}, $F(000) = 1436$, $T = 293$ K, $R = 0.046$, $wR = 0.076$ for 2027 reflections with $I \geq 3\sigma(I)$. The structure of (I) consists of dimerized organic layers, as known in the β-like stacking mode, separated by anionic sheets containing water molecules which act as bridges. The C—N···O1*W* contacts in (I) [2.82 (1) Å] are shorter than the corresponding van der Waals separation (2.9 Å). The mixed Pt(CN)$_4$ and H$_2$O layers could be considered as a one-dimensional polymer. Some intra- and interstack S···S contacts (3.496–3.645 Å) are observed. Compound (II) is isostructural with (I). The same two-dimensional character is observed.

Introduction. The salts described in this paper have been prepared in the course of our study of new conducting radical ion salts based on both tetracyanometallate dianions [M(CN)$_4^{2-}$, M = Pt$^{\rm II}$, Ni$^{\rm II}$ and Pd$^{\rm II}$] and organic donors (D) derived from TTF (tetrathiafulvalene) (Ouahab, Padiou, Grandjean, Garrigou-Lagrange, Delhaes & Bencharif 1989). In particular, the salts of general formula $[D]_4[M(CN)_4].x$H$_2$O, $x = 0 \rightarrow 2$, where D = symmetrical donor like BEDTTTF [or ET = bis(ethylenedithiotetrathiafulvalene)] or unsymmetrical donors such as MDTTTF (methylenedithiotetrathiafulvalene) and EDTTTF (ethylenedithiotetrathiafulvalene) (Mousdis, Ducasse, Fettouhi, Ouahab, Dupart, Garrigou-Lagrange, Amiell, Canet & Delhaes, 1992) have been of great interest after the recent observation of a superconducting transition at 2.5 K under pressure in [ET]$_4$[Pt(CN)$_4$].H$_2$O (Mori, Hirabayashi, Tanaka, Mori, Maruyama & Inokuchi, 1991) and the first κ-mode of packing in [MDTTTF]$_4$[Pt(CN)$_4$].2H$_2$O (Fettouhi, Ouahab, Grandjean, Mousdis & Delhaes, 1992).

Experimental. The preparation of the title compounds has been reported elsewhere (Mousdis *et al.*, 1992).

For compound (I), a crystal of approximate dimensions 0.4 × 0.1 × 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 Mo $K\alpha$ radiation. Three standard reflections monitored throughout the data collection showed very small changes in intensity (less than 5%). The cell dimensions were obtained and refined by least squares from setting angles of 25 centred reflections ($2\theta \leq 22°$) and 2721 reflections were recorded by a θ–2θ scan in the range $2 \leq 2\theta \leq 50°$ and $0 \leq h \leq 33$, $0 \leq k \leq 14$, $-10 \leq l \leq 10$. The intensities were corrected for Lorentz–polarization and absorption phenomena. The latter correction was performed using the *DIFABS* (Walker & Stuart, 1983) procedure (correction factors 0.358–1.471). The centrosymmetric space group $C2/m$ was suggested by the intensity statistics and confirmed by the successful structure solution performed by direct methods (*MULTAN*11/84; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and successive Fourier difference syntheses. 2068 independent reflections with $I \geq 3\sigma(I)$, after averag-

