Acta Cryst. (1981). B**37**, 1360–1363

Bis(oxamide oxime)palladium(II) Bis[(oxamide oximato)(oxamide oxime)palladium(II)] Bis(sulfate) Octahydrate

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(*Received* 15 *December* 1980; *accepted* 26 *January* 1981)

Abstract

$[Pd(C_2H_6N_4O_2)_2][Pd(C_2H_5N_4O_2)(C_2H_6N_4O_2)]_2(SO_4)_2.8H_2O$, $C_4H_{12}N_8O_4Pd^{2+}$. $2C_4H_{11}N_8O_4Pd^+$. $2SO_4^{2-}.8H_2O$, M_r = 1362·02, is triclinic, $P\bar{1}$, with a = 8·643 (4), b = 10·265 (4), c = 14·215 (4) Å, α = 107·09 (2), β = 94·00 (3), γ = 114·56 (3)°, V = 1069 Å^3, Z = 1, d_c = 2·11 Mg m^{-3}. Final R = 0·054 for 3846 independent diffractometer data. The unit cell contains one centrosymmetric dipositive and two monopositive noncentrosymmetric complex cations. In the crystal, stacks of triads of the complex cations are formed.

Introduction

We are presently investigating variability of the crystal structures of complexes of oxamide oxime (diaminoglyoxime, $oaoH_2$). The Ni, Pd, and Pt complexes of this ligand tend to form unusual crystal and molecular structures, compared to the normal behavior of the dioxime complexes of the Ni triad (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Endres (1980*a*) reported that crystal growth by a diffusion process gave two different forms of Pd oxamide oxime complexes, and the crystal structure of one form was described. The structure of the second form is the subject of this communication.

Experimental

Oxamide oxime was prepared according to Ephraim (1889). The crystal-growth procedure by which the title compound was obtained is described by Endres (1980*a*). A piece of a yellow column 0·1 × 0·1 × 0·15 mm was used for the investigations. Lattice constants were calculated by least squares (Berdesinski & Nuber, 1966) from diffractometrically determined θ values of 40 reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (Siemens AED, Mo $K\alpha$ radiation, θ–2θ scans, five-value method) up to $2\theta = 60°$. Reflections with $I < 3{\cdot}0\sigma(I)$ were regarded as unobserved, leaving 3846 independent reflections for the calculations. They were corrected for Lorentz and polarization factors, but not for absorption (μ = 14 mm^{-1}). Unit weights were assigned.

Calculations were carried out on a Nova 3 computer with the *SHELXTL* program system (Sheldrick, 1979); plots were drawn on a Tektronix plotter operated by the same program. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Anomalous dispersion was taken into account.

Structure determination and refinement

A Patterson synthesis favored the centrosymmetric space group $P1$ and yielded the Pd positions. Fourier syntheses revealed the positions of the other non-hydrogen atoms. Only 21 of the 25 H atoms could be detected on difference maps. They were refined with fixed isotropic temperature factors U = 0·08 Å^2, the temperature factors of the other atoms being refined anisotropically. Refinement by a cascade matrix procedure converged with R = 0·054 [mean (max.) shift/error = 0·03 (0·6)].†

Description of the structure and discussion

Table 1 contains the atomic coordinates, Table 2 the distances and angles involving H atoms. Distances within the sulfate ions are given in Table 3. O(11) to O(14) belong to the water molecules. The lattice accommodates two different Pd complex species: one is

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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 36013 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/071360-04$01.00

a centrosymmetic dication $[Pd(oaoH_2)]^{2+}$ (I) with Pd at the origin (Fig. 1). This species does not contain intramolecular H bridges which are very common in dioximato complexes. The second Pd complex species with Pd at a general position (Fig. 2) is monopositive $[Pd(oaoH)(oaoH_2)]^+$ (II) and deviates considerably from centrosymmetry. The O–O distances and H positions of the oxime groups mean that only one intramolecular H bridge has been formed. Such

