

O(61) from this plane is 0.298 (2) Å, that of O(62) is 0.258 (2) Å. The distances between O(61) in *A* and O(62) in *A'* are 3.285 (9) and 3.394 (8) Å. Each nitro O atom dips into the neighbouring layer in order to get closer to the positively charged N atom N(7).

In 6-nitrosaccharin all Na cations and water molecules form a layer with the plane (0.5 *y*, *z*) in the middle and with a thickness of about 5 Å (Fig. 2*b*). The Na cations are situated near an axis (0.5, *y*, 0.5) at a distance of 0.1466 (8) Å.

#### Concluding remarks

The results do not confirm the predicted correlation between the C(3)—O(3) bond length and taste quality. If there is such a correlation the corresponding variation of the bond length should be smaller than 1%. Each of the compounds including 4-hydroxy-saccharin has a different anion surrounding (except for the almost isostructural 5-chloro- and 5-nitrosaccharin), so that no characteristic interaction pattern for sweet- or bitter-tasting species can be recognized. No correlation between hydrogen bonds and Na coordination on one hand and taste quality on the other can be seen.

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## Structure at 293 and 135 K of $\beta$ -Tetrakis[bis(ethylenedithio)tetrathiafulvalene] Tetracyanoplatinate(II): $\beta$ -[BEDT-TTF]<sub>4</sub>[Pt(CN)<sub>4</sub>]

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#### Abstract

[C<sub>10</sub>H<sub>8</sub>S<sub>8</sub>]<sub>4</sub>[Pt(CN)<sub>4</sub>], *M<sub>r</sub>* = 1837.9. At 293 K: triclinic, *P* $\bar{1}$ , *a* = 9.721 (7), *b* = 11.127 (6), *c* = 16.552 (8) Å,  $\alpha$  = 76.90 (5),  $\beta$  = 81.52 (5),  $\gamma$  = 62.88 (5)°, *V* = 1550 Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.969 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71073 Å,  $\mu$  = 33.64 cm<sup>-1</sup>, *F*(000) = 914, *R* = 0.043

based on 4192 observed reflections with *I* ≥ 6σ(*I*). At 135 K: triclinic, *P* $\bar{1}$ , *a* = 9.693 (4), *b* = 10.890 (4), *c* = 16.521 (5) Å,  $\alpha$  = 77.12 (3),  $\beta$  = 81.84 (4),  $\gamma$  = 62.70 (3)°, *V* = 1509 Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 2.022 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71073 Å,  $\mu$  = 34.55 cm<sup>-1</sup>, *F*(000) = 914, *R* = 0.062 based on 4107 observed reflections with *I* ≥ 6σ(*I*). One carbon (C7 and C16) of the terminal ethylenic groups of each independent

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BEDT-TTF molecule shows disorder and/or high thermal motion at room temperature. This phenomenon disappears at 135 K. In addition the low-temperature X-ray structure shows that the BEDT-TTF molecules adopt a staggered conformation and develop tetrameric stacks along the [110] direction. This structure belongs to the  $\beta$  type of the BEDT-TTF series.

### Introduction

We recently reported the structures and properties of some new organic conducting salts prepared from TTF (TTF = tetrathiafulvalene) derivatives and planar tetracyanometallate dianions (Ouahab, Padiou, Grandjean, Garrigou-Lagrange, Delhaes & Bencharif, 1989; Ouahab, Triki, Grandjean, Bencharif, Garrigou-Lagrange & Delhaes, 1991; Garrigou-Lagrange, Ouahab, Grandjean & Delhaes, 1990). The two  $\beta$ -[BEDT-TTF]<sub>4</sub>[M(CN)<sub>4</sub>] [BEDT-TTF or ET = bis(ethylenedithio)tetrathiafulvalene and M = Pt, Ni] salts exhibit metallic behaviour down to 250 K where a broad metal-insulator transition occurs. This phase transition was evidenced by conduction measurements, and optical and ESR characterizations. In order to understand the nature of the transition we have determined the X-ray crystal structures of the platinate salt at room temperature and 135 K. Recently, a Pt(CN)<sub>4</sub><sup>2-</sup> salt having a different unit cell has been reported (Shibaeva, Lobkovskaya, Korotkov, Kushch, Yagubskii & Makova, 1988; Lobkovskaya, Kushch, Shibaeva, Yagubskii & Mokova, 1989). Physical characterization of the corresponding Ni(CN)<sub>4</sub><sup>2-</sup> salt has also been reported (Tanaka, Takeuchi, Sano, Enoki, Suzuki & Imaeda, 1989). The room-temperature structure of  $\beta$ -[BEDT-TTF]<sub>4</sub>[Pt(CN)<sub>4</sub>] was recently reported to have a modified unit cell (Gärtner, Heinen, Keller, Niebl, Nuber & Schweitzer, 1990). Although the authors assume their compound is different from that reported by Shibaeva *et al.* (1988) we believe the two compounds are in fact the same.\* We report here a more accurate room-temperature crystal structure, and the structure determined at 135 K. We also discuss the temperature dependence of the unit-cell parameters of the title compound.

