

β -Phase of 1-(4-bromobenzyl)pyridinium bis(1,2-dicyanoethene-1,2-dithiolato- κ^2S,S')platinate(III)Y.-C. Chen and X.-M. Ren*[‡]

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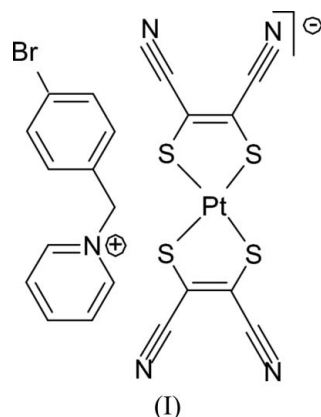
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Key indicatorsSingle-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.021$ Å
 R factor = 0.059
 wR factor = 0.138
Data-to-parameter ratio = 17.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $(C_{12}H_{11}BrN)[Pt(C_4N_2S_2)_2]$, is a new polymorphic modification, *viz.* the β -phase; the α -phase has been published recently [Ren *et al.* (2004). *Inorg. Chem.* **43**, 2569–2576]. In the β -phase, the anions and cations form segregated columnar stacks along the a axis, which is similar to the α -phase. Compared with the α -phase, the significant structural differences in the β -phase relate to the molecular conformation of the cation and the stacking architecture of both anions and cations.

Comment

Organic charge-transfer salts with segregated stacks are the subject of intensive study, due to their unusual properties in magnetism and conductivity (Coomber *et al.*, 1996; Kawamura *et al.*, 1997; Xie, Ren, Song, Zou & Meng, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie *et al.*, 2003). Recently, we reported the crystal structure of an ion-pair compound, 1-(4'-bromobenzyl)pyridinium bis(maleonitriledithiolato)platinate(III), which possesses segregated and regular stacks of cations and anions. Such an anionic stack behaves as a one-dimensional magnet with $S = \frac{1}{2}$ and undergoes a magnetostructural transition at *ca* 260 K, which results from the instability of the one-dimensional electron gas (Ren *et al.*, 2004). Here, we present the crystal structure of a new polymorph of the title compound, (I) (Fig. 1), which we have called the β -phase. The α -phase corresponds to the crystal form reported earlier (Ren *et al.*, 2004).



The β -phase crystallizes in a monoclinic space group, with one cation and one anion in the asymmetric unit. The anion, $[Pt(mnt)_2]^-$, shows a square-planar geometry (mnt is maleonitriledithiolate). The Pt–S bond lengths (Table 1) range from 2.249 (3) to 2.267 (3) Å. The S–Pt–S angles in the two chelate rings [89.79 (11) and 89.75 (11)°] are in good

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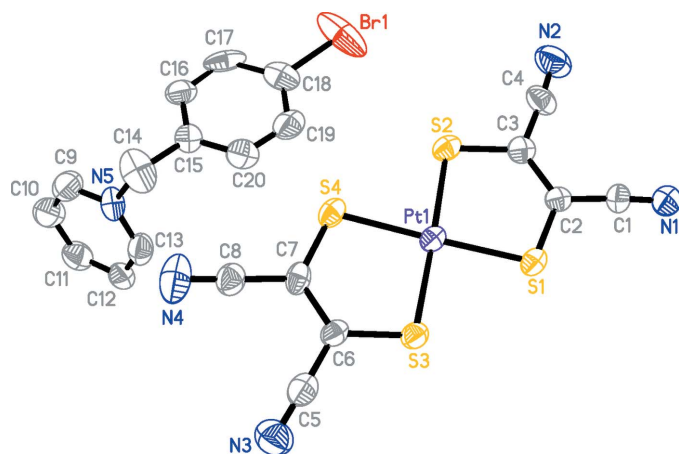


