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Redetermination of the Structure of *trans*-Diamminedibromoplatinum(II)-*trans*-diamminetetrabromoplatinum(IV), *trans*-[{$PtBr_2(NH_3)_2$}{$PtBr_4(NH_3)_2$}]

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Abstract. [$Pt_2Br_6(NH_3)_4$], orthorhombic, space group *Immm* (D_{2h}^{25}), $a = 7{\cdot}7596\ (9)$, $b = 8{\cdot}2342\ (9)$, $c = 5{\cdot}5525\ (7)$ Å, $Z = 1$, $V = 354{\cdot}4$ Å^3, $d_c = 4{\cdot}39$ Mg m^{-3}. The structure, refined to $R_w = 0{\cdot}044$ for 584 counter data, can best be described as a Wolffram's Salt analogue. Alternating Pt^{IV}–Br [2·485 (4) Å] and $Pt^{II}\cdots Br$ [3·068 (4) Å] distances are found along the neutral linear $Pt^{II}\cdots Br–Pt^{IV}$ chains. There are two statistically occupied Br positions in the chains.

Introduction. The title compound has been the subject of several investigations in recent years: After its first preparation (Grinberg & Filinov, 1937) three different X-ray investigations (Brosset, 1948; Hall & Williams, 1958; Wallén, Brosset & Vannerberg, 1961), three reports on its d.c. conductivity (Thomas & Underhill, 1971; Interrante, Browall & Bundy, 1974; Interrante & Browall, 1974) and a detailed analysis of its resonance Raman (RR) spectra (Clark & Turtle, 1978) were published. Nevertheless, some doubts concerning the correct structure of the compound remained after the most recent structural paper (Wallén, Brosset & Vannerberg, 1961). As pointed out explicitly by Clark (Clark & Turtle, 1978) the RR results on [$PtBr_2(NH_3)_2$][$PtBr_4(NH_3)_2$] indicate that the Pt–Br bond-length data of Wallén *et al.* 'are almost certainly in error'. Since many physical properties of these compounds depend strongly on the alternation of the $Pt^{II}\cdots X–Pt^{IV}$ distances along the chains (Keller, 1981) we reinvestigated the structure to resolve any ambiguity.

Rotating-crystal photographs around the *c* axis (needle axis) (Cu *Kα* radiation) showed all odd layers diffuse and even layers with Bragg reflections. The doubling of the *c* axis revealed by the diffuse layer lines was not considered further. Weissenberg photographs of all sharp layer lines showed orthorhombic symmetry and gave an estimate for the lattice parameters. Exact lattice parameters (see *Abstract*) were calculated from an orientation matrix derived from the setting angles of 25 reflections centred on a four-circle diffractometer (Syntex *R*3, monochromatic Mo *Kα* radiation). Data collection (θ–2θ scans background–peak–background, $2\theta_{\max.} = 60°$) yielded 898 independent observed reflections with $I > 3{\cdot}0\sigma(I)$. As the compound contains heavy elements, an empirical absorption correction was applied. The systematic absences ($h + k + l = 2n + 1$) correspond to the space groups *Immm* (D_{2h}^{25}), *I*222 (D_2^8), $I2_12_12_1$ (D_2^9), *Imm*2 (C_{2v}^{20}). Space group *Immm* was chosen, for the multiplicity and the point symmetry of the special positions fitted best with the composition of the compound. Calculations were carried out on a Nova 3 computer with the *SHELXTL* system (Sheldrick, 1979), plots were drawn by *ORTEP* (Johnson, 1965). The positions of Pt, N and Br were taken from a Patterson synthesis and were refined with anisotropic temperature factors. Refinement converged at $R_w = 0{\cdot}044$ ($R = 0{\cdot}055$). The weighting scheme was $w = 1/\sigma^2(F)$. Atomic coordinates are listed in Table 1.*

