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Bis[(oxamide oxime)(oxamide oximato)palladium(II)] Sulfate Hydrate

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Abstract

$[Pd(C_2H_5N_4O_2)(C_2H_6N_4O_2)]_2SO_4.H_2O$, $2C_4H_{11}N_8O_4Pd^+.SO_4^{2-}.H_2O$, M_r = 797·25, is triclinic, $P\bar{1}$ with a = 6·840 (1), b = 9·762 (3), c = 17·947 (3) Å, α = 92·79 (2), β = 97·95 (1), γ = 91·14 (2)°, V = 1185 Å^3, Z = 2, d_c = 2·23 Mg m^{-3}. Final R = 0·041 for 5677 independent diffractometer data. The complex molecules carry one positive charge each. The planar molecules form dimers, linked by the sulfate ions *via* H-bonding. The dimers are arranged in stacks along **a**. Each of the two independent complex molecules has one intramolecular H-bridge replaced by bridging H_2O or SO_4^{2-}.

Introduction

We are presently investigating the variability of the crystal structures of oxamide oxime (diaminoglyoxime, $oaoH_2$) complexes of Ni, Pd, Pt. Preceding papers have dealt with Ni and Pt complexes (Endres & Schlicksupp, 1980, 1979 and references therein). The crystal structures of two Co complexes are also known (Bekaroglu, Sarisaban, Koray & Ziegler, 1977; Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978). In the following, the first crystal structure of a Pd complex of $oaoH_2$ is described.

Experimental

Oxamide oxime was prepared according to Ephraim (1889) by reacting dithiooxamide with hydroxylammonium chloride. As the reaction of acetone solutions of $oaoH_2$ and Pd acetate yields $Pd(oaoH)_2$ as a yellow microcrystalline body which cannot be recrystallized, the growing of larger crystals by a diffusion process was tried. A glass fritt was placed into an Erlenmeyer beaker filled with H_2O. $PdCl_2$ was added outside the fritt, $oaoH_2$, which dissolves only slowly in cold H_2O, in the inner part of the fritt. In a few months large crystals had grown in low yield. They were contaminated by an amorphous precipitate. Two species of crystals could be discerned: large orange blocks, which are the subject of this paper, and a majority of yellow columns, the structure of which is presently being solved.

Lattice parameters were derived from the setting angles of 25 reflections centered on a diffractometer. Data collection (Syntex $R3$, Mo $K\alpha$ radiation, graphite monochromator, θ–2θ background-peak-background scans, $2\theta_{\max}$ = 60°) yielded 5677 independent reflections with $I > 3{\cdot}0\sigma(I)$. An empirical absorption correction was applied.

Calculations were carried out on an IBM 370/168 computer (Universitätsrechenzentrum Heidelberg) with the XRAY system (Stewart, Kundell & Baldwin, 1970) and scattering factors from *International Tables for X-ray Crystallography* (1974). Unit weights were used for all reflections. Plots were drawn by *ORTEP* (Johnson, 1965).

Structure determination and refinement

The Pd positions were derived from a Patterson synthesis. Fourier syntheses yielded the positions of the

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other nonhydrogen atoms. As it was not sure whether a tetrahedral species detected in the lattice was a sulfate or a perchlorate ion, a microprobe technique using X-ray fluorescence was carried out, which confirmed the presence of S and the absence of Cl in the crystals.* With anisotropic temperature factors R was 0·046. All but two of the H atoms became evident on a difference map. They were refined with individual isotropic temperature factors. Due to the large number of parameters, block-diagonal least-squares refinement (five blocks) was applied. It converged with R = 0·041.†