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

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

	x	y	z	B_{eq}
Compound (I)				
Pt	0	0	0	4.88 (1)
S1	0.10356 (8)	0.6503 (2)	0.2810 (3)	6.00 (5)
S2	0.20515 (7)	0.6248 (2)	0.5057 (2)	4.70 (4)
S3	0.31124 (7)	0.3750 (2)	0.7860 (2)	4.76 (4)
S4	0.36541 (8)	0.3505 (2)	0.3934 (3)	5.22 (4)
S5	0.26457 (7)	0.3752 (2)	0.1653 (2)	4.29 (4)
S6	0.15744 (7)	0.3749 (2)	−0.1102 (2)	4.81 (4)
O1*W*	0.5	0.1604 (9)	0.5	8.4 (3)
N1	−0.0203 (4)	−0.196 (1)	0.221 (1)	9.7 (3)
C1	−0.0133 (4)	−0.1236 (9)	0.143 (1)	6.6 (2)
C2	0.2364 (3)	0.5	0.586 (1)	3.8 (2)
C3	0.2803 (3)	0.5	0.702 (1)	3.9 (2)
C4	0.1512 (3)	0.5581 (7)	0.3835 (8)	4.2 (1)
C5	0.0556 (4)	0.553 (1)	0.199 (2)	13.9 (4)
C6	0.3604 (3)	0.4431 (8)	0.921 (1)	5.2 (2)
C7	0.1883 (4)	0.5	−0.028 (1)	3.9 (2)
C8	0.2332 (4)	0.5	0.087 (1)	3.7 (2)
C9	0.3182 (2)	0.4421 (6)	0.2885 (8)	3.8 (1)
C10	0.4133 (4)	0.4473 (9)	0.482 (2)	12.1 (4)
C11	0.1078 (3)	0.4432 (8)	−0.2452 (9)	5.0 (2)
Compound (II)				
Pd	0	0	0	4.15 (1)
S1	0.10388 (5)	0.6498 (1)	0.2815 (2)	5.78 (3)
S2	0.20580 (4)	0.6248 (1)	0.5056 (1)	4.56 (2)
S3	0.31163 (4)	0.3752 (1)	0.7863 (1)	4.47 (2)
S4	0.36492 (5)	0.35102 (9)	0.3929 (1)	4.82 (2)
S5	0.26407 (4)	0.37526 (9)	0.1637 (1)	3.84 (2)
S6	0.15707 (4)	0.37513 (9)	−0.1129 (1)	4.32 (2)
O1*W*	0.5	0.1622 (5)	0.5	7.5 (1)
N1	−0.0190 (2)	−0.1974 (5)	0.2217 (6)	8.7 (1)
C1	−0.0121 (2)	−0.1244 (5)	0.1458 (6)	5.9 (1)
C2	0.2369 (2)	0.5	0.5834 (6)	3.8 (1)
C3	0.2816 (2)	0.5	0.7049 (6)	3.8 (1)
C4	0.1516 (1)	0.5580 (4)	0.3839 (4)	4.34 (8)
C5	0.0543 (2)	0.5529 (6)	0.202 (1)	14.4 (2)
C6	0.3608 (2)	0.4428 (4)	0.9243 (5)	5.0 (1)
C7	0.1877 (2)	0.5	−0.0317 (6)	3.4 (1)
C8	0.2328 (2)	0.5	0.0866 (6)	3.3 (1)
C9	0.3181 (1)	0.4419 (3)	0.2862 (4)	3.42 (7)
C10	0.4137 (2)	0.4479 (5)	0.481 (1)	13.2 (2)
C11	0.1072 (2)	0.4430 (4)	−0.2499 (5)	4.71 (9)

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

Compound (I)			
Pt—C1	1.98 (1)	S6—C7	1.740 (5)
S1—C4	1.738 (7)	S6—C11	1.724 (8)
S1—C5	1.74 (1)	N1—C1	1.12 (2)
S2—C2	1.737 (5)	C2—C3	1.34 (1)
S2—C4	1.746 (7)	C4—C4	1.36 (1)
S3—C3	1.744 (5)	C5—C5	1.23 (2)
S3—C6	1.717 (7)	C6—C6	1.33 (1)
S4—C9	1.733 (6)	C7—C8	1.35 (1)
S4—C10	1.74 (1)	C9—C9	1.36 (1)
S5—C8	1.735 (5)	C10—C10	1.23 (2)
S5—C9	1.744 (6)	C11—C11	1.33 (1)
C1—Pt—C1	180. (0)	S1—C4—C4	128.4 (5)
C1—Pt—C1	94.2 (4)	S2—C4—C4	116.5 (5)
C4—S1—C5	100.3 (5)	S1—C5—C5	131 (1)
C2—S2—C4	96.1 (3)	S3—C6—C6	117.7 (6)
C3—S3—C6	95.3 (4)	S6—C7—S6	114.7 (5)
C9—S4—C10	101.1 (4)	S6—C7—C8	122.7 (2)
C8—S5—C9	96.0 (3)	S5—C8—S5	114.7 (5)
C7—S6—C11	95.0 (4)	S5—C8—C7	122.7 (2)
Pt—C1—N1	178. (1)	S4—C9—S5	115.1 (4)
S2—C2—S2	114.5 (4)	S4—C9—C9	128.2 (5)
S2—C2—C3	122.7 (2)	S5—C9—C9	116.7 (5)
S3—C3—S3	114.0 (5)	S4—C10—C10	130.5 (9)
S3—C3—C2	123.0 (2)	S6—C11—C11	117.6 (5)
S1—C4—S2	115.0 (5)		
Compound (II)			
Pd—C1	1.989 (6)	S6—C7	1.737 (3)
S1—C4	1.733 (4)	S6—C11	1.733 (4)
S1—C5	1.753 (7)	N1—C1	1.114 (8)
S2—C2	1.734 (3)	C2—C3	1.373 (7)
S2—C4	1.746 (4)	C4—C4	1.362 (7)
S3—C3	1.731 (3)	C5—C5	1.24 (1)
S3—C6	1.726 (4)	C6—C6	1.343 (7)
S4—C9	1.724 (4)	C7—C8	1.367 (6)
S4—C10	1.755 (6)	C9—C9	1.363 (5)
S5—C8	1.733 (3)	C10—C10	1.223 (9)
S5—C9	1.745 (3)	C11—C11	1.339 (7)
C1—Pd—C1	180	S1—C4—C4	128.4 (3)
C1—Pd—C1	94.4 (2)	S2—C4—C4	116.7 (3)
C4—S1—C5	100.7 (3)	S1—C5—C5	130.4 (5)
C2—S2—C4	95.6 (2)	S3—C6—C6	117.4 (3)
C3—S3—C6	94.8 (2)	S6—C7—S6	115.1 (3)
C9—S4—C10	101.1 (2)	S6—C7—C8	122.5 (1)
C8—S5—C9	95.7 (2)	S5—C8—S5	115.3 (3)
C7—S6—C11	95.1 (2)	S5—C8—C7	122.3 (1)
Pd—C1—N1	176.8 (5)	S4—C9—S5	115.1 (2)
S2—C2—S2	115.3 (3)	S4—C9—C9	128.2 (3)
S2—C2—C3	122.3 (1)	S5—C9—C9	116.6 (2)
S3—C3—S3	115.6 (3)	S4—C10—C10	130.4 (5)
S3—C3—C2	122.2 (1)	S6—C11—C11	117.3 (3)
S1—C4—S2	114.9 (3)		