\* The room-temperature crystal data reported for this compound are: (1)  $a = 11.002$  (9),  $b = 17.906$  (9),  $c = 16.625$  (7) Å,  $\alpha = 77.28$  (4),  $\beta = 84.17$  (5),  $\gamma = 81.26$  (6)°,  $V = 3149.9$  Å<sup>3</sup>, triclinic,  $P\bar{1}$ ,  $R = 0.073$  (Shibaeva *et al.*, 1988; Lobkovskaya *et al.*, 1989). (2)  $a = 9.721$  (7),  $b = 11.127$  (6),  $c = 16.552$  (8) Å,  $\alpha = 76.90$  (5),  $\beta = 81.52$  (5),  $\gamma = 62.88$  (5)°,  $V = 1550.1$  Å<sup>3</sup>, triclinic,  $P\bar{1}$ ,  $R = 0.032$  (Ouahab *et al.*, 1989). (3)  $a = 9.7280$  (30),  $b = 10.9237$  (27),  $c = 16.5432$  (60) Å,  $\alpha = 95.820$  (25),  $\beta = 98.296$  (26),  $\gamma = 115.215$  (24)°,  $V = 1547.56$  Å<sup>3</sup>, triclinic,  $P\bar{1}$ ,  $R = 0.082$  (Gärtner *et al.*, 1990). The transformation matrices are: (1) to (2) (-0.5, 0.5, 0 / 0.5, 0.5, 0 / 0, 0, 1); (1) to (3) (0.5, -0.5, 0 / -1.0, 0 / 0, 0, 1); (2) to (3) (-1, 0, 0 / 1, -1, 0 / 0, 0, 1).

### Experimental

The title compound was deposited on a platinum-wire electrode by anodic oxidation of the organic donor ( $5 \times 10^{-3} M$ ) under low constant current ( $I = 1 \mu A$ ) in the presence of the tetrabutylammonium salt of the dianion ( $10^{-2} M$ ), which acted as supporting electrolyte. The crystal growth solvent used was a mixture of DMF and CH<sub>2</sub>Cl<sub>2</sub> (ratio 4:1). The stoichiometries were determined by X-ray crystal structure analysis.

The X-ray crystal structures were solved at room temperature and 135 K using the same sample. A black crystal of approximate dimensions  $0.175 \times 0.175 \times 0.275$  mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation. The unit-cell parameters were determined and refined from the setting angles of 25 accurately centered reflections. Data were collected with  $\theta$ - $2\theta$  scans. The intensities were corrected for Lorentz and polarization effects. The room-temperature structure was solved by direct methods and successive Fourier difference synthesis. An empirical absorption correction was applied using the *DIFABS* procedure (Walker & Stuart, 1983), the correction factors ranged from 0.91 to 1.05 and 0.70 to 1.49 at 135 and 293 K respectively. The refinements (on  $F$ ) were performed by the full-matrix least-squares method [H atoms, both found by Fourier synthesis and placed at computed positions (C-H: 1.0 Å,  $B = 4$  Å<sup>2</sup>), were not refined]. The structure at 135 K was refined starting from the atomic coordinates of the room-temperature structure. Crystal characteristics and refinement data are summarized in Table 1. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP11/60 and a MicroVAX 3100 using the *SDP* programs (B. A. Frenz & Associates Inc., 1985). Atomic coordinates are given in Table 2. Comparative bond distances and the atomic numbering scheme are shown in Fig. 1.\*

The sample was cooled by a nitrogen stream. The temperatures were deduced by measuring the temperature of the nitrogen stream near the sample with a thermocouple. After stabilization of the temperature, the unit-cell parameters were refined by least squares following a *SETANG* procedure (Enraf-Nonius, 1985). Each point was measured during the decrease and increase of temperature. We observed complete reversibility in the measurements.