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

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

	x	y	z	U (Å^2)
Pd(1)	0	0	0	21·9 (3)
Pd(2)	8886 (1)	2342 (1)	8908 (1)	19·0 (2)
N(1)	2541 (8)	1488 (8)	428 (5)	27 (3)
N(2)	396 (8)	717 (8)	1501 (5)	27 (3)
N(3)	2397 (9)	2322 (9)	3020 (5)	38 (3)
N(4)	4896 (8)	3124 (8)	1800 (5)	32 (3)
N(5)	9207 (7)	2948 (7)	10399 (4)	21 (2)
N(6)	8320 (8)	1609 (8)	7385 (5)	31 (3)
N(7)	6395 (8)	827 (8)	8596 (5)	27 (3)
N(8)	11424 (7)	3943 (7)	9395 (5)	26 (2)
N(9)	11138 (9)	4527 (9)	11968 (5)	37 (3)
N(10)	13630 (8)	5690 (8)	10817 (5)	36 (3)
N(11)	3908 (9)	−954 (9)	7302 (5)	36 (3)
N(12)	6122 (10)	−175 (10)	5939 (5)	36 (3)
O(1)	3672 (7)	1962 (7)	−197 (4)	33 (3)
O(2)	−864 (7)	457 (7)	2091 (4)	38 (3)
O(3)	7921 (7)	2336 (7)	10894 (4)	31 (2)
O(4)	12618 (7)	4578 (7)	8852 (4)	34 (2)
O(5)	9334 (7)	2075 (9)	6715 (4)	47 (3)
O(6)	5519 (6)	508 (6)	9295 (4)	28 (2)
C(1)	1957 (9)	1720 (9)	2031 (5)	23 (3)
C(2)	3235 (9)	2131 (9)	1381 (6)	26 (3)
C(3)	10718 (9)	4009 (9)	10968 (5)	24 (3)
C(4)	12011 (9)	4599 (8)	10379 (5)	23 (3)
C(5)	6736 (9)	556 (8)	6938 (5)	23 (3)
C(6)	5591 (9)	127 (8)	7634 (5)	23 (3)
S	3363 (2)	2112 (2)	6611 (1)	29 (1)
O(7)	5263 (7)	2938 (8)	7001 (4)	44 (3)
O(8)	2841 (7)	516 (7)	6014 (4)	35 (2)
O(9)	2501 (9)	2163 (8)	7478 (5)	48 (3)
O(10)	2817 (10)	2840 (8)	6018 (6)	63 (4)
O(11)	187 (9)	2151 (9)	4457 (5)	52 (3)
O(12)	9613 (9)	4280 (10)	3703 (6)	62 (4)
O(13)	6943 (9)	3173 (10)	5341 (5)	58 (4)
O(14)	6062 (11)	4327 (9)	3964 (6)	64 (4)
H(1)	1041 (17)	433 (15)	1226 (10)	
H(2)	662 (16)	566 (14)	373 (9)	
H(3)	1365 (16)	606 (14)	1151 (10)	
H(4)	1425 (16)	570 (14)	1045 (9)	
H(5)	544 (16)	324 (14)	242 (10)	
H(6)	567 (16)	353 (14)	140 (9)	
H(7)	1233 (15)	461 (14)	1229 (9)	
H(8)	1023 (16)	222 (14)	690 (9)	
H(9)	−114 (16)	−52 (14)	203 (9)	
H(10)	1273 (16)	391 (14)	869 (9)	
H(11)	651 (16)	325 (14)	574 (9)	
H(12)	616 (16)	413 (14)	434 (9)	
H(13)	700 (16)	142 (14)	1028 (9)	
H(14)	649 (16)	12 (14)	570 (9)	
H(15)	867 (16)	427 (14)	363 (9)	
H(16)	989 (16)	341 (14)	408 (9)	
H(17)	420 (16)	137 (14)	−36 (9)	
H(18)	308 (16)	−109 (14)	782 (9)	
H(19)	352 (16)	−45 (14)	689 (9)	
H(20)	155 (17)	194 (14)	349 (9)	
H(21)	324 (16)	273 (14)	332 (9)	