ing the symmetry-related reflections ($R_{\text{int}} = 0.070$), were used for the full-matrix least-squares anisotropic (β_{ij}) refinements (on F). In the refinement the secondary-extinction coefficient $g = 2.5488 \times 10^{-7}$, and final $R = 0.056$, $wR = 0.076$ $\{w = 4F_o^2/[\sigma(I)^2 + (0.07F_o^2)^2]\}$, $S = 1.832$; $(\Delta/\sigma)_{\text{max}} = 0.11$; $(\Delta\rho)_{\text{max}} = 1.10$, $(\Delta\rho)_{\text{min}} = -1.54$ e Å^{-3}. H atoms were placed at computed positions (C—H = 1 Å; $B_{\text{eq}} = 5$ Å^2) and not refined.

For compound (II), a crystal of approximate dimensions 0.7 × 0.3 × 0.2 mm was selected for the intensity-data collection. Three standard reflections monitored throughout the data collection showed very small changes in intensity (less than 2%). The cell dimensions were obtained and refined by least squares from setting angles of 25 centred reflections ($2\theta \le 25°$). 4840 reflections were recorded by a θ–2θ scan in the range $2 \le 2\theta \le 50°$ and $0 \le h \le 10$, $0 \le k \le 13$, $-31 \le l \le 31$. The intensities were corrected for Lorentz–polarization and absorption phenomena. The latter correction was performed using the *DIFABS* (Walker & Stuart, 1983) procedure (correction factors 0.502–1.267). The centrosymmetric space group $P2_1/n$ was first adopted from observed symmetry and systematic absences and confirmed by the successful structure solution found by direct methods (Main *et al.*, 1984) and successive Fourier difference syntheses. 2729 independent reflections with $I \ge 6\sigma(I)$, after averaging the symmetry-related reflections ($R_{\text{int}} = 0.029$), were used for the full-matrix least-squares anisotropic (β_{ij}) refinements (on F), for which $g = 1.6935 \times 10^{-8}$, $R = 0.058$, $wR = 0.123$ $\{w = 4F_o^2/[\sigma(I)^2 + (0.07F_o^2)^2]\}$, $S = 3.245$, $(\Delta/\sigma)_{\text{max}} = 0.68$, $(\Delta\rho)_{\text{max}} = 0.78$, $(\Delta\rho)_{\text{min}} = -0.65$ e Å^{-3}. In a second step, owing to some correlations, the $C2/m$ space group was adopted, although a great number of observed reflections with $(h + k)$ odd suggested no centring, among them the following: ±140, ±180, ±380, $\bar{6}7\bar{1}$, $\bar{8}7\bar{1}$, $\bar{3}8\bar{3}$, $\bar{1}8\bar{3}$, $11,4,\bar{1}$, $\bar{6}3\bar{1}$, $52\bar{2}$ and $89\bar{2}$. The transformation matrix from $P2_1/n$ to $C2/m$ is (1 0 1; 0 1 0; −1 0 0). 2208 independent reflections with $I \ge 3\sigma(I)$, after averaging the symmetry related reflections ($R_{int} = 0.029$), were used for the full-matrix least-squares anisotropic (β_{ij}) refinements (on F), for which $g = 1.401 \times 10^{-7}$, $R = 0.046$, $wR = 0.076$, $w = 4F_o^2/[\sigma(I)^2 + (0.07F_o^2)^2]$, $S = 1.967$, $(\Delta/\sigma)_{max} = 0.33$, $(\Delta\rho)_{max} = 0.70$, $(\Delta\rho)_{min} = -0.65$ e Å^{-3}. H atoms were placed at computed positions (C—H = 1 Å; $B_{eq} = 5$ Å^2) and not refined. The refinement results are discussed below.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a 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.* The atomic numbering scheme is given in Fig. 1.

