

**The Structure of the Linear Chain**  
**Bis(1,2-diaminoethane)platinum(II)bis(1,2-diaminoethane)diiodoplatinum(IV)**  
**Tetraperchlorate**

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**Abstract.**  $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2\text{I}_2](\text{ClO}_4)_4$ ,  $\text{C}_8\text{H}_{32}\text{I}_2\text{N}_8\text{Pt}_2^{4+} \cdot 4\text{ClO}_4^-$ , monoclinic,  $A2/m$ ,  $a = 7.440$  (4),  $b = 5.827$  (4),  $c = 17.031$  (10) Å,  $\beta = 97.93$  (4)°,  $Z = 1$ ,  $d_c = 2.9$  Mg m<sup>-3</sup>. The structure was refined to  $R = 0.057$  for 857 counter intensities and can best be described as a statistical three-dimensionally-disordered Wolfram's salt analogue. The two alternating Pt–I distances along the Pt<sup>II</sup>...I–Pt<sup>IV</sup> chains are 3.036 (8) Å and 2.791 (8) Å.

**Introduction.** The structures of some three-dimensionally-ordered (Endres, Keller, Martin & Traeger, 1979, and references therein), one-dimensionally-ordered (Breer, Endres, Keller & Martin, 1978) and statistically three-dimensionally-disordered Wolfram's salt analogues (Endres, Keller, Martin & Traeger, 1979, and references therein) have recently been described. The Pt<sup>II</sup>...X–Pt<sup>IV</sup> distances in these linear-chain, mixed-valence platinum(II,IV) compounds differ greatly in some cases (Keller, Martin & Traeger, 1978) but so far have been found to be equivalent in two compounds, within experimental error (Endres, Keller, Martin & Traeger, 1979; Endres, Keller, Martin & Nötzel, 1979). We used platelet-shaped crystals of the title compound (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977) to investigate its structure, which is interesting in comparison with the bromine derivative, the latter being three-dimensionally ordered with equivalent Pt–Br–Pt distances along the chains. Rotating-crystal and Weissenberg photographs (Cu  $K\alpha$  radiation) showed the symmetry and systematic extinctions, and established approximate lattice constants. Exact lattice constants (see *Abstract*) were calculated by a least-squares procedure (Berdesinski & Nuber, 1966) from the  $\theta$  values of 45 reflections, measured on a diffractometer. Intensity measurements on an automatic single-crystal diffractometer (AED, Siemens, Mo  $K\alpha$  radiation,  $\theta$ – $2\theta$  scans, five-value method) with  $4^\circ < 2\theta < 30^\circ$  furnished 855 observed independent intensities. Reflections with  $I < 3.0\sigma(I)$  were classified as unobserved. Observed reflections were corrected for polarization and Lorentz factors. Because of the small crystal size

( $0.05 \times 0.1 \times 0.01$  mm), no absorption correction was carried out ( $\mu = 12.6$  mm<sup>-1</sup>). The systematic absences ( $hkl$  with  $k + l = 2n + 1$ ) correspond to the centrosymmetric  $A2/m$  ( $C_2^3$ ) and to the noncentrosymmetric  $Am$  ( $C_2^3$ ) and  $A2$  ( $C_2^3$ ) space groups. A Patterson synthesis showed the positions of Pt, Cl and I to be exactly midway between the two Pt sites ( $0, \frac{1}{2}, 0$ ). The positions of the N and O atoms were located in a Fourier synthesis. The C atoms were found in a difference Fourier map. For the refinement I was shifted away from its central position and the  $y$  parameter was left free to adjust. Least-squares refinement proved to be successful in the centrosymmetric space group  $A2/m$ . The noncentrosymmetric space group  $Am$  yields the same atomic positions as  $A2/m$ , and the noncentrosymmetric  $A2$  furnishes the same  $R$  value as  $A2/m$ , but the anisotropic temperature factor of N is not positive definite. Thus  $A2/m$  was chosen as the correct space group. The refinement in  $A2/m$  resulted in  $R = 0.117$  with isotropic temperature factors and  $R = 0.057$  with anisotropic. H atoms were not included. If I is kept fixed midway between the Pt atoms,  $R$  remains the same, but  $U_{22}$  increases by 25%. Hence it seems more reasonable to describe the structure by the split positions for I. Atomic coordinates are listed in Table 1.\* Calculations

