

## Bis(oxamide oxime)platinum(II) Bis(perchlorate) Dihydrate

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**Abstract.**  $[\text{Pt}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{C}_4\text{H}_{12}\text{N}_8\text{O}_4\text{Pt}^{2+} \cdot 2\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$ ,  $M_r = 666.22$ , is triclinic,  $P\bar{1}$ , with  $a = 7.780$  (4),  $b = 10.010$  (3),  $c = 12.919$  (8) Å,  $\alpha = 105.08$  (4),  $\beta = 102.75$  (4),  $\gamma = 103.15$  (4)°,  $V = 903.1$  Å<sup>3</sup>,  $Z = 2$ ,  $d_c = 2.45$  Mg m<sup>-3</sup>. Final  $R = 0.029$  for 2496 rapidly collected (within 12.5 h) diffractometer data. The complex cations form diadic stacks along **a**, connected by a network of H bridges involving the water molecules and the perchlorate ions.

**Introduction.** Recently we have shown (Endres & Weiss, 1981, and references cited therein) that the structural chemistry of complexes of oxamide oxime (diaminoglyoxime,  $\text{oaoH}_2$ ) with the metals of the Ni triad is very variable. This variability is caused by the amino groups, the influence of which is twofold: Firstly, they can help to fix additional molecules by forming H bridges, and secondly they reduce the acidity of the oxime H atoms by a mesomeric effect. As a consequence of this, charged complexes which have lost less than one H atom per dioxime ligand are formed readily. The positively charged complex species usually do not exhibit the two intramolecular H bridges otherwise common in bis(dioximato) metal complexes. The title compound is a further member in the family of positively charged oxamide oxime complexes of the Ni triad.

$\text{Pt}(\text{oaoH}_2)_2\text{Cl}_2$  is converted to  $\text{Pt}(\text{oaoH})_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$  when recrystallized from water. The dissolution of the dichloride is facilitated by adding a small quantity of perchloric acid. The title compound was obtained as yellow crystals when the mother liquid of such a recrystallization was allowed to evaporate on standing. These crystals are stable in dry air, but they decompose and develop a red color when they come in contact with moisture or are exposed to moist air. To avoid decomposition a rapid data collection was performed, a procedure inspired by a recent paper by Hope & Nichols (1981).

A block-like crystal mounted on top of a glass capillary was used for the investigation. Lattice parameters were derived from the setting angles of 13 reflections centered on a Syntex R3 diffractometer,

operating with monochromatic Mo  $K\alpha$  radiation. Data collection by fast  $\omega$  scans, background-peak-background, yielded 2496 observed  $[I > 2\sigma(I)]$  out of 2667 possible independent reflections with  $2\theta \leq 50^\circ$  within 12.5 h. They were corrected empirically ( $\psi$  scans) for absorption effects. Data collection was carried out at room temperature. The reflections were processed in the usual way by subtracting local background from the gross intensity.

The Pt position was taken from a Patterson synthesis. Subsequent Fourier syntheses revealed the positions of the other non-H atoms. Refinement with anisotropic temperature factors by 'cascade matrix' least squares gave a weighted (unweighted)  $R$  of 0.029 (0.031).\* A difference Fourier map revealed the positions of eleven out of sixteen H atoms; only the oxime hydrogen and one H atom of an amino group did not show up.

Inserting the detected H positions lowered  $R_w$  to 0.028, but as not all of the positions could be located, all H atoms were omitted in the final calculations. The weighting scheme was  $w = 1/\sigma^2(F)$ .

Calculations were carried out on a NOVA 3 computer, plots were drawn on a Tektronix plotter. The program package was *SHELXTL* (Sheldrick, 1979), which uses atomic scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account.

**Discussion.** Atomic coordinates are listed in Table 1. Fig. 1 shows the numbering scheme, bond distances and angles in the complex molecule. Table 2 contains the bond distances and angles of the perchlorate ions. The complex molecule is essentially planar, the mean (maximum) deviation of an atom from the least-squares plane is 0.05 Å [0.2 Å for O(2)]. The Pt complexes are arranged into stacks parallel to **a**, where adjacent

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36584 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

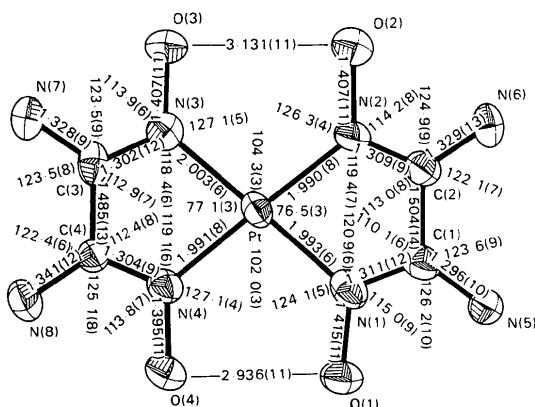


Fig. 1. The complex molecule with bond distances (Å) and angles (°). Thermal ellipsoids are at 50% probability.