\* Lists of bond distances and bond angles, structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54865 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0242]

Table 1. Crystal, data-collection and refinement information

	293 K	135 K
Crystal dimensions (mm)	0.175 × 0.175 × 0.275	
2θ range (°)	2 to 52	2 to 40
Range of h	-12 to 12	0 to 9
k	-13 to 13	-10 to 10
l	0 to 20	-15 to 15
Standard reflections	325	037
	215	133
	037	443
Average deviation (%)	-1.5	-3
μ(Mo Kα) (cm <sup>-1</sup> )	33.64	34.55
No. of unique reflections	5048	4652
R <sub>int</sub>	0.019	0.079
Reflections with I > 6σ(I)	4199	4107
No. of variables	368	368
Weighting scheme	w = 4F <sub>o</sub> <sup>2</sup> /[σ <sup>2</sup> (I) + (0.07F <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ]	
R, wR	0.043, 0.055	0.062, 0.092
S	1.34	2.37
Δ/σ	3.14	0.24
Δρ (e Å <sup>-3</sup> )	2.242	3.352

Table 2. Atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>)

The low-temperature atomic coordinates are given below the 293 K coordinates.  $B_{eq} = (4/3)\sum\beta_{ij}a_i \cdot a_j$ .

	x	y	z	B (Å <sup>2</sup> )
Pt	0	0	0	2.419 (7)
	0	0	0	0.98 (1)
C1	0.2146 (8)	-0.0385 (6)	0.0177 (4)	2.9 (2)
	0.217 (1)	-0.0392 (9)	0.0174 (6)	1.4 (2)
C2	0.0737 (8)	-0.1996 (7)	0.0049 (4)	3.3 (2)
	0.080 (1)	-0.209 (1)	0.0069 (6)	1.3 (2)
N1	0.3397 (7)	-0.0645 (7)	0.0297 (5)	4.8 (2)
	0.339 (1)	-0.060 (1)	0.0263 (6)	2.2 (2)
N2	0.1186 (7)	-0.3154 (6)	0.0078 (4)	4.1 (2)
	0.123 (1)	-0.3233 (9)	0.0120 (6)	1.8 (2)
S1	0.1855 (2)	0.4069 (2)	0.5678 (1)	3.54 (4)
	0.1846 (3)	0.4040 (3)	0.5708 (2)	1.48 (5)
S2	0.5195 (2)	0.2672 (2)	0.5870 (1)	3.53 (4)
	0.5208 (3)	0.2638 (3)	0.5900 (2)	1.56 (5)
S3	0.5800 (2)	0.3679 (2)	0.3955 (1)	3.39 (4)
	0.5816 (3)	0.3689 (3)	0.3994 (2)	1.40 (5)
S4	0.2479 (2)	0.5039 (2)	0.3699 (1)	3.39 (4)
	0.2471 (3)	0.5019 (3)	0.3717 (2)	1.37 (5)
S5	0.6746 (2)	0.4349 (2)	0.2219 (1)	3.69 (5)
	0.6764 (3)	0.4430 (3)	0.2254 (2)	1.28 (5)
S6	0.2764 (2)	0.5884 (2)	0.1890 (1)	3.46 (4)
	0.2779 (3)	0.5862 (3)	0.1905 (2)	1.40 (5)
S7	0.5031 (2)	0.1686 (2)	0.7671 (1)	3.40 (4)
	0.5051 (3)	0.1712 (3)	0.7713 (2)	1.38 (5)
S8	0.1017 (2)	0.3363 (2)	0.7432 (1)	3.72 (5)
	0.1010 (3)	0.3402 (3)	0.7481 (2)	1.54 (5)
S9	0.3557 (2)	0.1423 (2)	0.3394 (1)	3.62 (5)
	0.3592 (3)	0.1364 (3)	0.3367 (2)	1.51 (6)
S10	0.0223 (2)	0.3014 (2)	0.3207 (1)	3.36 (4)
	0.0231 (3)	0.3004 (3)	0.3186 (2)	1.47 (5)
S11	-0.0441 (2)	0.1968 (2)	0.5109 (1)	3.95 (5)
	-0.0438 (3)	0.1950 (3)	0.5094 (2)	1.64 (6)
S12	0.2884 (2)	0.0444 (2)	0.5367 (1)	3.90 (5)
	0.2916 (3)	0.0401 (3)	0.5358 (2)	1.66 (6)
S13	-0.1393 (2)	0.1031 (3)	0.6802 (1)	5.55 (6)
	-0.1397 (3)	0.0990 (3)	0.6797 (2)	2.12 (6)
S14	0.2564 (2)	-0.0731 (2)	0.7109 (1)	4.06 (5)
	0.2593 (3)	-0.0785 (3)	0.7109 (2)	1.54 (6)
S15	0.4393 (2)	0.1884 (2)	0.1597 (1)	3.61 (4)
	0.4427 (3)	0.1782 (3)	0.1564 (2)	1.55 (6)
S16	0.0398 (2)	0.3744 (3)	0.1394 (1)	4.73 (6)
	0.0388 (3)	0.3719 (3)	0.1361 (2)	2.03 (6)
C3	0.3692 (7)	0.3674 (7)	0.5216 (4)	2.9 (2)
	0.368 (1)	0.368 (1)	0.5248 (6)	1.4 (2)
C4	0.2493 (7)	0.3240 (7)	0.6675 (4)	3.0 (2)
	0.248 (1)	0.326 (1)	0.6712 (6)	1.4 (2)
C5	0.4038 (7)	0.2600 (6)	0.6768 (4)	2.4 (1)
	0.401 (1)	0.2649 (9)	0.6803 (6)	1.0 (2)