Figure 1
A view of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

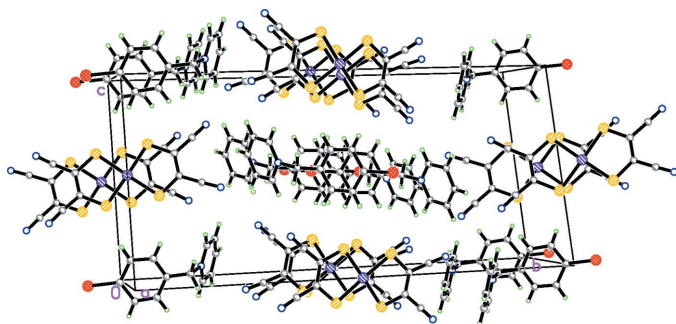


Figure 2
The crystal packing of (I), viewed approximately along the *a* axis.

agreement with the values observed in the α -phase. In the cation, the plane formed by atoms N5/C14/C15 makes dihedral angles with the benzene and pyridine rings of 72.6 (15) and 104.6 (10)°, respectively, while in the α -phase, the corresponding dihedral angles are 98.5 (6) and 93.1 (5)°. The dihedral angles between the benzene and pyridine rings in the β - and α -phases are 75.9 (4) and 114.1 (2)°, respectively. In the crystal structure of (I), the anions and cations stack into segregated columns along the *a* axis (Fig. 2).

There are remarkable differences in the crystal structures of the two polymorphs. The anionic stacks in the α - and β -phases are regular (Fig. 3*a*) and irregular (Fig. 3*b*), respectively. In the β -phase, two stacking patterns exist between adjacent anions, namely face-to-face overlap, and longitudinal and transverse offset. The face-to-face overlap involves an anionic pair containing atoms Pt1 and Pt1ⁱ [symmetry code: (i) 1 - *x*, 2 - *y*, 1 - *z*], in which the distance between the Pt^{III} ions [3.4838 (8) Å] is comparable with that between the corresponding mean planes defined by the four coordinating S atoms [3.489 (3) Å]. The longitudinal and transverse offset involves an anionic pair containing atoms Pt1 and Pt1ⁱⁱ [symmetry code: (ii) 2 - *x*, 2 - *y*, 1 - *z*], in which the distances between the Pt^{III} ions and between the corresponding mean planes are 4.3038 (9) and 3.6235 (4) Å,

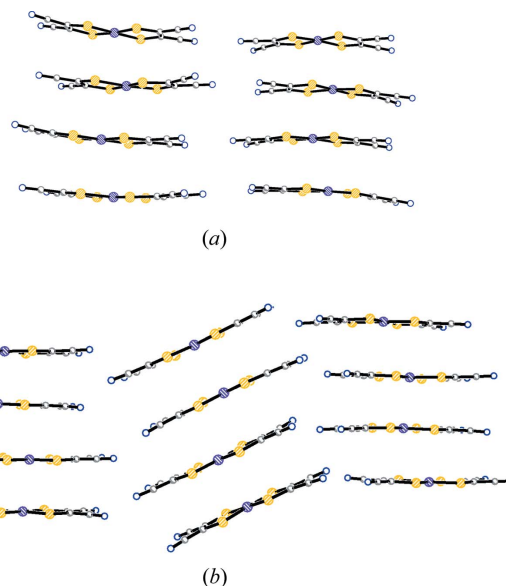


Figure 3
The anionic packing in (a) the α -phase and (b) the β -phase.

respectively. Within a cationic stack, neighbouring cations in the α - and β -phases are stacked in chair-conformation-like (Fig. 4*a*) and boat-conformation-like (Fig. 4*b*) fashions, respectively. In the β -phase, the anionic molecular planes in neighbouring stacks are inclined to each other with a dihedral angle of 27.73 (5)° [1.32 (5)° in the α -phase]. The dihedral angle between benzene rings in neighbouring cationic stacks is 21.94 (25)° [3.58 (18)° in the α -phase].

With respect to the $[M(\text{mnt})_2]^-$ -based compounds ($M = \text{Ni}$, Pd or Pt), their physical properties, such as conductivity and magnetism, are sensitive to the anionic stacking pattern. Therefore, the two polymorphs of (I) probably possess distinct conducting and magnetic behaviours, and such measurements are in progress.

