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Refinement of the Crystal Structure of Tetraethylammonium Tetrabromo-μ,μ′-dibromo-diplatinate(II)

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Abstract. $[C_8H_{20}N]_2[Pt_2Br_6]$, triclinic, space group $P\bar{1}$, $a=7{\cdot}567$ (7), $b=8{\cdot}401$ (8), $c=12{\cdot}415$ (12) Å, $\alpha=105{\cdot}3$ (3), $\beta=84{\cdot}5$ (4), $\gamma=111{\cdot}8$ (2)°, $U=707{\cdot}3$ Å^3, $Z=1$, $D_c=2{\cdot}65$ g cm^{-3}. The atomic positions have been refined by least-squares calculations, the final R being 0·085 for 2592 counter reflexions. Mean values for the bridging and terminal Pt–Br lengths are 2·443 and 2·413 Å respectively.

Introduction. The crystals commonly have the forms {100}, {001} and $\{0\bar{1}1\}$. Cell dimensions were determined from precession photographs of a small (maximum dimension < 0·02 cm) crystal taken with Mo $K\alpha$ radiation. The intensities of reflexions with $\theta < 30°$ were measured on a Stoe–Weissenberg diffractometer with monochromatic Mo $K\alpha$ radiation and an ω-scan technique with a crystal, 0·032 × 0·040 × 0·054 cm, mounted about **a**. The 2592 reflexions with $I > 3\sigma(I)$ and $\sin\theta/\lambda > 0{\cdot}1$ Å^{-1} were corrected for Lorentz and polarization effects, and for absorption [μ(Mo $K\alpha$) = 73 cm^{-1}) [de Meulenaer & Tompa (1965) as implemented by Alcock (1969)].

Scattering factors were from Cromer (1965). Atomic coordinates have already been obtained (Stephenson, 1964). Eight cycles of block-diagonal least squares reduced R to its final value of 0·085 [$R_w = \sum w(|F_o| - |F_c|)/\sum w|F_o| = 0{\cdot}087$]. Anisotropic temperature factors for Br and Pt were refined and the structure factors corrected for anomalous dispersion of these atoms (Cromer & Waber, 1965). H atoms were ignored. In the final cycles a weighting scheme, $w = (5{\cdot}811 - 0{\cdot}379|F_o| + 0{\cdot}017|F_o|^2)^{-1}$, was introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. The maximum shift in the final cycle was 0·02σ.* A difference synthesis calculated at the end of the refinement shows no features greater than 1·5 e Å^{-3}. The final atomic parameters are given in Table 1.

Discussion. The geometry of the anion is shown in Fig. 1. This redetermination differs in several significant details from the earlier determination by Stephenson (1964). The two bridging Pt–Br bonds are equal as are the two terminal Pt–Br bonds, both to within experimental error. The mean bridging bond length (2·443 Å) is significantly longer than the mean terminal length (2·413 Å). The differences in lengths between the two

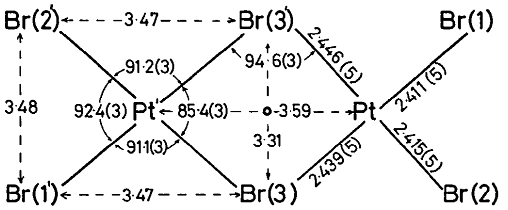

Fig. 1. Bond lengths (Å) and angles (°) in the anion with estimated standard deviations in parentheses.

Table 1. *Thermal parameters and final atomic positions with standard deviations derived from the least-squares refinement*

Temperature factors are in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pt	0·06835 (10)	0·09873 (8)	0·14387 (5)	3·35 (3)	2·35 (3)	2·47 (3)	1·08 (2)	0·17 (2)	1·53 (2)
Br(1)	−0·0499 (3)	0·2754 (3)	0·2978 (2)	5·18 (10)	3·84 (8)	3·48 (8)	0·56 (6)	0·12 (7)	2·65 (7)
Br(2)	0·3046 (3)	0·0947 (3)	0·2598 (2)	4·74 (10)	3·64 (8)	4·71 (10)	0·66 (7)	−1·22 (8)	2·15 (7)
Br(3)	0·1753 (3)	−0·0777 (3)	−0·0193 (2)	5·38 (10)	5·45 (10)	2·90 (8)	1·39 (7)	0·34 (7)	3·74 (7)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
N	−0·375 (2)	0·677 (2)	0·286 (1)	2·7 (2)	C(31)	−0·434 (3)	0·777 (3)	0·219 (2)	3·8 (3)
C(11)†	−0·208 (3)	0·812 (3)	0·357 (2)	3·7 (3)	C(32)	−0·605 (5)	0·663 (4)	0·145 (3)	6·3 (6)
C(12)	−0·118 (4)	0·735 (4)	0·426 (2)	5·4 (5)	C(41)	−0·538 (3)	0·591 (3)	0·361 (2)	4·4 (4)
C(21)	−0·323 (3)	0·526 (2)	0·212 (2)	3·4 (3)	C(42)	−0·606 (5)	0·727 (4)	0·446 (3)	6·8 (7)
C(22)	−0·164 (4)	0·575 (3)	0·133 (2)	5·3 (5)					

