

Fig. 2. Projection of the structure onto the *bc* plane.

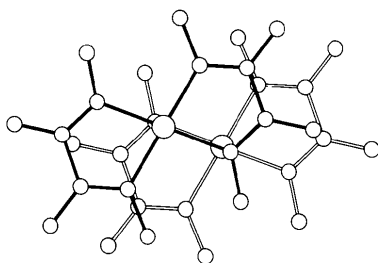


Fig. 3. Perpendicular projection of two adjacent molecules of a stack onto each other.

compared with  $82.2(2)^\circ$  in the Ni compound. As usual the intramolecular hydrogen bridge is considerably longer in the Pd complex [ $2.75(1) \text{ \AA}$ ] than in the Ni analogue [ $2.57(1) \text{ \AA}$ ].

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## Structure of Bis(ethylenediamine)diiodoplatinum(IV) Di- $\mu$ -iodo-bis[diiodoargentate(I)]

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**Abstract.**  $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2\text{I}_2]_2[\text{Ag}_2\text{I}_6]$ ,  $M_r = 2115.34$ , orthorhombic, *Fddd*,  $a = 15.576(3)$ ,  $b = 18.451(3)$ ,  $c = 24.645(4) \text{ \AA}$ ,  $V = 7082.79 \text{ \AA}^3$ ,  $Z = 8$ ,  $d_c = 3.96 \text{ Mg m}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 17.690 \text{ mm}^{-1}$ . The structure has been solved by Patterson and Fourier methods from diffractometer data and refined to  $R = 0.038$  for 1465

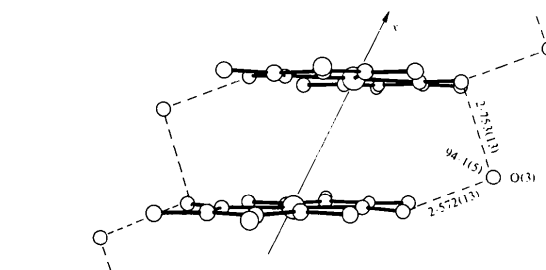


Fig. 4. Perspective view of two molecules of a stack showing the hydrogen-bonded water O atoms which lead to a ladder-like structure (distances in  $\text{ \AA}$ , angle in  $^\circ$ ).

The water molecule is attached by hydrogen bridges to oxime O atoms of adjacent molecules of a stack. This leads to a ladder-like structure, a section of which is shown in Fig. 4.

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Keller, Martin & Traeger, 1979), Pt(en)<sub>2</sub>Cl<sub>4</sub> (en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) was partially reduced by KI in an AgI/KI mixture. In detail 140 g KI were dissolved in 375 ml of water and heated to 363 K. A hot 363 K solution of 0.5 mmol Pt(en)<sub>2</sub>Cl<sub>4</sub> in 50 ml of water was added dropwise under stirring. The color of the solution turns brown because of the formation of molecular iodine. A boiling solution of 1 mmol freshly precipitated AgI in 50 ml of an aqueous half-concentrated KI solution was added immediately afterwards. The clear red-brown solution was cooled down slowly overnight. An analysis of the product of this reaction yielded the formula Ag<sub>5</sub>Pt<sub>3</sub>(en)<sub>6</sub>I<sub>14</sub>, but a closer examination of the substance revealed two kinds of crystals: long dichroic and lustrous needles, which are probably the Wolfram's salt analogue, and some small distorted octahedra. As there were not enough octahedral crystals for an analysis, an X-ray structure determination was carried out.

Preliminary cell parameters and systematic extinctions were derived from precession photographs. The cell parameters were refined with the setting angles of 25 reflections centered on a Syntex R3 diffractometer, which was also used for the data collection. Reflections in the range 3° ≤ 2θ ≤ 60° were measured by a θ/2θ scan (graphite monochromator, Mo Kα radiation). Empirical absorption corrections (crystal size 0.2 × 0.1 × 0.1 mm) were applied. For 39 of the 1504 measured reflections σ<sub>t</sub> (based on counting statistics) was greater than the intensity. These reflections were considered unobserved and not included in the refinement.