Description of the structure and discussion

Atomic coordinates are listed in Table 1. The numbering schemes, bond distances and angles in the two independent complex molecules are shown in Figs. 1 and 2. The presence of one sulfate ion per two metal complexes implies that a double positive charge is carried by the two complex molecules together. In each molecule one short intramolecular O—O contact signifies the presence of one H-bridge. The H atoms within the bridges could not be located, contrary to all the other H atoms. They are possibly distributed over two positions in each bridge. The two other O atoms of each molecule carry an H atom each. This means that each complex molecule has to be formulated as $[Pd(oaoH)(oaoH_2)]^+$. Instead of an H-bridge, a symmetrical water bridge exists between O(1) and O(4) of molecule 1 (Fig. 1). In molecule 2 (Fig. 2), the sulfate O(13) forms a symmetrical bridge between O(6) and O(7). It is a quite unusual feature in 1,2-dione dioximato complexes that the direct H-bridge between the O atoms is replaced by a bridge *via* a second molecule or ion. A similar case has been encountered in a modification of $Pt(oaoH)_2.2HCl$ (Endres & Schlicksupp, 1980), where bridging *via* Cl occurs.

As is evident from Figs. 1 and 2, the water molecule and the sulfate ion take part in several more H-bridges involving especially amino H atoms. Table 2 lists the bond distances and angles in the sulfate ion and short distances from SO_4^{2-} to neighbor atoms.

The complex molecules are planar. If the plane is defined by Pd and the four oxime N, the maximum deviation of an atom from the plane of molecule 1 is 0·31 Å [N(5)]. In molecule 2 the maximum deviation is

Table 1. *Positional parameters* ($\times 10^4$, H *parameters* $\times 10^3$) *and isotropic temperature factors equivalent to the refined anisotropic values*

	x	y	z	U (Å^2)
Pd(1)	2346·9 (5)	4136·4 (4)	211·1 (2)	0·018
Pd(2)	2601·2 (6)	5673·3 (4)	4944·4 (2)	0·019
S	2299 (2)	9389 (1)	7255·2 (7)	0·23
O(1)	1785 (7)	968 (4)	−139 (2)	0·034
O(2)	2564 (7)	5282 (4)	1794 (2)	0·031
O(3)	2599 (7)	7024 (4)	785 (2)	0·031
O(4)	1970 (8)	3408 (5)	−1525 (2)	0·037
O(5)	1237 (7)	2887 (4)	4314 (2)	0·033
O(6)	4565 (7)	6078 (4)	6622 (2)	0·031
O(7)	3828 (7)	8719 (4)	5390 (2)	0·032
O(8)	726 (6)	4823 (4)	3413 (2)	0·027
O(11)	203 (7)	9693 (4)	7321 (3)	0·035
O(12)	3311 (9)	617 (5)	7060 (3)	0·048
O(13)	2337 (8)	8292 (5)	6664 (3)	0·039
O(14)	3286 (8)	8927 (5)	7979 (2)	0·036
O(15)	4269 (7)	1328 (5)	8893 (3)	0·038
N(1)	2076 (7)	2097 (5)	383 (2)	0·024
N(2)	2371 (7)	4118 (5)	1316 (2)	0·025
N(3)	2615 (7)	6145 (5)	175 (2)	0·023
N(4)	2358 (8)	4354 (5)	−904 (2)	0·027
N(5)	1430 (8)	515 (5)	1274 (3)	0·030
N(6)	1941 (9)	2816 (5)	2351 (3)	0·030
N(7)	2875 (9)	8009 (5)	−575 (3)	0·035
N(8)	2526 (9)	5982 (5)	−1817 (3)	0·034
N(9)	2110 (7)	3679 (4)	4934 (3)	0·026
N(10)	3600 (7)	5245 (4)	6027 (3)	0·023
N(11)	2940 (7)	7718 (4)	4855 (2)	0·024
N(12)	1493 (7)	5883 (4)	3878 (2)	0·022
N(13)	2251 (9)	1668 (5)	5612 (3)	0·035
N(14)	4190 (8)	3477 (5)	6855 (3)	0·032
N(15)	2577 (9)	9490 (5)	4024 (3)	0·034
N(16)	891 (9)	7407 (5)	2898 (3)	0·032
C(1)	1833 (8)	1765 (5)	1059 (3)	0·020
C(2)	2043 (8)	2968 (5)	1617 (3)	0·023
C(3)	2719 (8)	6667 (5)	−474 (3)	0·021
C(4)	2548 (8)	5611 (6)	−1108 (3)	0·023
C(5)	2575 (8)	3032 (5)	5551 (3)	0·023
C(6)	3512 (8)	3955 (56)	6187 (3)	0·021
C(7)	2389 (8)	8172 (5)	4192 (3)	0·021
C(8)	1526 (8)	7112 (5)	3634 (3)	0·023
H(1)	105 (9)	−4 (6)	93 (3)	0·024
H(2)	66 (13)	21 (9)	171 (5)	0·071
H(3)	97 (13)	194 (9)	258 (5)	0·071
H(4)	193 (10)	349 (7)	262 (4)	0·038
H(5)	286 (11)	105 (8)	−44 (4)	0·045
H(6)	301 (13)	866 (9)	−17 (5)	0·062
H(7)	294 (9)	846 (6)	−108 (3)	0·019
H(8)	221 (10)	534 (7)	−222 (4)	0·030
H(9)	278 (13)	697 (9)	−202 (5)	0·065
H(10)	349 (8)	850 (6)	579 (3)	0·012
H(11)	166 (14)	114 (10)	520 (6)	0·075
H(12)	294 (16)	115 (11)	605 (7)	0·104
H(13)	490 (14)	255 (10)	697 (6)	0·079
H(14)	489 (10)	405 (7)	719 (4)	0·030
H(15)	394 (9)	675 (6)	667 (3)	0·022
H(16)	322 (19)	9 (13)	439 (7)	0·128
H(17)	134 (17)	997 (12)	353 (7)	0·109
H(18)	42 (11)	683 (7)	263 (4)	0·038
H(19)	29 (13)	838 (9)	281 (5)	0·068
H(20)	463 (14)	70 (10)	863 (5)	0·072
H(21)	320 (15)	272 (10)	869 (6)	0·087
H(22)	483 (12)	831 (9)	113 (5)	0·055

