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Bis(oxamide oximato)platinum(II)—$\frac{1}{3}$-Sodium Acetate—$\frac{1}{3}$-Sodium Chloride—2-Water

BY HELMUT ENDRES

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, *D*-6900 *Heidelberg* 1, *Federal Republic of Germany*

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Abstract

$C_4H_{10}N_8O_4Pt.\frac{1}{3}C_2H_3NaO_2.\frac{1}{3}NaCl.2H_2O$, M_r = 512·17, crystallizes in space group $P\bar{1}$, with a = 10·032 (3), b = 10·482 (5), c = 12·020 (5) Å, α = 116·16 (3), β = 85·32 (2), γ = 103·13 (2)°, V = 1105 Å^3, Z = 3, d_c = 2·31 Mg m^{-3}. The final R = 0·054 for 3557 reflections. The Pt complex units form stacks of triads along **a**, with Pt—Pt separations of 3·280 Å within a triad and 3·560 Å between triads. The complex molecules within a triad are linked by Pt—Pt interactions and by intermolecular H bridges between oxime O atoms.

Introduction

The structural variability of transition-metal complexes of oxamide oxime (diaminoglyoxime, oaoH$_2$) is presently being investigated (Bekaroglu, Sarisaban, Koray & Ziegler, 1977; Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978). In the search for new materials with highly anisotropic physical properties we are interested in the oaoH complexes of the Ni triad (Endres, 1978, 1979*a*,*b*), for the α,β-dione dioximato complexes of these metals are known to crystallize in stacked structures (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977).

Experimental

A solution of 415 mg $K_2[PtCl_4]$ and 2 g NH_4Cl in 100 ml H_2O was added dropwise to a refluxing solution of 260 mg oxamide oxime (Ephraim, 1889), kept 1 h under reflux and allowed to cool to room temperature. Dark-red crystals and a greenish-black amorphous body were filtered off. The mother liquor was buffered with a saturated Na acetate solution to pH 7, and another crop of red crystals were filtered off. These products are still under investigation. The filtrate was evaporated on a sand bath to about 15 ml and allowed to cool slowly. Large colourless crystals of the buffer substances and a small amount of red columnar crystals of the title compound precipitated and were collected by filtration. When the buffer substances were removed by washing with H_2O, the red crystals were attacked, too, and changed their habit. Hence analytical data are not available.

A crystal 0·18 × 0·05 × 0·06 mm was selected for the structure determination. Photographs (Cu $K\alpha$ radiation) showed the crystal to be triclinic. A rotation photograph exhibited a pattern with each third layer line strong, characteristic for a stacked structure with metal–metal separations roughly one third of the cell length. Lattice constants were calculated by least squares (Berdesinski & Nuber, 1966) from the diffrac-

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tometrically determined θ values of 57 reflections. Intensities were measured on a computer-controlled diffractometer (Siemens AED, Mo $K\alpha$ radiation, θ–2θ scans, five-value method) up to $2\theta = 60°$. The 3580 observed $[I > 3{\cdot}0\sigma(I)]$ independent reflections were corrected for Lorentz and polarization factors but not for absorption ($\mu = 10{\cdot}15$ mm^{-1}). In later refinement cycles several reflections with observed intensities just above the statistical threshold and with much lower calculated ones were rejected, as well as five strong reflections with abnormal $F_o - F_c$ differences. Final refinement was based on 3557 observations with unit weights. Calculations were carried out with the XRAY system (Stewart, Kundell & Baldwin, 1970) on an IBM 370/168 computer (Universitätsrechenzentrum Heidelberg). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Plots were drawn with *ORTEP* (Johnson, 1965).

