

in the observed conformation of KMTNB the 14 π -electron system undergoes only slight deformations. Evidently, the alternative way of relieving steric strain, that is an extensive rotation of the nitro groups with respect to the planar ring, is energetically less favoured, since it would imply a greater decrease in conjugation between the NO₂ groups and the ring.

The displacement of C(4) from plane *A* can be blamed mainly on packing effects. Indeed, the shortest heavy-atom contact within pairs of anions related to one another by centres of symmetry is C(3)···C'(4), 3.266 (2) Å. If the atom C(4) lay on plane *A*, this intermolecular distance would become even more critical, falling below 3.2 Å.

The water molecules are hydrogen bonded to the nitro groups in position 4. The distance O(*W*)···O(4) (at 1 - *x*, 1 - *y*, 1 - *z*) is 2.857 (2) Å, and the O-H···O angle is close to linear [172 (2)°]. The metal ions coordinate eight O atoms in an irregular polyhedron. Metal-oxygen distances lie in the range 2.765–2.990 Å.

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Bis[bromo(diethylenetriamine)platinum(II)] Tetrabromoplatinate(II)

BY R. MELANSON AND F. D. ROCHON

Département de Chimie, Université du Québec à Montréal, CP 8888, Montréal H3C 3P8, Canada

AND J. HUBERT

Département de Chimie, Université de Montréal, CP 6210 Montréal H3C 3V1, Canada

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Abstract. $2[\text{C}_4\text{H}_{13}\text{BrN}_3\text{Pt}]^+ \cdot [\text{Br}_4\text{Pt}]^{2-}$, $[\text{PtBr}(\text{C}_4\text{H}_{13}\text{N}_3)_2][\text{PtBr}_4]$, $M_r = 1271.1$, orthorhombic, $Pna2_1$, $a = 19.720$ (13), $b = 12.638$ (13), $c = 9.416$ (7) Å, $Z = 4$, $V = 2346$ (3) Å³, $D_x = 3.597$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 29.586$ mm⁻¹, $T = 295$ K. The refinement of the positional and thermal parameters, carried out by full-matrix least-squares calculations, converged to $R = 0.048$ and $R_w = 0.054$. The coordination around the platinum atoms is planar. The crystal structure is stabilized by hydrogen bonding.

Introduction. The complex salt $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ (dien = diethylenetriamine) was prepared by the following method. K₂PtCl₄ and an excess of HBr were mixed together in water overnight. The solution was then evaporated to dryness. The residue (K₂PtBr₄) was mixed with $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ in aqueous solution and

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References

- CRAMPTON, M. R. (1969). *Advances in Physical Organic Chemistry*, edited by V. GOLD, Vol. 7, pp. 211–257. New York: Academic Press.
- CRAMPTON, M. R. & GOLD, V. (1964). *J. Chem. Soc.* pp. 4293–4295.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DESTRO, R., GRAMACCIOLI, C. M. & SIMONETTA, M. (1968). *Acta Cryst.* **B24**, 1369–1386.
- FOSTER, R. (1959). *Nature (London)*, **183**, 1042–1043.
- FOSTER, R. & FYFE, C. A. (1965). *Tetrahedron*, **21**, 3363–3372.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GOLD, V. & ROCHESTER, C. H. (1964). *J. Chem. Soc.* pp. 1692–1697.
- MESSMER, G. G. & PALENIK, G. J. (1971). *Acta Cryst.* **B27**, 314–321.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- UEDA, H., SAKABE, N., TANAKA, J. & FURUSAKI, A. (1968). *Bull. Chem. Soc. Jpn*, **41**, 2866–2871.

crystals of $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ were obtained upon evaporation. A set of precession photographs indicated either space group $Pna2_1$ or $Pnam$.

The intensity data were collected from a crystal measuring 0.09 × 0.15 × 0.40 mm, elongated along the *c* axis, on a Syntex P1 diffractometer using graphite-monochromatized Mo *K* α radiation. The data were collected by the $2\theta/\theta$ scan technique (ω scan at half the speed of 2θ), in the region of $2\theta < 50^\circ$ at a variable speed (24 to 1° min⁻¹). Most reflexions were measured at a speed of 1° min⁻¹. The background-time to scan-time ratio was 0.40. The reflexions for which the intensity was less than $3\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as already described (Melanson, Hubert & Rochon, 1975). By this criteria, 1314 out of the 2155 measured reflexions were considered as observed. An absorption correction based on the equations of the

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crystal faces was applied to all the reflexions. The data were then corrected for Lorentz and polarization effects. The scattering factors were those of Cromer & Waber (1965) and the anomalous-dispersion terms (Cromer, 1965) of platinum and bromine were included in the calculations.

A set of normalized structure factors $|E|$ was obtained after isotropic temperature factor correction. Analysis of the $|E|$ statistics ($\langle |E| \rangle = 0.896$, $\langle |E|^2 - 1 \rangle = 0.722$) strongly indicated the non-centrosymmetric space group $Pna2_1$. The three-dimensional Patterson map clearly confirmed the $Pna2_1$ space group, which was used in the subsequent refinement.