Table 2 (cont.)

	x	y	z	B (Å <sup>2</sup> )
C6	0.350 (1)	0.184 (1)	0.8437 (5)	7.5 (3)
	0.350 (1)	0.205 (1)	0.8517 (6)	1.3 (2)
C7	0.208 (1)	0.226 (2)	0.8296 (6)	13.8 (5)
	0.212 (1)	0.196 (1)	0.8286 (7)	1.6 (2)
C8	0.3937 (7)	0.4101 (7)	0.4391 (4)	2.8 (2)
	0.393 (1)	0.412 (1)	0.4424 (6)	1.4 (2)
C9	0.5223 (7)	0.4476 (7)	0.2946 (4)	2.9 (2)
	0.521 (1)	0.455 (1)	0.2980 (6)	1.3 (2)
C10	0.3708 (7)	0.5082 (6)	0.2824 (4)	2.7 (1)
	0.375 (1)	0.5074 (9)	0.2850 (6)	1.2 (2)
C11	0.5815 (8)	0.4675 (8)	0.1283 (5)	4.0 (2)
	0.586 (1)	0.460 (1)	0.1315 (7)	1.4 (2)
C12	0.4329 (8)	0.5949 (8)	0.1179 (5)	4.1 (2)
	0.433 (1)	0.591 (1)	0.1180 (6)	1.3 (2)
C13	0.1710 (7)	0.1925 (7)	0.3861 (4)	2.9 (2)
	0.172 (1)	0.188 (1)	0.3842 (6)	1.2 (2)
C14	0.2937 (7)	0.2192 (7)	0.2384 (4)	3.0 (2)
	0.295 (1)	0.212 (1)	0.2350 (6)	1.5 (2)
C15	0.1411 (7)	0.2913 (7)	0.2300 (4)	2.8 (2)
	0.140 (1)	0.287 (1)	0.2273 (6)	1.2 (2)
C16	0.333 (1)	0.275 (2)	0.0713 (6)	12.8 (6)
	0.337 (1)	0.304 (1)	0.0682 (7)	1.8 (2)
C17	0.189 (1)	0.322 (1)	0.0609 (5)	7.1 (3)
	0.190 (1)	0.298 (1)	0.0574 (6)	1.8 (2)
C18	0.1439 (7)	0.1490 (7)	0.4678 (4)	3.0 (2)
	0.145 (1)	0.145 (1)	0.4656 (6)	1.3 (2)
C19	0.0122 (7)	0.0979 (7)	0.6083 (4)	3.1 (2)
	0.011 (1)	0.095 (1)	0.6081 (6)	1.5 (2)
C20	0.1637 (7)	0.0282 (7)	0.6206 (4)	2.9 (2)
	0.163 (1)	0.025 (1)	0.6196 (6)	1.2 (2)
C21	-0.047 (1)	0.044 (1)	0.7738 (5)	6.6 (3)
	-0.042 (1)	0.053 (1)	0.7752 (7)	1.7 (2)
C22	0.099 (1)	-0.071 (1)	0.7834 (5)	6.7 (3)
	0.101 (1)	-0.082 (1)	0.7838 (7)	1.7 (2)

