

Bis(1,2-diaminopropane)platinum(II) Diiodobis(1,2-diaminopropane)platinum(IV) Perchlorate – an Analogue of Wolfram's Red Salt

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Abstract. $[\text{Pt}(\text{C}_3\text{H}_{10}\text{N}_2)_2][\text{Pt}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{I}_2](\text{ClO}_4)_4$, orthorhombic, *Pcma*, $a = 7.609$ (3), $b = 5.726$ (2), $c = 19.645$ (5) Å, $Z = 1$, $V = 855.9$ Å³, $d_x = 2.56$ g cm⁻³. The structure was refined to $R = 0.062$ for 625 counter reflections. A rotating-crystal photograph shows one-dimensional order along the $M^{\text{IV}}-X-M^{\text{II}}$ chain. The $M-X$ distances are 2.956 (9) and 2.770 (9) Å. Optical-reflectivity data show a strongly anisotropic collective behaviour.

Introduction. In the course of the recent interest in the chemistry and physics of linear-chain transition-metal compounds (Miller & Epstein, 1976; Keller, 1977) attention was given to Wolfram's red salt, $[\text{Pt}(\text{NH}_2\text{C}_2\text{H}_5)_4][\text{Pt}(\text{NH}_2\text{C}_2\text{H}_5)_4\text{Cl}_2]\text{Cl}_4$, and its analogues (Bekaroglu, Breer, Endres, Keller & Nam Gung, 1977). These compounds contain linear $-\text{Pt}^{\text{IV}}-X-\text{Pt}^{\text{II}}-$ chains where Pt^{II} and Pt^{IV} can clearly be distinguished by the different metal-halogen distances.

During a programme to investigate such compounds we tried to prepare analogues of Wolfram's salt with equivalent or nearly equivalent metal centres (halogen exactly or nearly midway between the metal atoms). They should show enhanced cooperative electronic properties. Here we report the structure of the title compound (Bekaroglu *et al.*, 1977).

Rotating-crystal and Weissenberg photographs (Cu $K\alpha$ radiation) showed the symmetry and systematic extinctions. Lattice constants were calculated from the θ values of 28 reflections, measured on a diffractometer, by least squares (Berdiesinski & Nuber, 1966). Intensity measurements on an automatic single-crystal diffractometer (AED, Siemens, Mo $K\alpha$ radiation, $\theta-2\theta$ scan, five-value method) furnished 663 observed independent intensities in a 2θ range up to 55° , classifying reflections with $I < 2.58(I)$ as unobserved. Observed reflections were corrected for polarization and Lorentz factors only. The systematic absences ($hk0$ with $h = 2n + 1$; $0kl$ with $l = 2n + 1$) correspond to the centrosymmetric space group *Pcma* and to noncentrosymmetric *Pc2a*. A Patterson synthesis

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

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0	0	0
I	0	516 (2)	0
Cl	562 (1)	500	119 (1)
N(1)	402 (4)	0	400 (2)
N(2)	732 (4)	0	444 (1)
C(1)	543 (6)	-97 (9)	353 (2)
C(2)	707 (6)	47 (28)	374 (2)
C(3)	491 (8)	-23 (51)	280 (2)
O(1)	409 (5)	500	160 (3)
O(2)	707 (5)	500	162 (2)
O(3)	567 (3)	703 (4)	80 (1)