The structure was solved using the multiresolution method described by Germain, Main & Woolfson (1970) on 200 reflexions with $|E| \geq 1.50$. The E map calculated with the best set of phases revealed the three platinum and the six bromine atoms.

The refinement of the parameters was made by full-matrix least-squares calculations. In the early stages of refinement, unit weight was assigned to all observed reflexions. Individual weights w , according to the equation $1/w = a + bF_o$, were later calculated. a and b were adjusted to make the distribution of $w|\Delta F_o|^2$ almost constant with respect to $|F_o|$ and $\sin \theta/\lambda$ ($a = 151.0$, $b = -0.23$). An isotropic secondary-extinction correction (Coppens & Hamilton, 1970) was also introduced. The refinement of the scale factor, the coordinates, the anisotropic temperature factors of the heavy atoms and the isotropic temperature factors of the non-

hydrogen light atoms converged to $R = \sum (|F_o| - |F_c|)/\sum |F_o| = 0.048$ and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.054$.* The final difference Fourier map showed a few residual peaks between 1.4 and 2.0 e \AA^{-3} in the platinum positions and their close environments. The density of the crystals was so high that it could not be measured, but the infrared spectrum of the crystals showed the absence of any molecules of solvent.

The refined parameters are given in Table 1. The computer programs have already been described (Melanson, Hubert & Rochon, 1975).

Discussion. The atoms were labelled according to Fig. 1. The structure consists of an arrangement of complex cations $[\text{Pt}(\text{dien})\text{Br}]^+$ and of $[\text{PtBr}_4]^{2-}$ anions.

The bond distances and angles are listed in Table 2. As expected, the coordination around the platinum atoms is square-planar. The angles around the platinum atoms are close to the expected 90 and 180°, but there are some slight deviations in the cations. A slight strain caused by the tridentate ligand is responsible for these deviations from the ideal square-planar coordination of the platinum atom.

The Pt—Br bonds (2.41–2.42 Å) are of normal length (Bokii & Kukina, 1965; Melanson, Hubert & Rochon, 1975). The Pt—N bond lengths (1.95–2.08 Å) are also normal but the standard deviations are very high (0.05–0.06 Å) because of the great number of heavy atoms.

Fig. 2 illustrates the packing in the $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ crystal. The environment of the bromine atoms was examined to locate possible hydrogen bonding to the nitrogen atoms. Br—N distances within a range of 3.3 to 3.6 Å have been suggested for hydrogen bonding of this type (Hamilton & Ibers, 1968). Three short intermolecular contacts with favourable angles were

Table 1. Final positional parameters and estimated standard deviations ($\times 10^4$ for Pt and Br; $\times 10^3$ for N and C)

	x	y	z
Pt(1)	7185 (1)	4581 (2)	2830
Pt(2)	6001 (1)	890 (2)	4495 (4)
Pt(3)	9248 (1)	7934 (2)	3691 (4)
Br(1)	7962 (4)	3098 (6)	2910 (12)
Br(2)	6788 (4)	-237 (7)	3260 (9)
Br(3)	8794 (4)	6384 (6)	4860 (9)
Br(4)	191 (4)	7892 (8)	5341 (11)
Br(5)	8270 (4)	7984 (7)	2143 (10)
Br(6)	9737 (4)	9454 (6)	2526 (11)
N(1)	736 (3)	489 (4)	497 (6)
N(2)	661 (3)	583 (4)	296 (7)
N(3)	698 (3)	455 (4)	74 (6)
N(4)	884 (2)	722 (4)	838 (5)
N(5)	968 (3)	676 (5)	56 (7)
N(6)	933 (3)	475 (4)	91 (6)
C(1)	696 (4)	583 (7)	528 (10)
C(2)	680 (3)	655 (5)	398 (8)
C(3)	659 (5)	634 (8)	143 (12)
C(4)	650 (5)	541 (7)	35 (11)
C(5)	933 (4)	809 (6)	878 (11)
C(6)	-6 (3)	760 (5)	955 (8)
C(7)	26 (4)	599 (6)	97 (9)
C(8)	983 (4)	514 (7)	187 (10)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34063 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

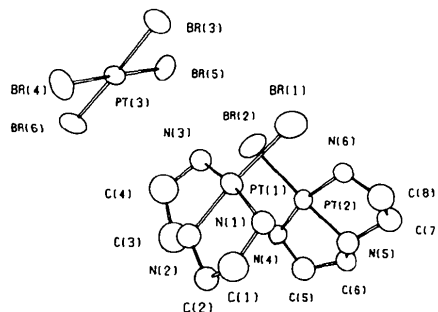


Fig. 1. $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ molecule.