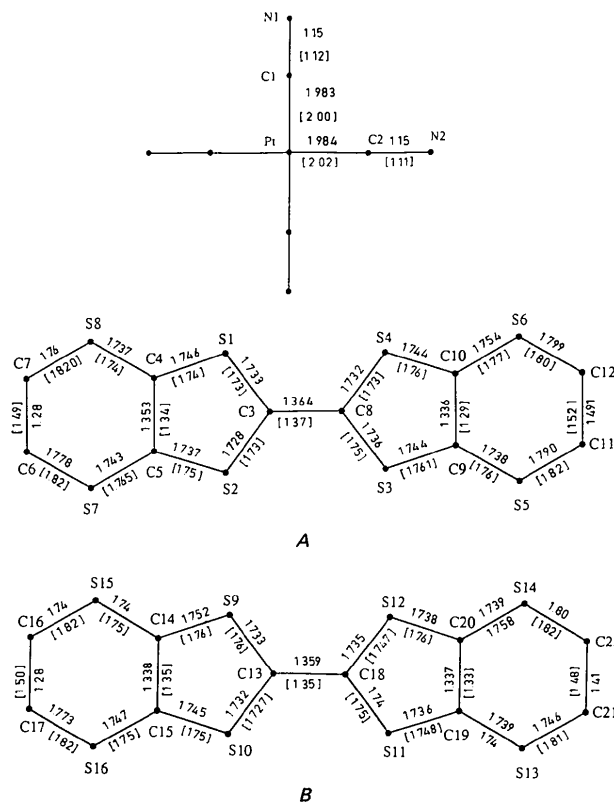
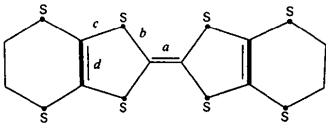


Fig. 1. Comparative bond distances (Å) at 293 [135] K and atomic numbering.

Table 3. Comparison of the averaged intramolecular distances (Å) for various observed charges on the BEDT-TTF molecules



	ET <sub>4</sub> Pt(CN) <sub>4</sub>				ET <sup>0</sup>	ET <sup>1/2+</sup>	ET <sup>+</sup>	ET <sup>2+</sup>
	293 K		135 K					
	A	B	A	B				
a	1.364 (7)	1.349 (7)	1.36 (1)	1.35 (1)	1.319 (10)	1.360 (10)	1.388 (14)	1.436 (7)
b	1.732 (5)	1.737 (5)	1.73 (1)	1.744 (9)	1.757 (10)	1.732 (9)	1.720 (11)	1.669 (6)
c	1.744 (5)	1.744 (5)	1.74 (1)	1.750 (9)	1.753 (10)	1.744 (9)	1.737 (10)	1.710 (6)
d	1.344 (7)	1.335 (7)	1.31 (1)	1.34 (1)	1.331 (10)	1.340 (10)	1.345 (15)	1.369 (7)
Ref.	This work				(1)	(2)	(3)	(4)

References: (1) Kobayashi *et al.* (1986); (2) Mallah *et al.* (1990); (3) Triki *et al.* (1991); (4) Shibaeva *et al.* (1988).

### Discussion

The crystal structure shown in Fig. 2 consists of Pt(CN)<sub>4</sub><sup>2-</sup> anions located at the origin of the lattice, and two ET molecules (denoted A and B) which together with the centrosymmetrically related molecules, form tetrameric stacks along the [110] direction in an AABBA... sequence.