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

	x	*y*	*z*	*U* (Å^2)
Pt	0	0	0	14·3 (3)
Br(1)	0	0	552 (6)	39·7 (18)
Br(2)	297 (2)	0	0	31·5 (7)
N	0	266 (21)	0	27·3 (52)

Discussion. The bond distances of the platinum complexes are listed in Table 2. As all the atoms are in special positions, all angles are 90° or 180°. Fig. 1(*a*) shows the experimentally found $Pt^{II}\cdots Br–Pt^{IV}$ chain with the two 'half-occupied' Br positions. It can be interpreted as a superposition of Fig. 1(*b*) and (*c*) which show segments of ordered linear chains. Since there is only a single Pt site in the lattice the earlier Fig. 1 in the paper by Hall & Williams (1958) is in error and should be replaced by Fig. 1 shown here.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35824 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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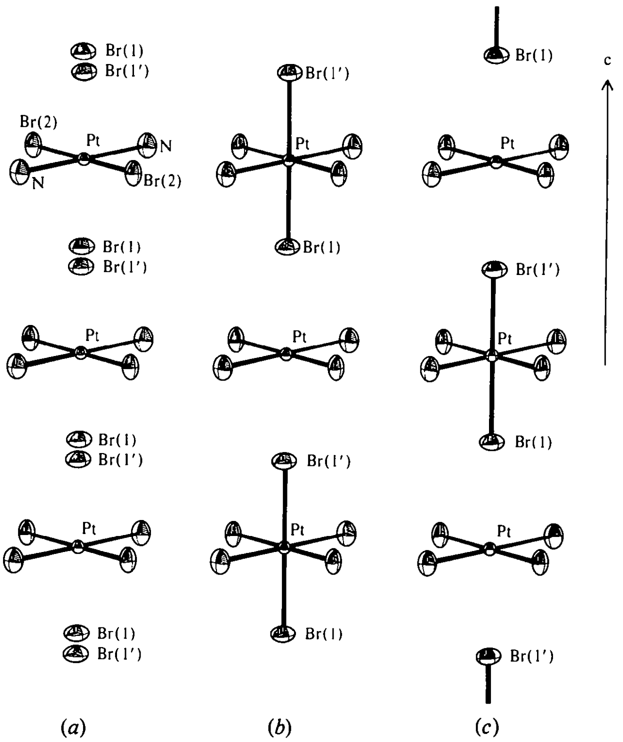

Fig. 1. (*a*) *ORTEP* plot (Johnson, 1965) of the chain rotated 20° around the *a* axis and 45° around the *c* axis. The Br(1) positions drawn are statistically half occupied. (*b*), (*c*) The same *ORTEP* plot showing the two possible bromine arrangements along the chain. The bromine positions drawn are fully occupied. (*a*) is a superposition of (*b*) and (*c*).

Table 2. *Bond distances* (Å)

Pt–Br(1)	2·485 (4)	Pt–Br(2)	2·445 (2)
Pt–Br(1′)	3·068 (4)	Pt–N	2·066 (17)

Two different aspects of the structural results presented here merit mention:

(i) The axial and equatorial Pt^{IV}–Br distances differ by only 0·04 Å showing, like the Br–Pt^{IV}–Br angles, the almost exact octahedral environment around the Pt^{IV} ions.

(ii) The Pt^{IV}–Br···Pt^{II} alternations are very close to those reported earlier by Hall & Williams (1958), Pt^{IV}–Br = 2·485 (4) Å and Pt^{II}···Br = 3·068 (4) Å. Compared to other 'dicationic' Pt^{IV}–Br···Pt^{II} chains the alternation and the sum of Pt^{IV}–Br and Pt^{II}···Br distances are 'normal' (Keller, 1981). The intense bronze lustre would have suggested less alternation and a shorter Pt^{IV}–Br···Pt^{II} distance (Clark, Kurmoo, Keller, Keppler & Traeger, 1980). Photoelectron spectra could help to clarify this point.

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