Structure solution and refinement

A Patterson synthesis confirmed the Pt positions at 0,0,0 and $\frac{1}{3}$,0,0, space group $P\bar{1}$ being assumed. The atoms of the ligands were found from the Patterson and Fourier syntheses. A difference map showed strong maxima outside the complex molecules. These maxima had to be attributed to species included from the solution. Possible species were Na^+, K^+, NH_4^+, Cl^-, acetate, unreacted starting material, and water. The possibility of unreacted starting material could be excluded by the distribution of the maxima which suggested the presence of acetate ion, and from the heights of the maxima the presence of Na^+, Cl^-, acetate ion, and water was made likely. R-factor calculations as well as bond distances and angles confirmed these assignments. The two anions occupy the same site in the crystal, and had to be inserted with multipliers = 0·5. As this seemed improbable, refinement in the non-centrosymmetric $P1$ was tried, where the double occupancy of the anion sites can be avoided. For isotropic refinement, R became 0·104, compared to $R = 0{\cdot}108$ in $P\bar{1}$, but with nearly twice the number of parameters, and with e.s.d.'s in bond length three times as large as in the centrosymmetric case. Therefore, calculations were continued in $P\bar{1}$. In a test for the occupancy ratio of the anion site the multipliers of the relevant atoms were varied independently. They scattered from 0·4 to 0·6, reflecting the interdependence of multiplier and temperature factor. For further refinement the multipliers were again fixed at 0·5. Refinement with anisotropic temperature factors for all atoms except the acetate anion converged with $R = 0{\cdot}054$ (maximum shift/error = 0·78, average shift/error = 0·10).* Refinement of the acetate anion with anisotropic temperature factors resulted in neither a better R nor better e.s.d.'s. H atoms could not be located unambiguously on a difference map.

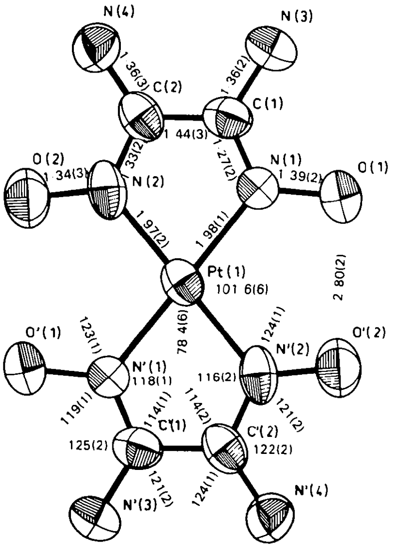

Fig. 1. Bond distances (Å) and angles (°) in the central molecule A of the triad.

Description of the structure and discussion

Atomic coordinates are listed in Table 1. The numbering scheme, bond distances and angles are shown in Figs. 1 and 2. The oaoH is coordinated to Pt in the usual way, *via* the oxime N atoms. There are two independent complex molecules in the cell: molecule A with Pt(1) at the inversion centre at 0,0,0, and molecule B with Pt(2) roughly at $\frac{1}{3}$,0,0. A is therefore centrosymmetric; in B a pronounced deviation from centrosymmetry is imposed by the different N(8)–Pt(2)–N(5) and N(7)–Pt(2)–N(6) angles, which lead to the very different O(4)–O(5) and O(3)–O(6) distances. Remarkable is the long O(3)–O(6) distance in Fig. 2, 3·21 (2) Å.

The inversion centre at 0,0,0 generates B' at roughly $-\frac{1}{3}$,0,0. B'–A–B form a distinct triad of complex units with interplanar separations of 3·25 Å and Pt–Pt distances of 3·280 (1) Å. Fig. 3 shows a perpendicular projection of B on to A. It is evident that the Pt(1)–Pt(2) axis is nearly perpendicular to the molecular planes. Angles Pt(1)–Pt(2)–N are: N(5) 87·5 (4), N(6) 95·9 (5), N(7) 92·0 (4), N(8) 85·6 (4)°. Angles Pt(2)–Pt(1)–N are: N(1) 85·4 (5), N(2) 93·0 (4)°. Therefore, a direct electronic Pt–Pt interaction can be assumed, as in the M–M forms of α,β-dione dioximato complexes of the Ni triad (Endres, Keller, Lehmann,