Discussion. For compound (I), Fig. 2 shows a stereoscopic view of the crystal structure which is built of alternating layers of organic molecules and anionic layers containing the water molecules.

There are two independent EDTTTF molecules, denoted *A* and *B*, having *m* symmetry as they are located at the 4(*i*) position of the *C*2/*m* space group (see Table 1 and Fig. 1). The six-membered heterocyclic ring appears to have a slight boat conformation. The geometrical parameters of each molecule are in the range of those observed in [EDTTTF]$_2$[AuI$_2$] in which the molecules have a formal valence state averaged to +0.5 (Hountas, Terzis, Papavassiliou, Hilti, Burkle, Meyer & Zambounis, 1990). The EDTTTF molecules stack with their centrosymmetrically related ones along the **c** direction. The adjacent stacks present strong interactions through short S···S contacts and present a β-type packing (see Fig. 3).

The Pt(CN)$_4^{2-}$ units are located at the origin of the lattice. The Pt—C bond distances and bond angles

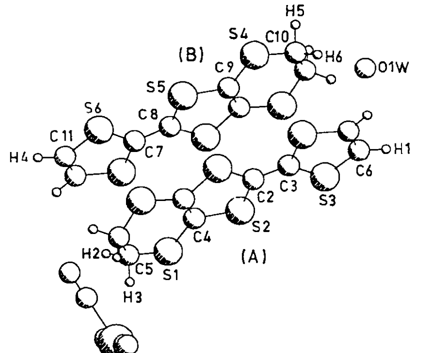

Fig. 1. Atomic numbering scheme for (EDTTTF)$_4M$(CN)$_4$(H$_2$O)$_2$, M = Pt, Pd.

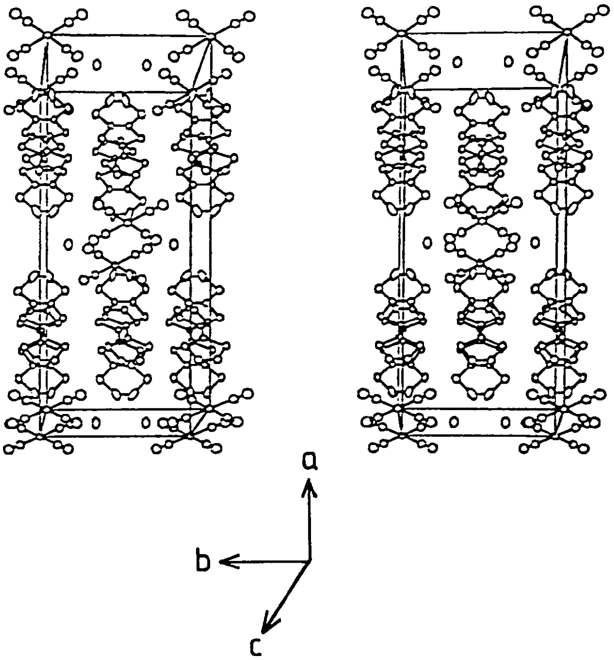

Fig. 2. Stereoscopic view of the crystal structure showing alternating layers of EDTTTF molecules and M(CN)$_4^{2-}$ units.