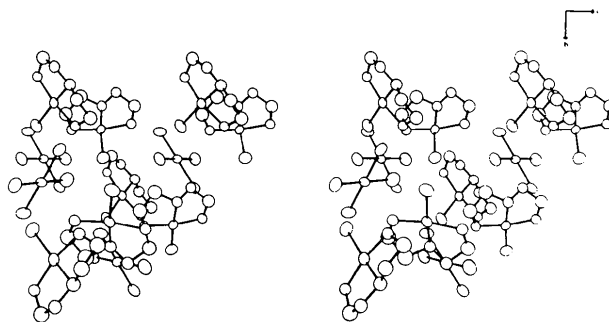
Table 2. Bond distances and bond angles in [Pt(dien)Br]₂[PtBr₄]

Pt(1)—Br(1)	2.421 (8) Å	Br(3)—Pt(3)—Br(4)	88.6 (3)°
Pt(2)—Br(2)	2.408 (9)	Br(3)—Pt(3)—Br(5)	90.0 (3)
Pt(3)—Br(3)	2.418 (8)	Br(3)—Pt(3)—Br(6)	178.2 (3)
Pt(3)—Br(4)	2.424 (10)	Br(4)—Pt(3)—Br(5)	177.2 (3)
Pt(3)—Br(5)	2.418 (9)	Br(4)—Pt(3)—Br(6)	90.1 (3)
Pt(3)—Br(6)	2.414 (9)	Br(5)—Pt(3)—Br(6)	91.4 (3)
Pt(1)—N(1)	2.08 (5)	Br(1)—Pt(1)—N(1)	90.4 (15)
Pt(1)—N(2)	1.95 (5)	Br(1)—Pt(1)—N(2)	173.5 (17)
Pt(1)—N(3)	2.01 (6)	Br(1)—Pt(1)—N(3)	98.1 (16)
Pt(2)—N(4)	2.01 (5)	Br(2)—Pt(2)—N(4)	98.3 (14)
Pt(2)—N(5)	2.01 (6)	Br(2)—Pt(2)—N(5)	176.9 (17)
Pt(2)—N(6)	2.07 (5)	Br(2)—Pt(2)—N(6)	95.9 (14)
N(1)—C(1)	1.47 (10)	N(1)—Pt(1)—N(2)	84 (2)
N(2)—C(2)	1.38 (9)	N(1)—Pt(1)—N(3)	170 (2)
N(2)—C(3)	1.57 (12)	N(2)—Pt(1)—N(3)	88 (2)
N(3)—C(4)	1.49 (11)	N(4)—Pt(2)—N(5)	85 (2)
N(4)—C(5)	1.50 (9)	N(4)—Pt(2)—N(6)	166 (2)
N(5)—C(6)	1.50 (9)	N(5)—Pt(2)—N(6)	81 (2)
N(5)—C(7)	1.54 (10)	Pt(1)—N(1)—C(1)	105 (4)
N(6)—C(8)	1.42 (10)	Pt(1)—N(2)—C(2)	115 (4)
C(1)—C(2)	1.56 (11)	Pt(1)—N(2)—C(3)	107 (5)
C(3)—C(4)	1.56 (14)	Pt(1)—N(3)—C(4)	111 (5)
C(5)—C(6)	1.52 (11)	Pt(2)—N(4)—C(5)	112 (4)
C(7)—C(8)	1.60 (12)	Pt(2)—N(5)—C(6)	107 (4)
		Pt(2)—N(5)—C(7)	106 (4)
		Pt(2)—N(6)—C(8)	113 (4)
		N(1)—C(1)—C(2)	116 (6)
		N(2)—C(2)—C(1)	103 (6)
		N(2)—C(3)—C(4)	107 (7)
		N(3)—C(4)—C(3)	108 (7)
		N(4)—C(5)—C(6)	109 (6)
		N(5)—C(6)—C(5)	109 (6)
		N(5)—C(7)—C(8)	100 (6)
		N(6)—C(8)—C(7)	105 (6)
		C(2)—N(2)—C(3)	112 (6)
		C(6)—N(5)—C(7)	112 (5)

noted (Table 3). One amino group of each dien is hydrogen bonded to [PtBr₄]²⁻, N(1)—H...Br(5) and N(6)—H...Br(4). The second amino group of one dien is hydrogen bonded to the bromine atom of the other cation, N(3)—H...Br(2). All the Br...Br distances are equal to or greater than the van der Waals distance (3.9 Å) except of course the intramolecular distances within the [PtBr₄]²⁻ ion.

Table 3. Distances and angles of atoms involved in hydrogen bonds

	Distance (Å)		Transformation on Br
	N...Br	Angle (°)	
C(1)—N(1)...Br(5)	3.40 (5)	105 (4)	x, y, z + 1
Pt(1)—N(1)...Br(5)		113 (2)	
C(4)—N(3)...Br(2)	3.37 (5)	104 (4)	x, y, z
Pt(1)—N(3)...Br(2)		122 (2)	
C(8)—N(6)...Br(4)	3.52 (5)	104 (4)	½ + x, ½ - y, z
Pt(2)—N(6)...Br(4)		130 (2)	

Fig. 2. Packing in the [Pt(dien)Br]₂[PtBr₄] crystal.

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References

- BOKII, G. B. & KUKINA, G. A. (1965). *J. Struct. Chem. (USSR)*, **5**, 670–677.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 15. New York: Benjamin.
- MELANSON, R., HUBERT, J. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.