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34356 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^3$ )

|      | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Pt   | 0       | 0       | 0       |
| I    | 0       | 479 (1) | 0       |
| Cl   | 526 (1) | 0       | 360 (1) |
| O(1) | 366 (5) | 0       | 305 (2) |
| O(2) | 678 (4) | 0       | 318 (2) |
| O(3) | 463 (2) | 301 (3) | 92 (1)  |
| N(1) | 137 (2) | 0       | 112 (1) |
| N(2) | 779 (3) | 0       | 61 (1)  |
| C(1) | 836 (4) | 44 (7)  | 147 (2) |
| C(2) | 15 (5)  | 60 (4)  | 172 (2) |

were carried out on an IBM 370/168 computer (Universitätsrechenzentrum Heidelberg) with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970) using scattering factors derived from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The numbering scheme, bond distances and angles are shown in Fig. 1. The complex units are arranged in chains along *b*, along which Pt and I alternate. I is distributed over two half occupied positions near the center of symmetry at (0,  $\frac{1}{2}$ , 0). These two positions are 0.25 Å apart, the two Pt—I distances being 3.036 (8) and 2.791 (8) Å. These values can be compared with the corresponding distances in the 1,2-diaminopropane derivative (Breer, Endres, Keller & Martin, 1978) of 2.956 (9) and 2.770 (9) Å.

Of much more interest is a comparison of these data with the Br analogue, which is ordered three dimensionally (Endres, Keller, Martin & Traeger, 1979). This three-dimensional ordering was supposed to be caused by hydrogen bridges between the ligand and the perchlorates. Fig. 2 shows the shortest approaches between ligand N and perchlorate O atoms in [Pten<sub>2</sub>]<sub>2</sub>[Pten<sub>2</sub>I<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>. These distances of 3.04 Å between N(2) and O(3) or 3.05 Å between N(1) and O(3) do not suggest appreciable hydrogen bonding in the title compound. This is additionally substantiated by the equal Cl—O distances [1.42 (3) Å] within the perchlorate ion. These differences between [Pten<sub>2</sub>]<sub>2</sub>[Pten<sub>2</sub>Br<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> and [Pten<sub>2</sub>]<sub>2</sub>[Pten<sub>2</sub>I<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> in ligand-perchlorate interactions and in the ordering of the full structure further suggest that the hydrogen bridges play an important role in the three-dimensional correlations in these systems.

After this paper had been submitted, we received a preprint of a paper by Professor S. Kida which describes the same structure (Matsumoto, Yamashita,

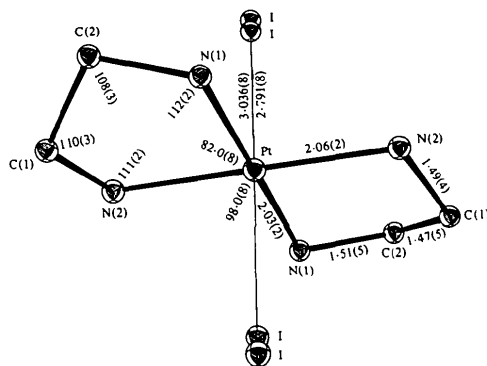


Fig. 1. ORTEP plot (Johnson, 1965) of the complex molecule with bond distances (Å) and angles (°). The two Pt—I separations are indicated. As there is no crystallographic distinction between Pt<sup>IV</sup> and Pt<sup>II</sup> sites, the plot in fact shows a superposition of the two different species. Only one of the two disordered positions for each C atom is shown.

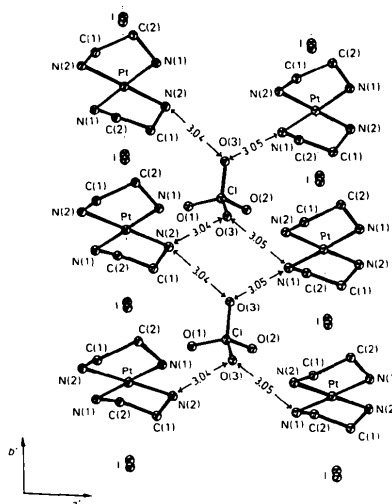


Fig. 2. View of two Pt<sup>IV</sup>—I...Pt<sup>II</sup> chains. The figure is derived from a projection on to the *ab* plane by rotations of 20° about *a* and *b*. The two half-occupied iodine positions between the Pt atoms are indicated by two 'overlapping' spheres. The shortest ClO<sub>4</sub><sup>-</sup> ligand contacts are shown between arrows. Only one of the two possible positions for C(1) and C(2) is shown.

Kida & Ueda, 1979). The differences are as follows: We tried all the possible space groups and were successful with anisotropic refinement in only the centrosymmetric space group *A2/m*. Kida has not considered this space group and has assumed the non-centrosymmetric space group *C2*, in which the atoms of the ligand were refined with isotropic temperature factors only. Not being constrained by the mirror plane of *A2/m*, the Pt in Kida's work is shifted markedly out of the plane of the four ligand N atoms. This does not happen in *A2/m*, but the shortcoming of this space group is that it implies the C atoms to be distributed statistically over two sites above and below the mirror plane. This means that the complex molecule statistically adopts two orientations. In Kida's work two different Pt—I distances from the same Pt result, whereas we constrained the refinement to give identical Pt—I distances.