showed the position of Pt, Cl and I exactly midway between two Pt sites. For the refinement I was shifted away from this central $(0, \frac{1}{2}, 0)$ position and the *y* parameter was left free to adjust. N and C atoms could be located from difference maps; O atoms could only be found in a Fourier synthesis calculated with those reflections for which the Pt contributions were systematically extinct. Least-squares refinement was tried in both space groups. In *Pc2a* anisotropic refinement proved impossible; mixed refinement with isotropic temperature factors for C, N and O resulted in abnormally large temperature factors for these atoms. Anisotropic refinement was successful in *Pcma*. To corroborate the space group a statistical centrosymmetry test was calculated. For this test the contributions of the Pt atoms, which alone form a centrosymmetric arrangement, were subtracted from the observed structure factors. This test supported the choice of the centrosymmetric space group. Refinement in *Pcma* gave $R = 0.122$ with isotropic and $R = 0.062$ with anisotropic temperature factors. Several reflections with an abnormally high difference between observed and calculated structure factors were omitted during the last refinement cycles. Atomic coordinates are listed in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33318 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Calculations were carried out on an IBM 370/168 computer (Universitätsrechenzentrum Heidelberg) with the XRAY system (Stewart, Kundell & Baldwin, 1970) and scattering factors from Hanson, Herman, Lea & Skillman (1964).

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 centre of symmetry at (0, $\frac{1}{2}$, 0). These two positions are 0.19 Å apart, the two Pt—I distances being 2.956 (9) and 2.770 (9) Å respectively.

On rotating-crystal photographs around **b**, diffuse layer lines are observed between the Bragg layer lines. This shows a doubling of **b** with a one-dimensional order along **b** only. This feature is often found with analogues of Wolfram's salt and is usually discussed in terms of Pt^{II}—X—Pt^{IV}—X—Pt^{II} chains, where the chains are shifted statistically in the chain direction by one Pt—Pt separation (Bekaroglu *et al.*, 1977). The difference between the two Pt—I separations in the title compound is the smallest observed so far in this class of compounds. This suggests the possibility that the difference could be made zero and thus the Pt atoms equivalent by an appropriate combination of ligands,

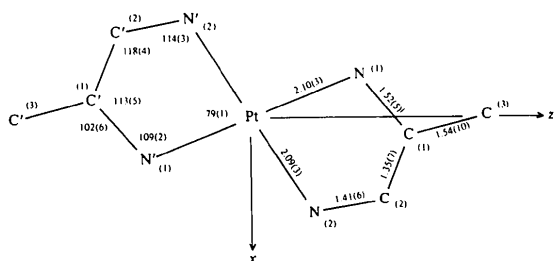


Fig. 1. The complex molecule with bond distances (Å) and angles (°).

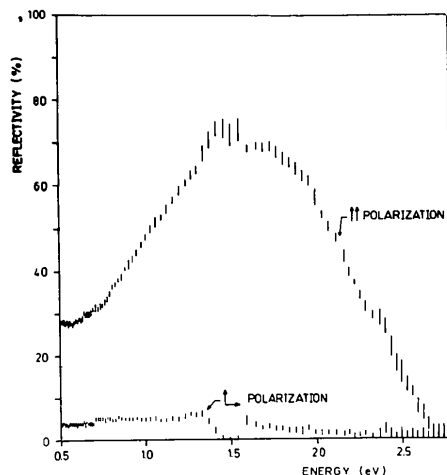


Fig. 2. Single-crystal optical reflectivity of the title compound.

halogens and counter-ions. The strong electronic interaction along the *M*—*X*—*M* chains is shown by the optical reflectivity of single crystals (Fig. 2): The crystals reflect strongly in a wide energy range if the incident beam is polarized parallel to the chains. The reflectivity is nearly zero for a perpendicular polarization.

As Pt occupies a crystallographic *2/m* position, the ligand has to adopt statistically two possible orientations

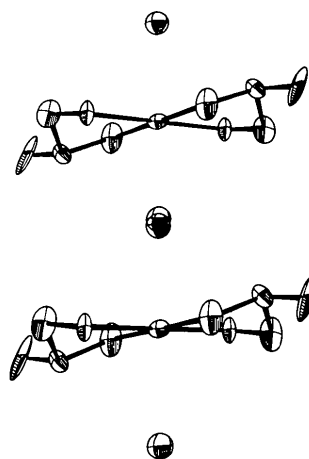


Fig. 3. ORTEP plot of part of the chain structure. Only one of the possible ligand orientations is shown. The split positions of iodine are indicated in the central part.