Table 2. *Distances* (Å) *and angles* (°) *involving* H *atoms*

N(3)–H(20)	1·06 (14)	C(6)–N(11)–H(18)	120 (5)
H(21)	0·70 (11)	H(19)	97 (6)
C(1)–N(3)–H(20)	123 (6)	H(18)–N(11)–H(19)	106 (>10)
H(21)	126 (>10)	N(12)–H(14)	0·56 (13)
H(20)–N(3)–H(21)	108 (>10)	C(5)–N(12)–H(14)	116 (9)
N(4)–H(5)	0·92 (14)	O(1)–H(17)	0·89 (16)
H(6)	0·96 (13)	N(1)–O(1)–H(17)	110 (9)
C(2)–N(4)–H(5)	123 (8)	O(2)–H(9)	0·91 (14)
H(6)	121 (7)	N(2)–O(2)–H(9)	100 (9)
H(5)–N(4)–H(6)	114 (>10)	O(3)–H(13)	1·04 (11)
N(9)–H(1)	0·77 (15)	N(5)–O(3)–H(13)	99 (7)
H(7)	1·06 (14)	O(4)–H(10)	0·71 (15)
C(3)–N(9)–H(1)	119 (10)	N(8)–O(4)–H(10)	90 (>10)
H(7)	116 (7)	O(5)–H(8)	0·73 (14)
H(1)–N(9)–H(7)	116 (>10)	N(6)–O(5)–H(8)	109 (>10)
N(10)–H(3)	0·92 (13)	O(12)–H(15)	0·81 (15)
H(4)	0·77 (14)	H(16)	1·26 (16)
C(4)–N(10)–H(3)	119 (8)	H(15)–O(12)–H(16)	122 (>10)
H(4)	112 (7)	O(13)–H(11)	0·71 (14)
H(3)–N(10)–H(4)	126 (>10)	O(14)–H(2)	1·40 (15)
N(11)–H(18)	1·06 (14)	H(12)	0·64 (16)
H(19)	1·02 (17)	H(2)–O(14)–H(12)	139 (9)

Table 3. *Distances* (Å) *and angles* (°) *in the sulfate anion*

S–O(7)	1·470 (6)	O(7)–S–O(8)	109·0 (4)
O(8)	1·457 (6)	O(9)	108·7 (4)
O(9)	1·483 (8)	O(10)	110·6 (4)
O(10)	1·449 (11)	O(8)–S–O(9)	108·6 (4)
		O(10)	110·8 (4)
		O(9)–S–O(10)	108·1 (5)

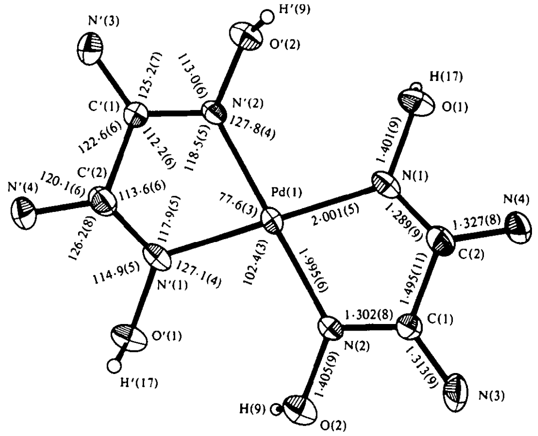

Fig. 1. The centrosymmetric $[Pd(oaoH_2)]^{2+}$ cation with numbering scheme, bond distances (Å) and angles (°). Distances and angles to H atoms are listed in Table 2. Thermal ellipsoids are at the 50% probability level; H atoms are drawn with an arbitrary temperature factor.

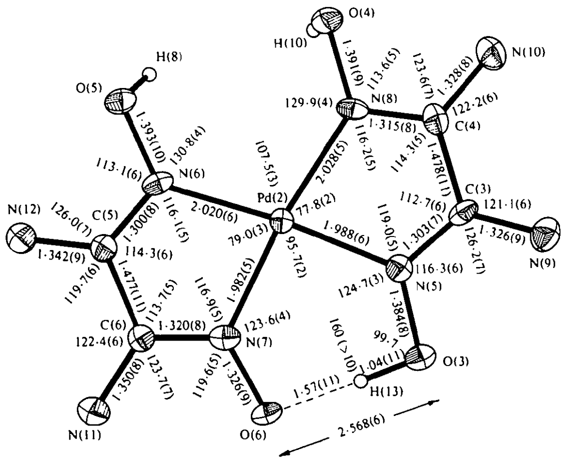

Fig. 2. The noncentrosymmetric $[Pd(oaoH)(oaoH_2)]^+$ cation with numbering scheme, bond distances (Å) and angles (°).