As the composition of the crystals was not known, the Patterson map was searched for short vectors, which could be assigned to intramolecular bonds. Some strong maxima could be interpreted as an I—Pt—I group. A difference Fourier map based on these atoms revealed the remaining atoms, other than H. The structure was refined by least-squares methods. The weight *w* was set equal to σ<sub>F</sub><sup>-2</sup>. The final *R* values were (Pt, I, Ag anisotropic; N, C isotropic): for the 1465 observed reflections, *R* = 0.038, *R*<sub>w</sub> = 0.036; and for all 1504 reflections, *R* = 0.039.

Table 1. Atomic coordinates and isotropic thermal parameters with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
Pt	0.375	0.375	0.11189 (2)	0.0163
Ag	0.25024 (10)	0.625	0.125	0.0389
I(1)	0.24153 (5)	0.28487 (6)	0.11200 (3)	0.0337
I(2)	0.125	0.50738 (6)	0.125	0.0260
I(3)	0.35372 (5)	0.62273 (5)	0.21928 (3)	0.0325
N(1)	0.4302 (7)	0.3167 (6)	0.0490 (4)	0.026 (2)
N(2)	0.3221 (7)	0.4342 (6)	0.1754 (4)	0.024 (1)
C(1)	0.3876 (11)	0.3339 (8)	-0.0035 (6)	0.041 (3)
C(2)	0.3693 (10)	0.4165 (6)	0.2267 (5)	0.025 (3)

Table 2. Distances (Å) and angles (°) in [Pt(en)<sub>2</sub>I<sub>2</sub>]<sub>2</sub>[Ag<sub>2</sub>I<sub>6</sub>]

The numbering is as shown in Figs. 1 and 2.

Pt—N(1)	2.073 (10)	N(1)—Pt—N(1)'	83.2 (6)
Pt—N(2)	2.079 (10)	N(2)—Pt—N(2)'	82.3 (6)
Pt—I(1)	2.662 (1)	I(2)—Ag—I(2)'	96.10 (6)
Ag—I(2)	2.918 (1)	Ag—I(2)—Ag'	83.90 (6)
Ag—I(3)	2.828 (1)	I(2)—Ag—I(3)	111.71 (2)
Ag—Ag'	3.902 (3)	I(2)—Ag—I(3)'	113.08 (2)
N(1)—C(1)	1.49 (2)	I(3)—Ag—I(3)'	110.51 (5)
C(1)—C(1)'	1.57 (3)	Pt—N(1)—C(1)	110.7 (8)
N(2)—C(2)	1.50 (2)	N(1)—C(1)—C(1)'	108.6 (9)
C(2)—C(2)'	1.55 (2)	Pt—N(2)—C(2)	109.1 (8)
		N(2)—C(2)—C(2)'	105.8 (9)

Scattering factors were taken from the tables of Cromer & Mann (1968). For Pt, I, and Ag the dispersion corrections (Cromer & Liberman, 1970) were included. Coordinates are listed in Table 1,\* distances and angles in Table 2.

**Discussion.** The structure is built up by [Pt(en)<sub>2</sub>I<sub>2</sub>]<sup>2+</sup> and [Ag<sub>2</sub>I<sub>6</sub>]<sup>4-</sup> units. Intermolecular distances shorter than the sum of the corresponding van der Waals radii exist only between the [Pt(en)<sub>2</sub>I<sub>2</sub>]<sup>2+</sup> cations, which are connected by weak I...I contacts (3.69 Å) forming zig-zag chains along the *a* axis. A similar I—I bridge was found in bis(butyl dithiocarbamate)platinum diiodide (I—I 3.729 Å, Willemsse, Cras, Wijnhoven & Beurskens, 1973). The Pt atom has a distorted octahedral coordination with the two I atoms in a *trans* position (Fig. 1). The distances and angles have the expected values and the configuration of the cation is in good agreement with that in [Pt(en)<sub>2</sub>I<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O (Freckmann & Tebbe, 1981).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36673 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