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^3$ ) equivalent to the refined anisotropic values

$U_{\text{eq}}$  is defined as  $U_{\text{eq}} = \frac{1}{3} \text{trace } \tilde{U}$ ,  $\tilde{U}$  signifying the diagonalized  $U$  matrix.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ (Å <sup>2</sup> )
Pt	3804.1 (5)	244.6 (4)	11065.0 (3)	27.6 (1)
N(1)	5871 (11)	1995 (8)	12086 (6)	37 (3)
N(2)	4822 (10)	-376 (8)	12352 (6)	36 (3)
N(3)	1713 (11)	-1495 (8)	10026 (6)	39 (5)
N(4)	2815 (10)	923 (8)	9805 (6)	33 (3)
N(5)	8159 (12)	3094 (9)	13804 (6)	51 (4)
N(6)	6949 (12)	278 (9)	14126 (6)	53 (4)
N(7)	-629 (11)	-2501 (9)	8334 (6)	47 (4)
N(8)	695 (11)	319 (9)	8027 (6)	44 (4)
O(1)	6448 (9)	3280 (6)	11824 (5)	45 (3)
O(2)	4324 (10)	-1790 (7)	12413 (5)	56 (3)
O(3)	965 (10)	-2773 (7)	10246 (6)	56 (3)
O(4)	3471 (10)	2283 (7)	9698 (5)	52 (3)
C(1)	6822 (14)	2012 (10)	13065 (7)	39 (4)
C(2)	6170 (13)	559 (10)	13215 (7)	36 (4)
C(3)	762 (13)	-1409 (10)	9093 (7)	34 (4)
C(4)	1446 (12)	20 (9)	8946 (7)	31 (4)
Cl(1)	9856 (3)	3417 (3)	7168 (2)	41 (1)
O(5)	10013 (11)	4041 (8)	6302 (5)	63 (4)
O(6)	9158 (12)	4258 (9)	7958 (6)	76 (4)
O(7)	11636 (10)	3388 (9)	7756 (6)	72 (4)
O(8)	8613 (10)	1939 (7)	6672 (6)	59 (3)
Cl(2)	2930 (4)	2634 (3)	4604 (2)	49 (1)
O(9)	2751 (13)	4044 (9)	4829 (9)	97 (5)
O(10)	1249 (13)	1659 (10)	4637 (9)	106 (6)
O(11)	3140 (13)	2162 (14)	3531 (7)	121 (7)
O(12)	4481 (12)	2580 (10)	5395 (7)	88 (5)
O(13)	6804 (10)	4449 (8)	9829 (6)	63 (4)
O(14)	4630 (12)	5075 (10)	12451 (7)	100 (5)

molecules are related by inversion centers midway between the Pt sites. Two different overlap patterns occur alternately along a stack, so the stacks may be termed 'diadic'. These two modes of overlap are shown in Figs. 2 and 3. The two interplanar distances ( $\sim 3.4$  Å) are practically identical.

Table 2. Bond distances (Å) and angles (°) in the perchlorate ions

Cl(1)—O(5)	1.431 (9)	Cl(2)—O(9)	1.411 (10)
O(6)	1.432 (10)	O(10)	1.460 (10)
O(7)	1.435 (8)	O(11)	1.403 (9)
O(8)	1.454 (6)	O(12)	1.420 (9)
O(5)—Cl(1)—O(6)	110.3 (5)	O(9)—Cl(2)—O(10)	108.4 (6)
O(7)	110.1 (5)	O(11)	109.7 (8)
O(8)	109.5 (4)	O(12)	112.1 (5)
O(6)—Cl(1)—O(7)	108.4 (5)	O(10)—Cl(2)—O(11)	109.0 (6)
O(8)	109.6 (5)	O(12)	109.3 (6)
O(7)—Cl(1)—O(8)	109.0 (5)	O(11)—Cl(2)—O(12)	108.3 (6)

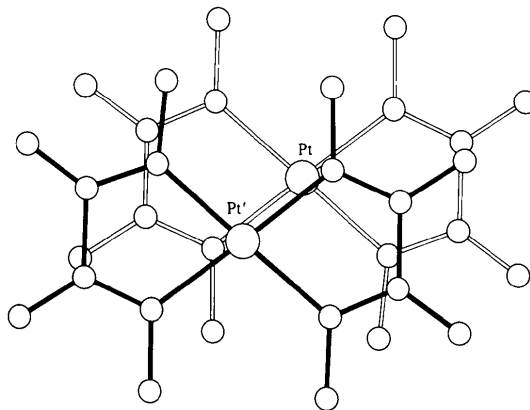


Fig. 2. Perpendicular projection of two complex molecules of a stack, related by the inversion center 0.5, 0. Pt is at 0.38, 0.02, 1.11, Pt' at 0.62, -0.02, 0.89.