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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 35139 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

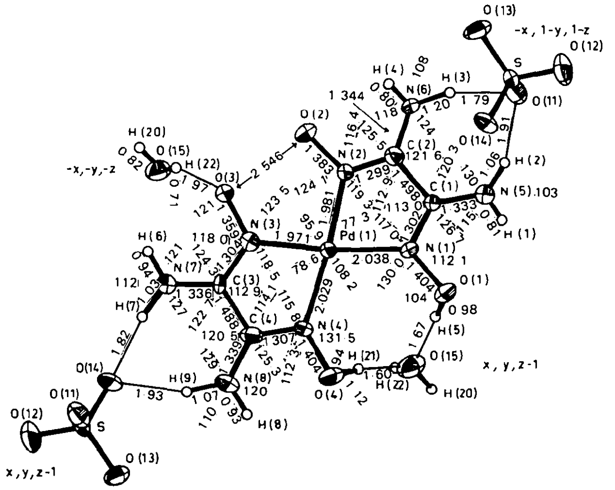

Fig. 1. *ORTEP*-plot of molecule 1 with bond distances (Å) and angles (°). E.s.d.'s for bonds range from 0·002 to 0·007 Å, for distances to H from 0·06 to 0·13 Å. For angles excluding H, e.s.d.'s range from 0·01 to 0·04°, involving H they are around 5°. The symmetry operations which generate O(15) and S from the positions given in Table 1 are indicated.

