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A Hydrogen-Bridged Dimeric Stacked Structure in a Dioximato Complex: (Oxamide oximato)(oxamide oxime)platinum(II) Iodide Dihydrate, $[Pt(C_2H_5N_4O_2)(C_2H_6N_4O_2)]I.2H_2O$

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Abstract. $M_r = 593{\cdot}21$, triclinic, $P\bar{1}$, $a = 7{\cdot}116\ (1)$, $b = 9{\cdot}424\ (2)$, $c = 11{\cdot}848\ (3)$ Å, $\alpha = 71{\cdot}95\ (2)$, $\beta = 89{\cdot}06\ (2)$, $\gamma = 70{\cdot}98\ (2)°$, $V = 711$ Å^3, $Z = 2$, $D_x = 2{\cdot}77$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 115{\cdot}5$ cm^{-1}, $F(000) = 548$, room temperature, final $R = 0{\cdot}049$ for 4720 observed reflections. Strong intermolecular H bridges [$O\cdots O = 2{\cdot}74\ (2)$ Å] lead to phane-like deviations of the complex cations from planarity and to pronounced pairing of the complexes in the stacks. The shortest intrastack Pt—Pt separation is 3·241 (5) Å. Further intra- and interstack H bridges involve the water molecules. Pt—N bond lengths are 1·971 (6)–2·006 (6) Å.

Introduction. Dioximato complexes of the d^8 metal ions of the Ni triad are normally planar, forming stacks of equally spaced molecules in the solid state. One of two stacking modes is usually observed (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977): In the '*M*—*M* form' the stacking axis is perpendicular to the molecular planes, the metal atoms are in close contact along the stacks, and adjacent complexes of a stack are rotated with respect to each other, probably for steric reasons. Consequently, the unit-cell length along the stacking axis comprises two metal—metal separations. It had been proposed that an attractive metal—metal interaction stabilizes this form (Endres *et al.*, 1977), but recent theoretical work contradicts this assumption (Böhm, 1983), at least for Ni complexes. The highest occupied molecular orbital is considered to be ligand centred, and partial reduction (rather than partial oxidation) may lead to increased electronic conductivity along the stacks (Alvarez & Canadell, 1984). In the '*M*–*L* form' the stacking direction is inclined to the molecular plane, there are no direct metal—metal contacts, and the unit-cell length equals one metal—metal distance.

The complexes of oxamide oxime ['diaminoglyoxime, oaoH$_2$', HON=C(NH$_2$)—C(NH$_2$)=NOH], however, often differ from this simple behaviour: The mesomeric effect of the free electron pair of the amino groups enhances the basicity of the oxime O atoms, giving them a pronounced capability of forming strong intermolecular H bonds. The amino groups tend to be involved in H bridges as well. Such intermolecular H bridges lead to a rich structural chemistry in the solid state (Endres, 1980, 1982*a*,*b*) and allow the synthesis of new molecular electron conductors (Endres, Bongart, Nöthe, Hennig, Schweitzer, Schäfer, Helberg & Flandrois, 1985). The title compound is another example of the unusual stacking patterns found in oxamide oximato complexes.

Experimental. Preparation: [Pt(oaoH$_2$)$_2$]Cl$_2$ (Endres & Schlicksupp, 1980) dissolved in boiling H$_2$O, diluted HI solution added, slow cooling to room temperature, long (≈ 10 mm) dark-red column-like crystals filtered off after three days.

Section of a column, 0·15 × 0·19 × 0·23 mm, mounted on end of glass capillary; lattice parameters from setting angles of 50 reflections (Siemens–Stoe AED2 diffractometer, monochromated Mo $K\alpha$ radiation);

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θ–2θ scans; $2\theta \leq 65°$; 5377 reflections measured; index range −10, −13, 0 to 10, 13, 17; 2 check reflections every 3 h, intensity variation ±3·5%; empirical absorption correction using ψ scans of 8 reflections with $9{\cdot}6° < 2\theta < 45{\cdot}9°$, min. transmission 0·42 (max. = unity); equivalent reflections merged ($R_{\rm int} = 0{\cdot}025$); 5088 unique reflections, 4720 observed with $I > 2{\cdot}5\sigma(I)$. Pt position from Patterson map, other non-H atoms from Fourier maps, H positions not determined; refinement by blocked-matrix least squares based on F; $w = 1/\sigma^2(F)$; all atoms anisotropic; 181 parameters, $wR = 0{\cdot}066$, $R = 0{\cdot}049$, $S = 5{\cdot}71$; max. $\Delta/\sigma = 0{\cdot}08$; largest features in final difference Fourier map +1·69 and −3·7 e Å^{-3} (close to I and Pt); *STRUCSY* (1984) program system on an Eclipse computer; scattering factors including anomalous dispersion from *International Tables for X-ray Crystallography* (1974); plots on a Tektronix plotter using *SHELXTL* (Sheldrick, 1983) on a Nova 3 computer.