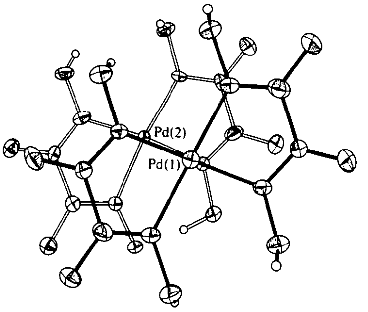

Fig. 3. Perpendicular projection of the central and the outer molecule of a triad.

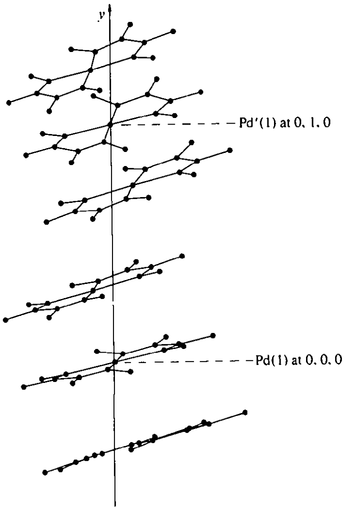

Fig. 4. Perspective view of the triads stacking along **b**.

asymmetric complexes are rare in dioxime chemistry, but have been observed in several Pd^{II} and Pt^{II} complexes with $oaoH_2$ ligands (Endres, 1979, 1980*b*; Endres & Schlicksupp, 1980).

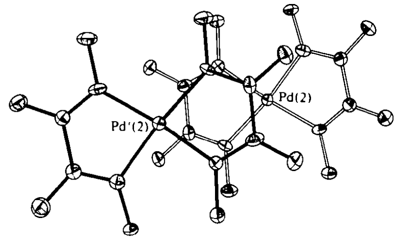

Fig. 5. Perpendicular projection of two adjacent molecules of different triads.

Table 4. *Possible* H *bridges*

Distances < 3·0 Å are listed together with distances (Å) and angles (°) involving H atoms when known.

N(3)–O(11)	2·89 (1)	O(11)–H(20)	1·89 (15)
	N(3)–H(20)–O(11)	155 (>10)	
N(3)–O(14)	2·90 (1)	O(14)–H(21)	2·22 (12)
	N(3)–H(21)–O(14)	165 (>10)	
N(4)–O(14)	2·88 (1)	O(14)–H(5)	2·06 (12)
	N(4)–H(5)–O(14)	148 (>10)	
N(4)–O(4)	2·896 (9)	O(4)–H(6)	2·04 (13)
	N(4)–H(6)–O(4)	148 (>10)	
N(9)–O(12)	2·90 (1)	O(12)–H(1)	2·21 (15)
	N(9)–H(1)–O(12)	150 (>10)	
N(10)–O(1)	2·98 (1)	O(1)–H(4)	2·47 (3)
	N(10)–H(4)–O(1)	125 (>10)	
N(10)–O(7)	2·093 (9)	O(7)–H(3)	1·99 (12)
	N(10)–H(3)–O(7)	174 (>10)	
N(12)–O(8)	2·95 (1)	O(8)–H(14)	2·50 (13)
	N(12)–H(14)–O(8)	140 (>10)	
O(1)–O(6)	2·61 (1)	O(6)–H(17)	1·73 (16)
	O(1)–H(17)–O(6)	169 (>10)	
O(2)–O(9)	2·75 (1)	O(9)–H(9)	1·97 (14)
	O(2)–H(9)–O(9)	143 (>10)	
O(4)–O(9)	2·625 (9)	O(9)–H(10)	2·02 (12)
	O(4)–H(10)–O(9)	144 (>10)	
O(5)–O(9)	2·83 (11)	O(9)–H(8)	2·11 (15)
	O(5)–H(8)–O(9)	167 (>10)	
O(6)–O'(6)	2·57 (12)		
O(7)–O(13)	2·87 (1)	O(7)–H(11)	2·19 (14)
	O(7)–H(11)–O(13)	164 (>10)	
O(8)–O(11)	2·741 (8)		
O(10)–O(11)	2·76 (1)		
O(10)–O(14)	2·65 (1)	O(10)–H(2)	1·33 (15)
	O(10)–H(2)–O(14)	152 (10)	
O(11)–O(12)	2·89 (2)	O(11)–H(16)	1·64 (17)
	O(11)–H(16)–O(12)	174 (7)	
O(12)–O(13)	2·902 (9)		
O(13)–O(14)	2·78 (1)	O(13)–H(12)	2·16 (16)
	O(13)–H(12)–O(14)	162 (>10)	