The distances and angles in the basal plane of the coordination bipyramid around Pt are identical within standard deviations in both papers, but significant differences in the Pt—I distances occur: We obtain 2.791 (8) and 3.036 (8) Å; Kida reports 2.704 (11)/2.726 (9) and 3.115 (11)/3.039 (9) Å, respectively. Our picture of the H-bonding pattern (Fig. 2) is correct, the representation in Kida's paper is wrong.

It is difficult to compare the *R* factors (0.057 in this paper, 0.054 in Kida's work), for we have more free thermal parameters, while Kida calculates with more independent positions.

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## Structure of Dibromobis(1,2-diaminoethane)platinum(IV) 3,4-Dihydroxy-3-cyclobutene-1,2-dionate Dihydrate

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**Abstract.** [PtBr<sub>2</sub>(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>][C<sub>4</sub>O<sub>4</sub>].2H<sub>2</sub>O, C<sub>4</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>4</sub>Pt<sup>2+</sup>.C<sub>4</sub>O<sub>4</sub><sup>2-</sup>.2H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.038 (19), *b* = 14.289 (4), *c* = 6.983 (12) Å, β = 132.24 (10)°, *V* = 815.6 Å<sup>3</sup>, *d* = 2.57 Mg m<sup>-3</sup>, *Z* = 2. The structure was refined to *R* = 0.079 for 1553 counter data and consists of six-coordinate [PtBr<sub>2</sub>en<sub>2</sub>]<sup>2+</sup> units (en = 1,2-diaminoethane) with planar [C<sub>4</sub>O<sub>4</sub>]<sup>2-</sup> counterions which are strongly hydrogen bonded to each other and to the water molecules in the lattice. The reduced cell has *a* = 6.984, *b* = 14.290, *c* = 8.184 Å, β = 93.07°.

**Introduction.** In recent papers we have reported the structure of mixed-valence Wolfram's salt analogues (Endres, Keller, Martin, Nam Gung & Traeger, 1979). In some cases *three*-dimensional order is observed in the *linear* chain compounds (Endres, Keller, Martin & Traeger, 1979), and it was suggested that this ordering is caused by hydrogen bridges between the complex ligands and the perchlorate counterions. We therefore investigated the system [PtBr<sub>2</sub>en<sub>2</sub>]<sup>2+</sup>–[Pten<sub>2</sub>]<sup>2+</sup>–C<sub>4</sub>H<sub>2</sub>O<sub>4</sub> (squaric acid) – the latter compound being well known for its ability to form hydrogen bridges – in the hope of strengthening the interchain coupling in Wolfram's salt analogues. After hot aqueous solutions

containing 0.5 mmol [PtBr<sub>2</sub>en<sub>2</sub>]<sup>2+</sup> and 0.5 mmol [Pten<sub>2</sub>]<sup>2+</sup> are mixed with a hot aqueous solution of 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), the title compound crystallizes in red platelets. {Analysis for [PtBr<sub>2</sub>en<sub>2</sub>][C<sub>4</sub>O<sub>4</sub>].2H<sub>2</sub>O, *M<sub>r</sub>* = 622.9: calculated: C 15.40, N 8.98, H 3.46, Pt 31.31%; found: C 15.40, N 8.26, H 3.41, Pt (residue) 32.44%.}

Rotating-crystal and Weissenberg photographs (Cu *K*α radiation) showed the symmetry and systematic extinctions and established approximate lattice constants. Exact lattice constants (see *Abstract*) were calculated by least squares (Berdesinski & Nuber, 1966) from the θ values of 33 reflections, measured on a diffractometer. Intensity measurements on an automatic single-crystal diffractometer (AED, Siemens, Mo *K*α radiation, θ–2θ scans, 'five-value method', 4° < 2θ < 60°) furnished 1553 observed independent intensities. Reflections with *I* < 3.0σ(*I*) were classified as unobserved. Owing to the small crystal size (0.04 × 0.05 × 0.03 mm), no absorption correction was applied (μ = 14.5 mm<sup>-1</sup>). Observed reflections were corrected for polarization and Lorentz factors. The systematic absences (*h*0*l* with *h* + *l* = 2*n* + 1 and 0*k*0 with *k* = 2*n* + 1) correspond to the space group *P*2<sub>1</sub>/*n* (*C*<sub>2h</sub><sup>2</sup>). A Patterson synthesis showed the positions of Pt and Br. The positions of N, O and C atoms could be located by distance and angle calculations from the

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