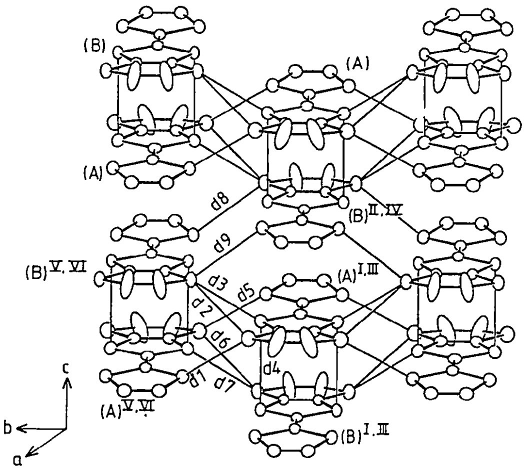

Fig. 3. Packing mode of the EDTTTF molecules with intra- and interstack S···S contacts lower than 3.65 Å. Contact distances (Å) [value for (I) followed by that for (II) in square brackets]: $d1 = d5 = 3.645$ (3) [3.617 (2)]; $d2 = d6 = 3.540$ (3) [3.570 (2)]; $d3 = d7 = 3.496$ (3) [3.489 (2)]; $d4 = 3.632$ (3) [3.611 (2)]; $d8 = d9 = 3.503$ (3) [3.511 (2)]. Symmetry code: (I) x, y, z; (II) $x, y, 1+z$; (III) $x, 1-y, z$; (IV) $x, 1-y, 1+z$; (V) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (VI) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and results of the refinement in the $P2_1/n$ space group, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55339 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0279]

compare well with those found, for instance, in the $[BEDTTTF]_4[Pt(CN)_4]$ (BEDTTTF = bisethylenedithiotetrathiafulvalene) salt (Fettouhi, Ouahab, Grandjean & Toupet, 1992). The water molecules act as bridges between the $Pt(CN)_4^{2-}$ units in the anionic layers (Fig. 4). Strong interactions between the C—N groups of the anion and the O atom of the water molecule are observed [C1—N1···OW1 = 2.82 (1) Å]. This contact is similar to that observed in κ-$[MDTTTF]_4[Pt(CN)_4].2H_2O$ (Fettouhi, Ouahab, Grandjean, Mousdis & Delhaes, 1992) and is shorter than the value [3.415 (7) Å] observed in the superconducting salt $[BEDTTTF]_4[Pt(CN)_4].H_2O$ (Mori *et al.*, 1991). The anionic layers could be considered as one-dimensional polymers through hydrogen bonds (see Fig. 4).

For compound (II), taking into account the strongly observed reflections with $(h+k)$ odd which are inconsistent with the $C2/m$ group, the comparison of the structural results relating to the space groups $P2_1/n$ and $C2/m$ allows one to think that the $C2/m$ symmetry is broken by the terminal ethylenic C atoms, which are disordered. Indeed, when the m symmetry is imposed for the EDTTTF molecules in the $C2/m$ space group, a slight boat conformation for the six-membered heterocyclic ring is observed and high temperature factors are obtained for C5 and C10. But when placed at general positions of the $P2_1/n$ space group, more reasonable temperature factors are obtained and a slight chair conformation is observed as is known for this kind of salt (Hountas *et al.*, 1990). Owing to the improved values of the R and wR factors, the results of the refinements performed in the $C2/m$ space group are given here. Those concerning the $P2_1/n$ space group may be obtained as supplementary material.*

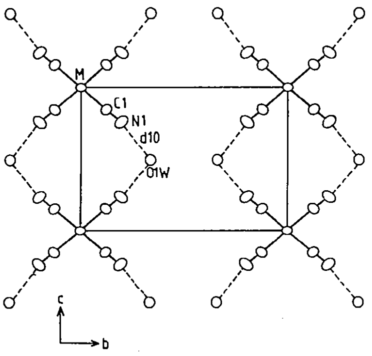

Fig. 4. Arrangement of anions and water molecules in the anionic layer parallel to the (100) face for $[EDTTTF]_4[M(CN)_4].2H_2O$ with the N···OW1 contacts (Å): $d10 = 2.822\,(3)$ for (I) and 2.817 (7) for (II).

The crystal structure of (II) is the same as in (I). It is built of dimerized organic layers parallel to the (100) face based on two independent molecules (A and B) presenting a β-type packing (Fig. 2). The S···S contacts are in the range 3.48–3.61 Å. The anionic sheets contain water molecules which act as bridges between the anionic units through short N···O1W contacts of the order of 2.817 Å (see Fig. 4).

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* See deposition footnote.

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