Table 2. *Distances (Å) and angles (°) in the* SO_4^{2-} *ion, and distances to its nearest neighbors*

S–O(11)	1·489 (5)	O(11)–S–O(12)	109·7 (3)
S–O(12)	1·455 (5)	O(13)	108·6 (3)
S–O(13)	1·473 (5)	O(14)	109·6 (3)
S–O(14)	1·473 (4)	O(12)–S–O(13)	110·0 (3)
		O(14)	109·4 (3)
		O(13)–S–O(14)	109·5 (3)
O(11)–H(2)	1·91 (10)	O(12)–H(12)	1·89 (12)
O(11)–N(5)	2·910 (7)	O(12)–N(13)	2·845 (8)
O(11)–H(3)	1·79 (9)	O(12)–H(13)	1·97 (10)
O(11)–N(6)	2·955 (7)	O(12)–N(14)	2·895 (7)
O(11)–H(17)	1·78 (11)		
O(11)–N(15)	3·009 (7)		
O(11)–H(19)	1·94 (9)		
O(11)–N(16)	1·974 (7)		
O(13)–O(5)	2·982 (6)	O(14)–H(7)	1·82 (6)
O(13)–H(10)	1·87 (6)	O(14)–N(7)	2·836 (7)
O(13)–O(7)	2·677 (7)	O(14)–H(9)	1·93 (9)
O(13)–H(15)	1·88 (6)	O(14)–N(8)	2·961 (7)
O(13)–O(6)	2·673 (7)	O(14)–H(20)	2·16 (9)
		O(14)–O(15)	2·810 (6)

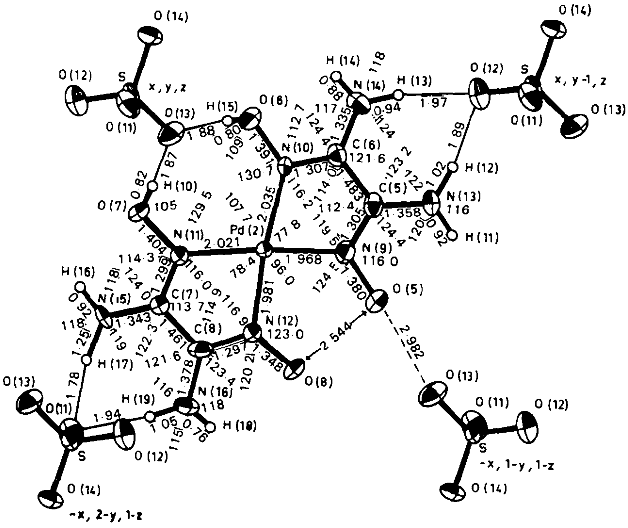

Fig. 2. *ORTEP*-plot of molecule 2. For e.s.d.'s see caption of Fig. 1.

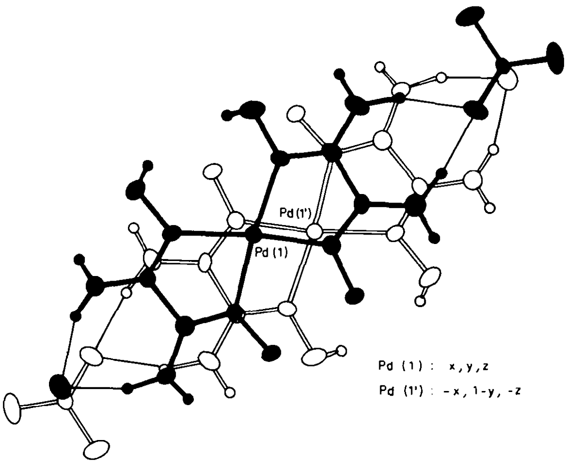

Fig. 3. Overlap pattern of two molecules 1 generated by the indicated symmetry operations. The two molecules are linked by SO_4^{2-}.