† Corresponding atom numbering according to Stephenson (1964) is C(6), C(8), C(4), C(2), C(3), C(1), C(5) and C(7).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31152 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

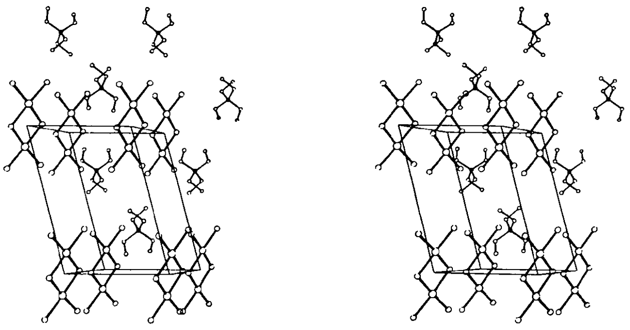

Fig. 2. Stereoscopic drawing of the unit-cell contents viewed approximately along **a**.

determinations are due largely to changes in positional parameters but are, in part, due to a small difference in cell parameters. It may be that the lack of an absorption correction has introduced a systematic error into the derived coordinates of the earlier refinement (see, for example, Mais, Owston & Wood, 1972). Our results confirm that there are slight deviations from planarity in the anion, with Br(1) and Br(2) 0·13 and −0·03 Å respectively from the plane defined by the Pt and bridging Br atoms. The angles at Pt and Br appear to be controlled primarily by the non-bonded contacts marked on Fig. 1. Thus the Br(1)···Br(2), Br(1)···Br(3) and Br(2)···Br(3′) contacts are approximately equal and the Pt···Pt′ and Br(3)···Br(3′) contacts are in proportion to their respective van der Waals diameters (Pauling, 1960). The revised geometry of the anion is now consistent with other halogen-bridged species. The conformation of the cation is controlled by eight C(α)···C(β) contacts with a mean value of 3·03 (1) Å. The remaining four C(α)···C(β) contacts have a mean value of 3·82 (1) Å. The lengths and angles in the cation are unexceptional and have been deposited with the structure factors. The packing is illustrated in Fig. 2. There are no interionic contacts shorter than 2·77 Å; a list of shorter contacts has been deposited with the structure factor table.

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Cadmium(II) Thiodiacetate Hydrate

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Abstract. $C_4H_6O_5SCd$, monoclinic, $P2_1$, a=8·009 (1), b=5·352 (1), c=9·143 (2) Å, β=116·03 (1), (20°C), Z=2, D_x=1·31 g cm^{-3}. The complex is tridentate, cadmium being bonded to sulphur as well as to oxygen atoms at both ends of the thiodiacetate ligand. Additional bonds to a water molecule and to two adjacent ligands complete a distorted octahedral arrangement about cadmium. The Cd–S bond length is 2·663 (2) Å and Cd–O distances are in the range 2·258 (5) to 2·287 (6) Å.

Introduction. Cadmium thiodiacetate, prepared from a stoichiometric mixture of $Cd(NO_3)_2$ and thiodiacetic acid in aqueous solution, crystallizes as pale-yellow prisms with the (100) face prominent. After preliminary X-ray photographs, a crystal measuring 0·20 × 0·12 × 0·25 mm was selected for intensity measurements. It was mounted in a random orientation on an automated Picker diffractometer. Accurate unit-cell parameters were derived by a least-squares method from the positions of 38 high-angle reflexions (monochromatized Mo $K\alpha_1$ radiation, λ=0·70926 Å) with a 1·5° take-off angle. 0k0 reflexions with k odd were systematically absent and the non-centrosymmetric space group $P2_1$ was indicated by reflexion statistics. Intensity data were collected by θ–2θ scans for all hkl and $\bar{h}kl$ reflexions with $2\theta \leq 60°$. Scans of $(1{\cdot}9+0{\cdot}60 \tan\theta)°$ were measured at 2° min^{-1} with 60s backgrounds. Of 1139 observations, 1124 with $I > 1{\cdot}65\sigma$ (σ based on counting statistics) were used in the analysis. The intensities of three standard reflexions monitored during data collection varied < 5% during the course of the measurements. Lorentz and polarization factors were applied to the data but no corrections for absorption were