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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 34786 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z
Pt(1)	0	0	0
Pt(2)	330·6 (1)	14·2 (1)	−19·0 (1)
Cl*	−845 (1)	−249 (1)	−625·9 (8)
Na	423·6 (6)	324·5 (5)	608·2 (4)
O(1)	49 (1)	112 (1)	272 (1)
O(2)	−5 (1)	188 (2)	−121 (1)
O(3)	266 (1)	−177 (1)	117 (1)
O(4)	418 (1)	331 (1)	110 (1)
O(5)	381 (1)	224 (1)	−124 (1)
O(6)	248 (2)	−311 (1)	−180 (1)
O(7)*	966 (4)	344 (4)	672 (3)
O(8)*	770 (3)	195 (3)	610 (3)
O(9)	161 (2)	408 (2)	547 (1)
O(10)	365 (2)	615 (2)	174 (2)
O(11)	278 (4)	475 (3)	896 (2)
N(1)	41 (2)	148 (1)	174 (1)
N(2)	19 (1)	183 (2)	−16 (1)
N(3)	102 (2)	395 (2)	309 (1)
N(4)	62 (2)	438 (2)	92 (2)
N(5)	314 (1)	−40 (1)	121 (1)
N(6)	383 (2)	207 (1)	124 (1)
N(7)	347 (1)	79 (1)	−150 (1)
N(8)	284 (1)	−172 (1)	−173 (1)
N(9)	347 (2)	49 (1)	336 (1)
N(10)	438 (2)	335 (1)	336 (1)
N(11)	319 (2)	19 (2)	−361 (1)
N(12)	243 (2)	−278 (2)	−386 (1)
C(1)	62 (2)	281 (2)	197 (2)
C(2)	49 (2)	304 (2)	89 (2)
C(3)	349 (2)	66 (2)	232 (1)
C(4)	395 (2)	212 (2)	232 (1)
C(5)	316 (2)	−14 (2)	−265 (1)
C(6)	278 (2)	−165 (2)	−278 (1)
C(7)*	904 (4)	215 (5)	614 (4)
C(8)*	983 (4)	102 (5)	560 (4)

* Half-occupied positions.

Table 2. *Bond distances* (Å) *and angles* (°) *in the acetate anion*

C(7)–C(8)	1·46 (7)	C(8)–C(7)–O(7)	119 (4)
C(7)–O(7)	1·25 (5)	C(8)–C(7)–O(8)	126 (3)
C(7)–O(8)	1·32 (5)	O(7)–C(7)–O(8)	115 (4)

Poveda, Rupp & van de Sand, 1977). A quite unusual feature is the additional linkage of the molecules within a triad by short O(2)–O(3) distances [2·60 (2) Å], typical for a H bridge. These contacts are indicated, together with further information, in Fig. 4, a projection of the structure parallel to the molecular plane of *A*. The interpretation of this short contact as a H bond is supported by the long O(3)–O(6) distance, which signifies no H bridging between these oxime O atoms. A similar pattern has been found in the NH_4Cl adduct of $[Pt(oaoH)_2]$ (Endres, 1979*b*), where also an intramolecular H bridge has opened to give an intermolecular H bond to an oxime O of an adjacent stack.

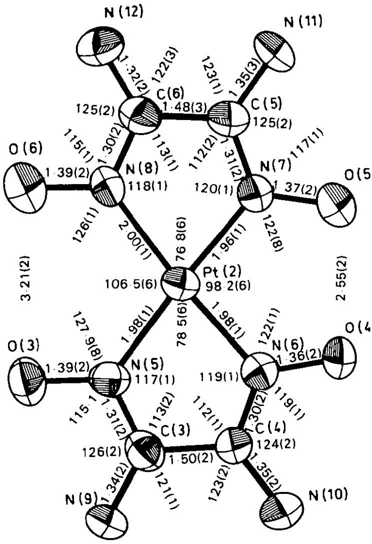

Fig. 2. Bond distances (Å) and angles (°) in the outer molecule *B* of the triad.

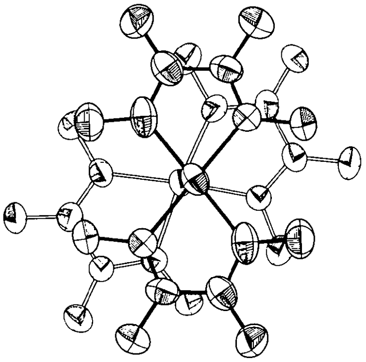

Fig. 3. Perpendicular projection of an outer molecule on to the central molecule of a triad.