The Pt—C bond distances and bond angles compare well with those found, for instance, in the K<sub>2</sub>Pt(CN)<sub>4</sub>·3H<sub>2</sub>O salt (Waschecheck, Peterson, Reiss & Williams, 1976). A small increase in the Pt—C bond lengths is observed with decreasing temperature.

The charge on each ET molecule has been assumed to be +0.5, based on a comparison (Table 3) of its geometrical parameters with those found for a variety of oxidation states for that molecule *i.e.* ET<sup>0</sup> (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986), ET<sup>0.5+</sup> (Mallah, Hollis, Bott, Kurmoo, Day, Allan & Friend, 1990) and ET<sup>+</sup> (Triki, Ouahab, Grandjean & Fabre, 1991). In support of this, the 4:1 stoichiometry of this salt suggests that the ET molecules bear a mean charge of +0.5.

Table 4. Comparative intermolecular interactions (Å) in  $\beta$ -(BEDT-TTF)<sub>4</sub>Pt(CN)<sub>4</sub> at 293 and 135 K

E.s.d.'s on the last digit at 293 [135] K are 0.003 [0.004] for S...S, 0.009 [0.011] for Pt...C and 0.010 [0.012] for other distances.

Interstack interaction	293 K		135 K		Anion-cation contacts	
	293 K	135 K	293 K	135 K	293 K	135 K
S1—S10 <sup>v</sup>	3.695	3.659	Pt—C21 <sup>v,vi</sup>	3.733	3.681	
S2—S13 <sup>iii</sup>	3.380	3.321	Pt—C22 <sup>v,vi</sup>	3.738	3.761	
S3—S14 <sup>iiii</sup>	3.665	3.605	Pt—H15 <sup>v,vi</sup>	3.144	2.727	
S4—S8 <sup>i</sup>	3.615	3.650	N1—C16 <sup>viii</sup>	3.436	3.486	
S5—S10 <sup>ii</sup>	3.502	3.419	N1—S7 <sup>vii</sup>	3.622	3.587	
S5—S16 <sup>ii</sup>	3.425	3.414	N1—C17	> 4.	3.622	
S5—S14 <sup>iiii</sup>	3.690	3.648	N2—S6 <sup>i</sup>	3.302	3.246	
S6—S8 <sup>i</sup>	3.446	3.429	N2—S16 <sup>v</sup>	3.389	3.338	
S7—S13 <sup>iii</sup>	3.374	3.366	N2—C17 <sup>v</sup>	3.382	3.264	
S7—S15 <sup>iii</sup>	3.681	3.541	N2—C16	> 4.	3.572	
S8—S10 <sup>i</sup>	3.583	3.481				
S8—S16 <sup>i</sup>	3.748	3.655				
S9—S14 <sup>iiii</sup>	3.497	3.456				
S9—S12 <sup>iiii</sup>	3.755	3.720				
S14—S15 <sup>iiii</sup>	3.485	3.490				
Intrastack interaction						
S1—S12 <sup>ii</sup>	3.828	3.768				
S2—S6 <sup>i</sup>	3.791	3.693				
S4—S9 <sup>ii</sup>	3.803	3.774				
S5—S7 <sup>i</sup>	3.976	3.747				

Symmetry code: (i)  $-x, 1-y, 1-z$ ; (ii)  $1+x, y, z$ ; (iii)  $1-x, -y, 1-z$ ; (iv)  $-x, -y, -z$ ; (v)  $x, -1+y, z$ ; (vi)  $x, y, -1+z$ ; (vii)  $-x, -y, 1-z$ ; (viii)  $1-x, -y, -z$ ; (ix)  $x, y, z$ ; (x)  $1-x, 1-y, 1-z$ .