Discussion. Atom coordinates are listed in Table 1;* Fig. 1 shows the numbering scheme and bond distances and angles in the $[Pt(oaoH)(oaoH_2)]^+$ complex cation. As usual for these monopositive complex species the molecule is not centrosymmetric, as only one intramolecular H bond, O(1)···O(4), is found (see Fig. 1), as, for example, in $[Pt(oaoH_2)_2]^{2+}\{[Pt(oaoH)(oaoH_2)]^+\}_2$-$(SO_4^{2-})_2.8H_2O$ (Endres, 1982*c*). Furthermore, the cation exhibits an unusually large deviation from planarity: The dihedral angle between the two planes through Pt and each of the chelate rings is 7 (1)°. The reason for this becomes evident from Fig. 2, which shows the stacking of the complex cations along **a**, They are 'clamped' together in pairs by intermolecular H bridges between the oxime O(1) and O(3) atoms of adjacent complexes. (Although the H positions could not be determined directly, H bridges are evident from the interatomic distances.) These H bridges cause the bending of the cations (and lead to a short Pt—Pt separation), giving the pair of molecules a cyclophane-like appearance. The linking of these diads into stacks occurs *via* H bridges involving the O(5) water molecules. Geometrical information is included in Fig. 2.

Similar features are never observed in complexes of other dioximes where the tendency to form intermolecular H bridges is much less pronounced. Some other oxamide oxime complexes, however, show analogous behaviour: Intermolecular H bridges perpendicular to the molecular planes occur within the triples of the triadic stacks of a compound containing

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3) *equivalent to the refined anisotropic values*

$U_{\rm eq} = \frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Pt	2801·8 (4)	−135·4 (3)	220·6 (2)	17·1 (1)
I	8247 (1)	3504·7 (9)	4358·2 (6)	37·9 (4)
O(1)	1331 (9)	2161 (6)	−2162 (5)	33 (3)
O(2)	4047 (10)	−3706 (6)	671 (5)	37 (3)
O(3)	4925 (9)	−2177 (6)	2731 (5)	32 (3)
O(4)	1251 (11)	3384 (7)	−478 (6)	38 (3)
N(1)	1801 (9)	605 (7)	−1475 (6)	26 (2)
N(2)	3164 (10)	−2166 (7)	−92 (5)	27 (3)
N(3)	3816 (10)	−680 (7)	1924 (5)	25 (2)
N(4)	2157 (10)	1970 (7)	449 (6)	26 (3)
N(5)	993 (13)	−104 (9)	−3115 (7)	39 (4)
N(6)	2593 (12)	−3341 (8)	−1480 (7)	35 (4)
N(7)	4161 (12)	319 (9)	3467 (7)	37 (4)
N(8)	2093 (12)	3433 (9)	1705 (7)	38 (4)
C(1)	1715 (11)	−428 (9)	−1974 (7)	26 (3)
C(2)	2519 (11)	−2064 (8)	−1159 (7)	25 (3)
C(3)	3524 (11)	486 (8)	2347 (7)	27 (3)
C(4)	2501 (11)	2068 (8)	1471 (7)	27 (3)
O(5)*	2554 (11)	5948 (8)	2693 (6)	40 (3)
O(6)*	3564 (14)	2608 (8)	4586 (7)	56 (4)

* Water O atoms.

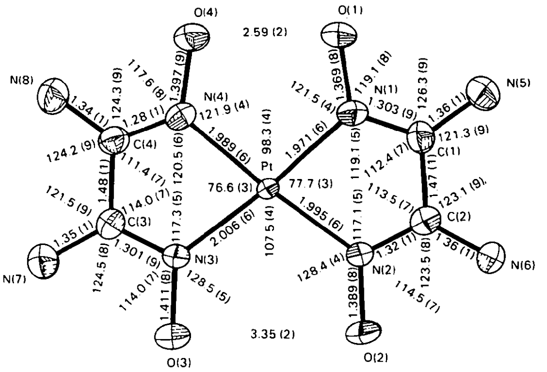

Fig. 1. The $[Pt(oaoH)(oaoH_2)]^+$ complex cation with bond distances (Å) and angles (°). Thermal contours are at 50% probability.