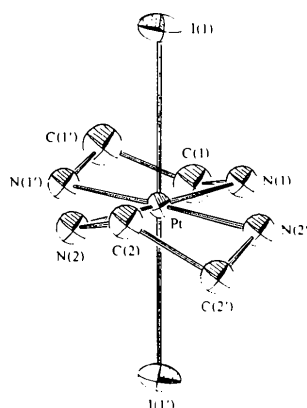


Fig. 1. ORTEP (Johnson, 1965) plot of the [Pt(en)<sub>2</sub>I<sub>2</sub>]<sup>2+</sup> cation.

As the [Ag<sub>2</sub>I<sub>6</sub>]<sup>4-</sup> anion has no intermolecular distance shorter than 4.3 Å, it may be characterized as an isolated di- $\mu$ -iodo-bis[diiodoargentate(I)], which consists of two AgI<sub>4</sub> tetrahedra sharing a common edge (Fig. 2). In all known structures of iodoargentates the Ag atom is tetrahedrally coordinated by four I atoms, but the tetrahedra are connected over common corners, edges or planes building polymeric chains, layers or three-dimensional networks (Gilmore, Tucker & Woodward, 1971, and references therein; Coetzer, 1975; Coetzer & Thackeray, 1975; Thackeray & Coetzer, 1975*a*,*b*, 1978, and references therein; Geller, 1972; Geller & Dudley, 1978; Geller, Skarstad & Wilber, 1975). Structures with isolated iodoargentates have not yet been reported, though the existence of Ag<sub>2</sub>I<sub>6</sub><sup>4-</sup> in melts has been postulated by Holmberg (1973). The connection of the two tetrahedra in [Ag<sub>2</sub>I<sub>6</sub>]<sup>4-</sup> causes a distortion of the tetrahedral coordination around Ag with the angle I(2)–Ag–I(2)' becoming much smaller than the others. The bridging Ag–I distance is longer than the terminal ones. These features are found for other M<sub>2</sub>X<sub>6</sub> metal halides. The Ag–I distances lie in the range found for polymeric structures. The calculation of the bond-valence sum for Ag (Brown, Howard-Lock & Natarajan, 1977) yielded a value somewhat too small (0.93 instead of 1.00), again comparable to polymeric iodoargentates with values in the range 0.9 to 1.0.

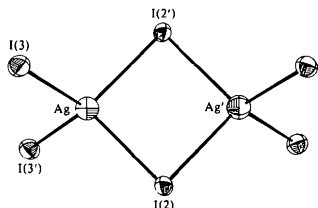


Fig. 2. ORTEP plot of the [Ag<sub>2</sub>I<sub>6</sub>]<sup>4-</sup> anion.

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## Bis[ $\mu$ -(2-methylaminopyridine 1-oxide)- $\mu$ -O]-bis[dichloro(2-methylaminopyridine 1-oxide)copper(II)]

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**Abstract.** [Cu<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O)<sub>4</sub>Cl<sub>4</sub>], C<sub>24</sub>H<sub>32</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>4</sub>, *M<sub>r</sub>* = 765.4, triclinic, *P*1, *a* = 11.0483 (11), *b* = 9.2975 (9), *c* = 9.4998 (9) Å,  $\alpha$  = 124.61 (1),  $\beta$  = 92.85 (1),  $\gamma$  = 99.26 (1)°, at 298 K, *Z* = 1, *D<sub>m</sub>* =

1.63 (2), *D<sub>c</sub>* = 1.628 Mg m<sup>-3</sup>. The structure was solved by a combination of direct methods and Fourier synthesis techniques which led to a conventional *R* of 0.041 for the 255 parameters varied and 2147