The $[Pt(oaoH)_2]$ triads are arranged in stacks along **a** (Fig. 4), generated by the inversion centre at $\frac{1}{2}$,0,0. The Pt(2)–Pt′(2) separation between triads is 3·560 (1) Å; the corresponding interplanar spacing is 3·44 Å. The mode of overlap of two *B* molecules of adjacent triads is shown in Fig. 5. There should be only van der Waals interactions between these molecules. Their relative orientation is typical for the *M–L–M* form of *α,β*-dione dioximato complexes of the Ni triad (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Thus, the two characteristic overlap patterns of the two forms of *α,β*-dione dioximato complexes of the Ni triad are realized in this compound.

The parallel stacks include channels in the lattice which accommodate the H_2O, Na^+, Cl^- and CH_3COO^-. The H_2O O(10) and O(11) link the stacks in the y direction by short contacts [O(10)–O(4) 2·89 (2); O(10)–O(5) and O(10)–O(3) of the

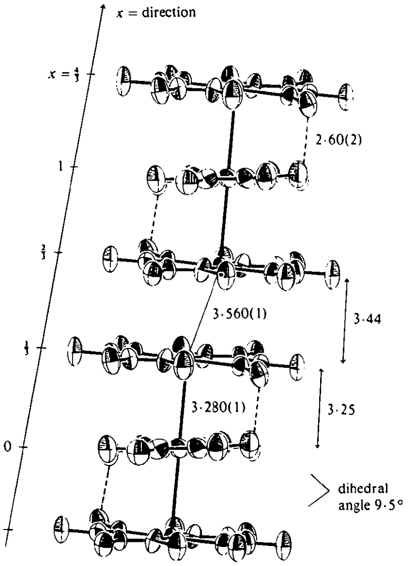

Fig. 4. Projection of two triads parallel to the plane of the central molecule indicating relevant interplanar and intermolecular distances (Å).

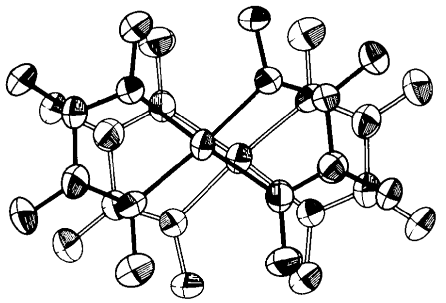

Fig. 5. The overlap of two adjacent outer molecules of two different triads.

neighbour stack 2·90 (2) and 2·94 (3); O(11)—O(6) 2·84 (5) and O(11)—O(5) of the neighbour stack 2·95 (5) Å]. Linkage of the stacks in the *z* direction is brought about by the acetate anion. Short distances are O(8)—N(9) 2·89 (4) Å, and O(8)—N(11) of the neighbour stack 2·89 (3) Å. Na^+ has no contacts <3·2 Å to atoms of the complex molecules; its nearest neighbour is H_2O O(9) at 3·19 (2) Å. O(9) links two stacks over the short diagonal of the unit cell by contacts to N(3) and N(12) of different stacks, 2·90 (3) and 2·95 (2) Å. Another short contact links O(9) to the acetate O(7): 2·52 (4) Å. Bond distances and angles of the acetate anion are listed in Table 2.

Apparently, the inclusion of voluminous ions makes a regularly stacked structure energetically unfavourable, as in the $AgClO_4$ adduct of bis(1,2-benzoquinone dioximato)platinum(II) (Endres, Mégnamisi-Bélombé, Keller & Weiss, 1976), in the dimethylformamide adduct of $[Ni(oaoH)_2]$ (Endres, 1978), where the regularly stacked structure of $[Ni(oaoH)_2].2H_2O$ (Endres, 1979*a*) has completely collapsed, and in the NH_4Cl adduct of $[Pt(oaoH)_2]$ (Endres, 1979*b*).

Nevertheless, a columnar structure of complex molecules will be favoured if the formation of an inclusion compound is connected with an oxidation of the metal chain. This has been found in the iodine oxidation products of bis(diphenylglyoximato)nickel (Gleizes, Marks & Ibers, 1975), bis(1,2-benzoquinone dioximato)nickel (Endres, Keller, Mégnamisi-Bélombé, Moroni, Pritzkow, Weiss & Comès, 1976) and bis(glyoximato)palladium (Endres, Keller, Lehmann & Weiss, 1976). In bis(diphenylglyoximato)platinum(III) perchlorate, the columnar structure is also retained (Endres, Keller, van de Sand & Vu Dong, 1978).

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