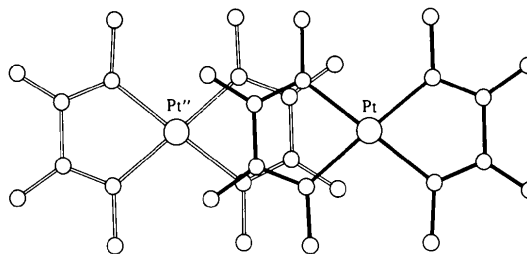


Fig. 3. Perpendicular projection of two adjacent complex molecules related by the inversion center at 0, 0, 1. Pt is at 0.38, 0.02, 1.11, Pt'' at -0.38, -0.02, 0.89.

The composition of the compound implies that the complex molecules are dipositive ions with all four oxime H atoms present. In such a case the otherwise typical intramolecular H bridges are usually not formed. The long O—O distances support this idea. The yellow color is also in agreement with a formulation of the complex cation as  $[\text{Pt}(\text{oaoH}_2)_2]^{2+}$ , as the oxamide oxime complexes of Pt<sup>II</sup> become orange and finally red when the charge is reduced.

The structure is held together by an extended network of H-bonding interactions, as illustrated in Fig. 4. To make this H-bonding network more evident,

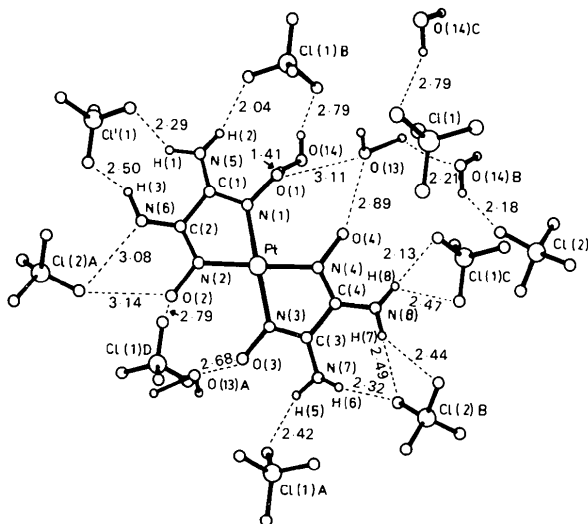


Fig. 4. A complex cation and surrounding perchlorate ions and water molecules showing possible H-bonding interactions. Where H positions could be found on a difference Fourier map, unrefined H to heavy atom distances are indicated, otherwise the corresponding heavy atom to heavy atom distances. Standard deviations for the heavy atoms may be estimated from Fig. 1. The coordinates of the complex molecule are those of Table 1. Round-off coordinates for the other molecules are: Cl(1) 0.98, 0.34, 0.72; Cl'(1) 0.98, 0.34, 1.72; Cl(1)A -0.02, -0.66, 0.72; Cl(1)B 1.02, 0.66, 1.28; Cl(1)C -0.02, 0.34, 0.72; Cl(1)D 0.02, -0.34, 1.28; Cl(2) 0.29, 0.26, 0.46; Cl(2)A 0.71, -0.26, 1.54; Cl(2)B -0.29, -0.26, 0.54; O(13) 0.68, 0.44, 0.98; O(13)A 0.32, -0.44, 1.02; O(14) 0.46, 0.50, 1.24; O(14)B 0.54, 0.50, 0.76; O(14)C 1.54, 0.50, 0.76. (Distances are in Å.)

those H positions which could be found on a difference Fourier map are included, even if they were not considered in the final refinement. The figure shows a complex cation and the surrounding perchlorate ions and water molecules which exhibit possible H-bonding interactions. The oxime groups in particular have remarkably short distances to water or perchlorate O atoms, indicating strong H bonding, e.g. O(2)-O(8) 2.79 (11), O(3)-O(13) 2.68 (11), O(4)-O(13)

2.89 (11) Å. Together with the long intramolecular O-O distances of the oxime group, these observations strongly hint at the presence of intermolecular instead of intramolecular H bridges of the oxime H atoms, as is usually observed in charged oxamide oxime complexes. A remarkable exception is Ni(oaoH)<sub>2</sub>·HCl·H<sub>2</sub>O (Endres, 1982), where an intermolecular H bridge coexists with the usual intramolecular bridges.

The successful structure determination and especially the rather low *R* factor justify the approach of Hope & Nichols (1981), who state that for normal structural problems a rapid data collection (within a couple of hours) is sufficient. These authors emphasize the importance of low-temperature data collection to offset the loss of precision. Nevertheless, the data for the present structure have been collected at room temperature. The low *R* factor indicates that room-temperature data collected at high speed may well give reasonable results, provided the crystal is of sufficient quality. The reduced accuracy in the data collection has the main effect of increasing the standard deviations. In the present case the standard deviations are about 50% higher than in comparable structures.

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#### References

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