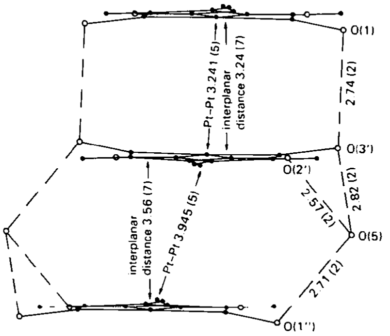

Fig. 2. Section of a stack along **a** with relevant distances (Å). The complex cations are related in pairs by inversion centres, the top and bottom molecules by a unit-cell translation **a**. Interplanar distances refer to the planes through the four oxime N atoms.

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* Lists of structure factors, anisotropic thermal parameters and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42139 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[Pt(oaoH)$_2$] (Endres, 1980). No bending of the molecules is observed in this case, as there is only one H bridge between each pair of molecules. H bridges *via* water molecules, leading to a ladder-like structure, are found in the regular stacks of M(oaoH)$_2$.2H$_2$O, M = Ni or Pd (Endres, 1982*a*).

As in some other complexes it is not possible to discriminate between 'M—M' and 'M—L' forms. The arrangement between adjacent pairs of H-bonded dimers, with the long metal–metal distance, is reminiscent of the M—L type of stacking, while the geometry within a dimer is different from the usual M—M pattern, despite the short Pt—Pt distance. There is no twist of adjacent complexes relative to each other and the molecules are nearly eclipsed. The Pt—Pt vector makes an angle of 9·9 (5)° with respect to the normal of the plane through Pt and the four coordinated N atoms. A perpendicular projection of the two molecules of a dimer (Fig. 3, deposited) reveals that it is not an attractive Pt—Pt interaction which leads to the observed arrangement, but the link between the H-bridged O(1) and O(3) atoms of adjacent complexes. The other atoms tend to avoid close intermolecular interactions as far as possible, without losing the bonding O(1)···O(3) contacts.

Further H bridges link the stacks in the other two dimensions (Fig. 4). In the y direction these bridges involve amino and oxime groups, in the z direction the bridging occurs *via* O(6) water molecule.

From a chemical point of view it is interesting to note that the treatment with iodine-containing HI solution does not lead to oxidation of the complex.

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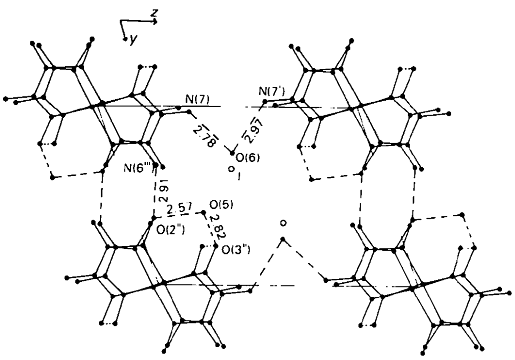

Fig. 4. Parallel projection of the structure along **a** showing probable intermolecular H bridges. The corresponding distances are given, e.s.d. 0·02 Å. Symmetry operations are: (i) $1-x$, $-y$, $1-z$; (ii) x, $1+y$, z; (iii) $1-x$, $-y$, $-z$.

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Structure of an Organoamidoplatinum(II) Compound

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Abstract. Chloro[*N*,*N*-dimethyl-*N'*-(2,3,5,6-tetrafluorophenyl)-1,2-ethanediaminato(1−)]pyridineplatinum(II), [PtCl($C_{10}H_{11}F_4N_2$)(C_5H_5N)], $M_r = 544·85$, triclinic, $P\bar{1}$, $a = 12·296$ (2), $b = 13·014$ (1), $c = 5·679$ (1) Å, $\alpha = 91·88$ (2), $\beta = 111·74$ (1), $\gamma = 96·23$ (1)°, $V = 836·5$ Å^3, $Z = 2$, $D_m = 2·16$ (2), $D_x = 2·16$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 8·26$ mm^{-1}, $F(000) = 516$, $T = 293$ K. Final $R = 0·037$ for 3798 counter reflections. The structure consists of molecules of the title compound in which approximately square-planar Pt$^{\text{II}}$ is

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