0·09 Å. The complex molecules form irregular stacks parallel to **a**. The normal of the plane of molecule 1 is inclined at 8·4° to the stacking axis. Two different interplanar distances occur (defined as the distance of adjacent Pd to the molecular plane as defined above): 3·33 and 3·44 Å. In the stacks formed by molecule 2 the inclination of the molecular planes is 16·9° and there is practically no difference in the interplanar distances, 3·26 and 3·28 Å. The angle between the planes of molecules 1 and 2 is 22·6°. Figs. 3–6 show the overlap patterns of adjacent molecules in the two

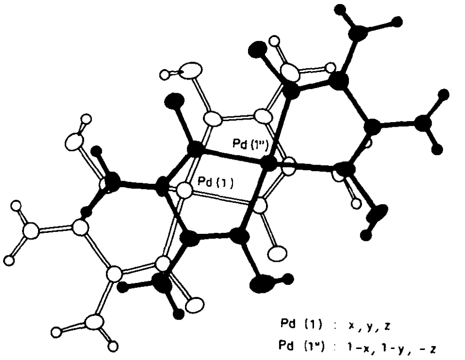

Fig. 4. Overlap pattern of two molecules 1 not linked by SO_4^{2-}.

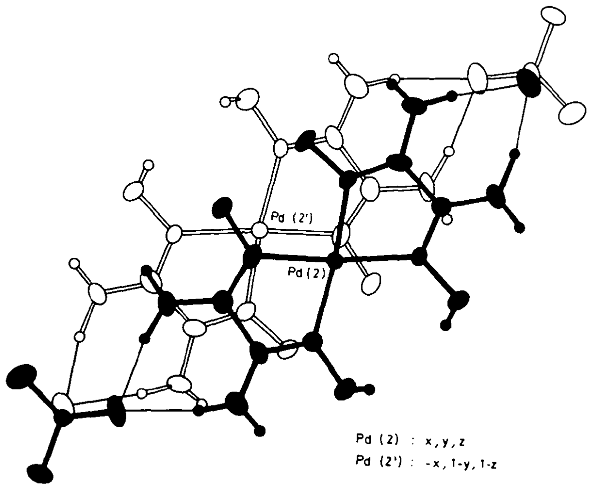

Fig. 5. Overlap pattern of two molecules 2 linked by SO_4^{2-}.

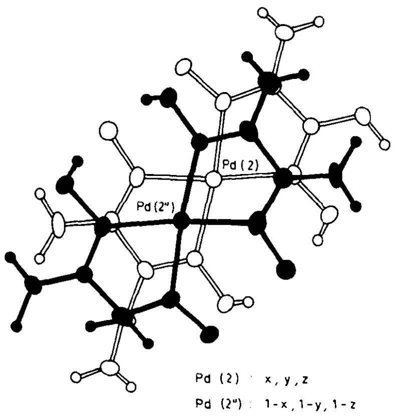

Fig. 6. Overlap pattern of two molecules 2 not linked by SO_4^{2-}.

kinds of stacks. In both stacks the two molecules which exhibit the shorter interplanar distances are linked by SO_4^{2-} *via* H-bridges to amino H atoms. This is shown schematically in Fig. 7 and is indicated in Figs. 3 and 5. This bridging between molecules within a stack is reminiscent of the feature found in $Ni(oaoH)_2.2H_2O$ (Endres, 1979), where regular stacks of the complex molecules are formed. The molecules within a stack are linked by H_2O *via* H-bridges to oxime O atoms.

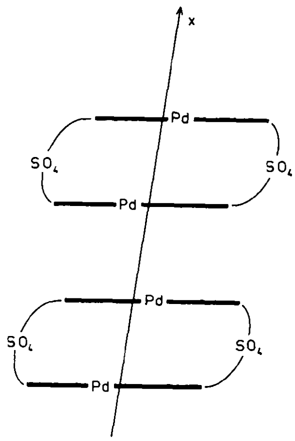

Fig. 7. Schematic drawing of the stacking sequence within one stack.

The SO_4^{2-} ions, which have purposely not been added, most likely were present as a contamination in the oxamide oxime batch, which was prepared from a sulfur-containing compound.

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