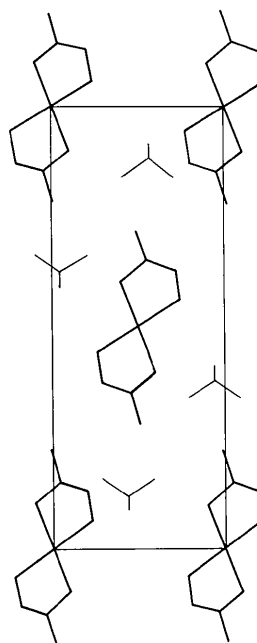


Fig. 4. Projection of the unit cell along **b**.

tations to fulfil the symmetry requirements. Theoretically this could also be the cause of the diffuse scattering. An *ORTEP* plot (Johnson, 1965) of one chain is presented in Fig. 3, showing one possible ligand orientation only and the splitting of the I position between two Pt atoms. A projection of the structure along the chains is given in Fig. 4.

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Structure of Tetrakis(thiourea)zinc(II) Nitrate

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Abstract. Zn[SC(NH₂)₂]₄(NO₃)₂, *M_r* = 493, orthorhombic, *Pnaa*, *a* = 22.434 (23), *b* = 9.465 (2), *c* = 8.859 (1) Å, *V* = 1880.9 Å³, *Z* = 4, *D_m* = 1.72, *D_c* = 1.73 g cm⁻³, *F*(000) = 1008, *μ* = 17.9 cm⁻¹. The structure was solved by single-crystal X-ray diffraction with the heavy-atom technique and refined by full-matrix least squares to *R* = 0.072 for 1435 independent reflections [*I* > 2σ(*I*)]. Four S atoms from thiourea molecules coordinate to Zn in a tetrahedral arrangement: Zn–S = 2.361 (3) and 2.324 (3) Å. Packing is determined by N–H⋯O hydrogen bonds which the NH₂ thiourea groups form with the nitrate O atoms.

Introduction. This investigation was undertaken because of our interest in the molecular conformation of thiourea and selenourea complexes with divalent metal salts. We have already studied several complexes {Ni[SC(NH₂)₂]₄Cl₂ (Truter & López-Castro, 1963), Hg[SC(NH₂)₂]₂(CN)₂ (Moreno & López-Castro, 1971) and Hg[SC(NH₂)₂]₄Cl(SH) (Criado, Conde, Moreno & Márquez, 1975)} by three-dimensional X-ray analysis. In continuing this research, the crystal structure of

tetrakis(thiourea)zinc nitrate has been studied and the results of this analysis are reported here.

Single crystals were grown by slow evaporation of a 1:4 mixture of solutions of Zn(NO₃)₂ and thiourea. They are colourless prisms elongated along *c*. The cell parameters were determined and the intensities of the reflections were recorded up to sin θ/λ = 0.70 Å⁻¹ with monochromated Mo *K*α radiation (λ = 0.7107 Å) on a Philips PW 1100 automatic four-circle diffractometer. Systematic absences of reflections were observed in the diffractometer data. The observed reflections obey the conditions: *hkl* (no condition), *0kl* (*k* + *l* = 2*n*), *hk0* (*h* = 2*n*), and *h0l* (*h* = 2*n*); the space group consistent with these observations is *Pnaa* [this corresponds to *Pccn* (*D*_{2h}¹⁰, No. 56) (*International Tables for X-ray Crystallography*, 1952) by a transformation involving a permutation of the *a* and *c* axes].

The intensities were only corrected for Lorentz and polarization factors. Of the 2734 independent reflections recorded, 1435 intensities greater than 2σ(*I*), as estimated from counting statistics, were regarded as 'observed' and used for the refinement. No absorption correction was applied.