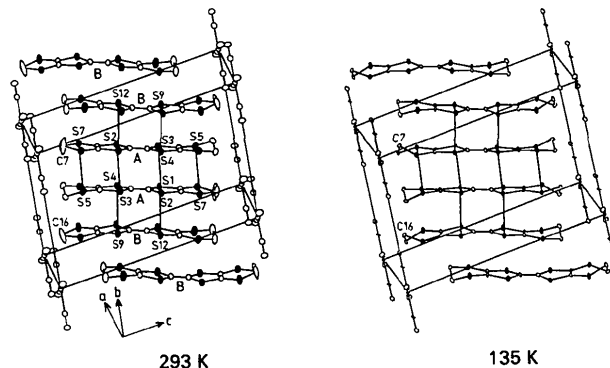


Fig. 2. Unit-cell contents, intermolecular S...S interactions at both temperatures and comparison of the conformations of the terminal ethylenic groups.

Variations in the unit-cell parameters at different temperatures down to 100 K are plotted in Fig. 3. There is no hysteresis effect during variation of the temperature (increasing or decreasing). Two small modifications may be observed: the first around 230–260 K, the second around 150–160 K. These two modifications may be explained by the 'condensation' of the motions of the two disordered ethylenic group carbon atoms. This indicates the absence of a fundamental crystal structure transition. However, we observe a point of inflection in the variation of the volume at 250 K which corresponds to the temperature of the phase transition deduced from other physical characterizations (Shibaeva *et al.*, 1988; Garrigou-Lagrange *et al.*, 1990; Garrigou-Lagrange, Amiel, Dupart, Delhaes, Ouahab, Fet-

touhi, Triki & Grandjean, 1991; Gärtner *et al.*, 1990).

A stereoscopic view of the packing of the ET molecules is given in Fig. 4. This arrangement belongs to the  $\beta$ -type (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1985). As commonly observed in these quasi-two-dimensional types of compound, the most significant intermolecular S $\cdots$ S contacts are established between adjacent stacks. The intrastack S $\cdots$ S interactions are greater than 3.8 Å (see Fig. 4 and Table 4).

The difference between the structures at 293 and 135 K lies in the conformations of the terminal ethylenic groups of the ET molecules. In fact, the carbon atoms (C7 and C16) of the ethylenic groups exhibit high thermal motion (perpendicular to the plane of the ET molecules) and/or disorder at 293 K, and the exact conformation of the ET molecules cannot be determined at that temperature. These carbon atoms were unambiguously located at 135 K, showing that the ET molecules are staggered. The anion $\cdots$ cation interactions and the environment of the Pt atom are given in Fig. 5. We observe, in particular, short