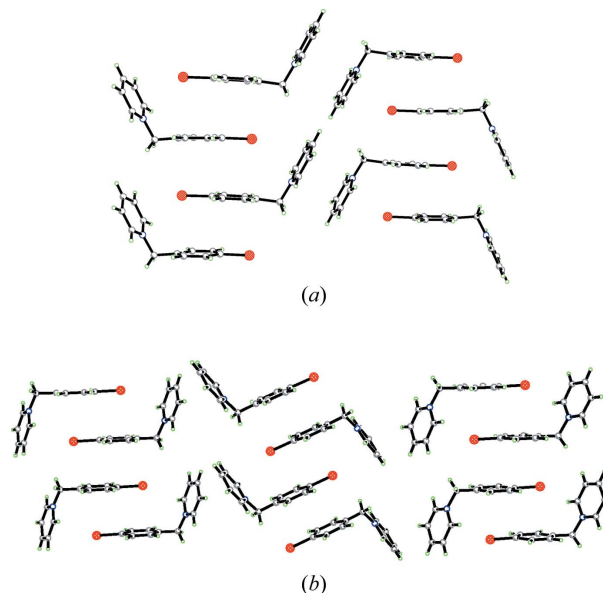


Figure 4
The cationic packing in (a) the α -phase and (b) the β -phase.

Experimental

Disodium maleonitriledithiolate (Na_2mnt) was prepared following the known procedure of Davison & Holm (1967). 1-(4-Bromobenzyl)pyridinium chloride was prepared by reacting 4-bromobenzylchlorine with 1.5 equivalents of pyridine in refluxing acetone for 4 h. The resulting product, containing white microcrystals, was filtered and washed with acetone and diethyl ether in turn, and then dried *in vacuo*, with a yield *ca* 80%. K_2PtCl_4 , Na_2mnt and 1-(4'-bromobenzyl)pyridinium chloride (equivalent molar ratio 1:2:2) were mixed in water. The red product which precipitated was separated, washed with water and then dissolved in MeCN. Iodine (1.5 molar equivalents) was added to the boiling solution with stirring. Five times the resulting volume of MeOH was then added and the mixture allowed to stand for 24 h. The microcrystals which formed were separated, washed with MeOH and dried *in vacuo*, with a yield *ca* 55%. A saturated MeCN solution of (I) at room temperature was placed in a refrigerator at 277 K for one week, and single crystals of (I) suitable for X-ray crystal structure analysis were obtained.

Crystal data

$(\text{C}_{12}\text{H}_{11}\text{BrN})[\text{Pt}(\text{C}_4\text{N}_2\text{S}_2)_2]$
 $M_r = 724.58$
 Monoclinic, $P2_1/c$
 $a = 7.3814$ (8) Å
 $b = 26.180$ (3) Å
 $c = 12.6488$ (14) Å
 $\beta = 105.739$ (2)°
 $V = 2352.7$ (5) Å³
 $Z = 4$

$D_x = 2.046$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 851 reflections
 $\theta = 2.9\text{--}23.8^\circ$
 $\mu = 8.04$ mm⁻¹
 $T = 293$ (2) K
 Block, black
 0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.24$, $T_{\max} = 0.45$
 13418 measured reflections

4851 independent reflections
 2886 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$
 $\theta_{\max} = 26.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -32 \rightarrow 28$
 $l = -13 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.138$
 $S = 0.92$
 4851 reflections
 280 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.86$ e Å⁻³
 $\Delta\rho_{\min} = -1.58$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pt1—S4	2.249 (3)	Pt1—S1	2.262 (3)
Pt1—S2	2.255 (3)	Pt1—S3	2.267 (3)
S4—Pt1—S2	88.78 (11)	S4—Pt1—S3	89.75 (11)
S4—Pt1—S1	178.45 (11)	S2—Pt1—S3	177.76 (10)
S2—Pt1—S1	89.79 (11)	S1—Pt1—S3	91.70 (11)

All H atoms were placed in geometrically calculated positions and refined as riding, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The residual electron density of 1.86 e Å⁻³ and the deepest hole of -1.58 e Å⁻³ are situated at 1.04 and 1.74 Å from Pt1, respectively.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXL97.

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