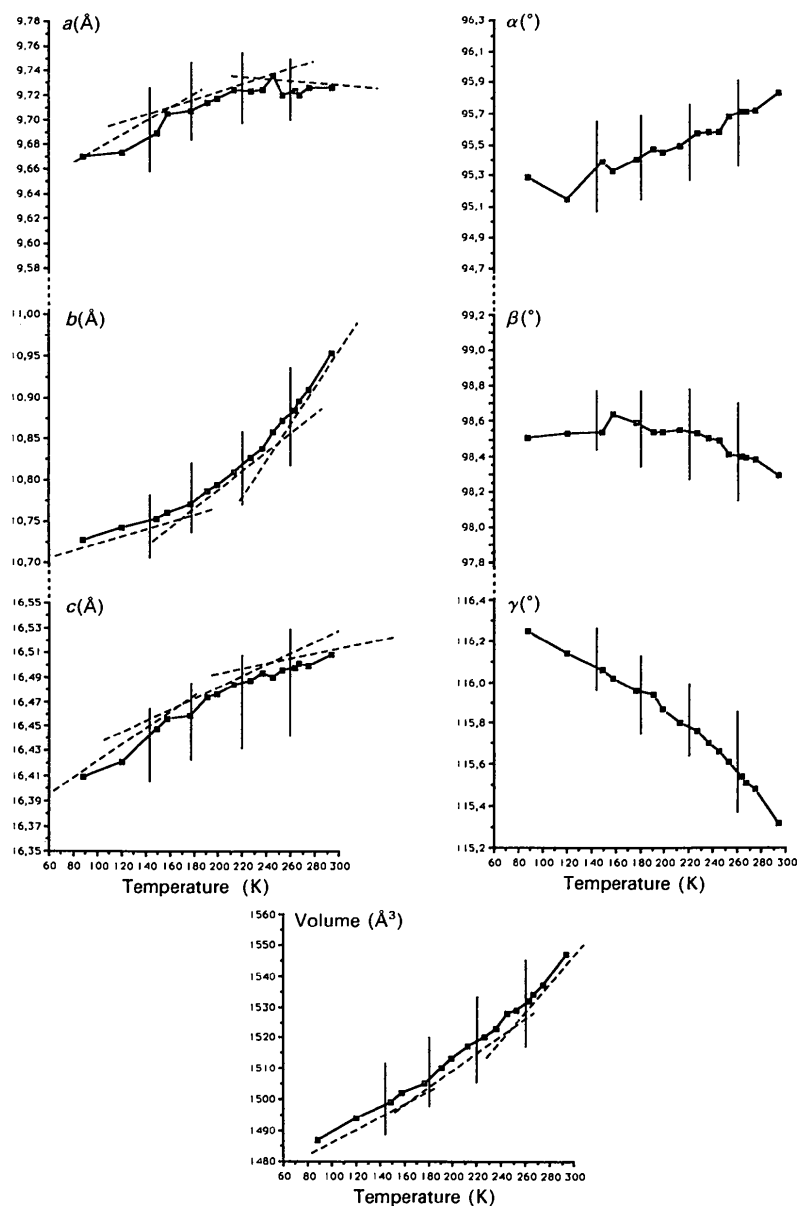


Fig. 3. Variation of the unit-cell parameters versus temperature.

Pt...H contacts (2.727 Å) involving hydrogen atoms of the ethylenic groups which are located on both sides of the anion plane. This kind of weak anion/cation bonding interaction involving hydrogen atoms has previously been observed in other BEDT-TTF salts (Emge, Wang, Leung, Rust, Cook, Jackson, Carlson, Williams, Whangbo, Venturini, Schirber, Azevedo & Ferraro, 1986) in which the short X...H (X = halogen atom) contacts can be described as

classical hydrogen bonds (Novoa, Mota, Whangbo & Williams, 1991). However, this is not the case in the title compound for which the Pt...H bonding interaction is better described as a Pt...HC agostic bond, *i.e.* a weak dative bond from a ligand (CH bond) to an electron-deficient metal (Brookhart & Green, 1983).

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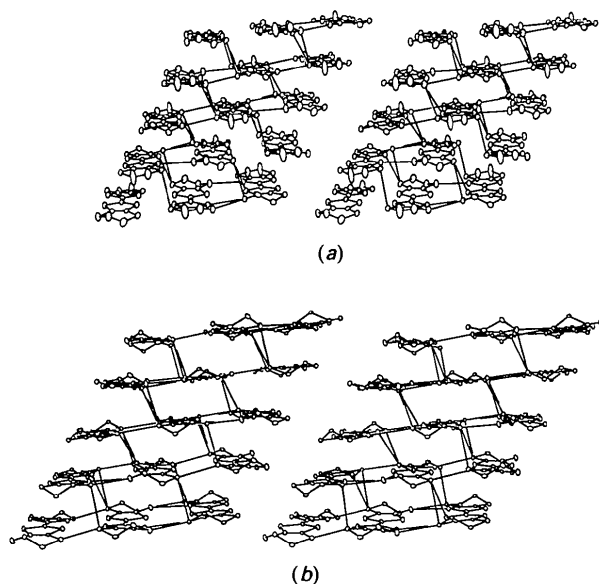


Fig. 4. Stereoscopic view of the ET packing at (a) 293 K and (b) 135 K. Interstack S...S contacts  $\leq 3.8$  Å (see Table 4) are drawn.

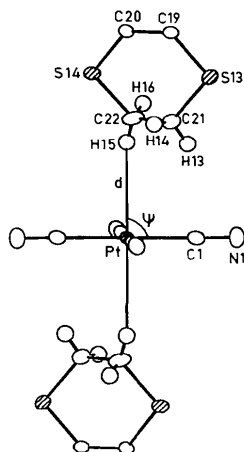


Fig. 5. Environment of the Pt atom and evidence of Pt...H interactions. At 293 K:  $d = 3.144$  Å,  $\psi = 89.32^\circ$ . At 135 K:  $d = 2.727$  Å,  $\psi = 80.70^\circ$ . E.s.d.'s on the last digit are 0.001.

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