The complex species are practically planar. (For the following discussion the molecular plane is defined as the plane through the four oxime N.) In (I) the average deviation of a non-H atom from the plane is 0·05 Å; the maximum deviation is 0·205 Å for O(2). Corresponding values for (II) are 0·03 Å and 0·116Å for N(12). (I) and (II) are arranged in triads with (I) at the center and two species (II) forming the outer molecules of the triad. The molecular planes of (I) and (II) are nearly parallel, the dihedral angle being 3·8°. The average distance of the atoms of (II) to the molecular plane of (I) is 3·3 Å; minimum [maximum] values are 3·11 Å for O(6) [3·58 Å for O(4)]. The mode of molecular overlap of (I) and (II) within a triad is shown in Fig. 3. These triads are arranged in stacks along **b**, Fig. 4. The molecular overlap between two species (II) of adjacent triads is given in Fig. 5. The molecular planes are parallel by symmetry and the mean [min./max.] distances of the non-H atoms of one species to the molecular plane of the adjacent one are 3·35 Å [3·28 Å for N(10)/3·48 Å for N(12)]. In terms of the usual stacking modes of 1,2-dioximato complexes of the Ni triad (Endres *et al.*, 1977), the title compound is composed of triads of *M–L* form stacked in an *M–L* fashion, with a more pronounced slip of adjacent molecules between triads than within triads. Stacks of triads occur in a Pt(oaoH)$_2$ species as well (Endres, 1980*b*), but with a pronounced difference: in the Pt compound the stacking pattern corresponds to the *M–M* form in accordance with the greater tendency of Pt complexes to arrange in this form (Endres *et al.*, 1977).

In [Pd(oaoH)(oaoH$_2$)]$_2$SO$_4$ which crystallizes simultaneously with the title compound (Endres, 1980*a*), the complex species arrange in stacks of diads where the diads are linked by SO_4^{2-} ions *via* H bridges involving the amino substituents. A similar kind of linking does not occur in the title compound, but the sulfate ion and the water molecules are involved in a network of H bridges to each other and to the complex molecules. Relevant distances and angles are summarized in Table 4. H bridges involving the oxime groups also link the different complex cations, as is evident from the short distances O(1)–O(6) 2·61 (1) Å involving H(17) with O(6)–H(17) 1·73 (16) Å and an O–H–O angle of 169°, and O(6)–O′(6) 2·57 (12) Å. In the latter case it is not evident where the bridging H comes from, as there should not be an H atom bound to O(6), nor has an H been found in the structure analysis. There might be a statistically occupied site between O(6) and O′(6) together with statistical vacancies at the H(13) or H(17) positions. Similar intermolecular linking has been found in other oaoH$_2$ complexes (Endres, 1979, 1980*b*).

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Acta Cryst. (1981). B**37**, 1363–1366

Hydrogen-Bond Length in Homomolecular Organic Crystals

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(*Received* 13 *December* 1979; *accepted* 17 *December* 1980)

Abstract

A statistical analysis of X-ray data on the intermolecular hydrogen bond (H bond) in organic homomolecular crystals has been carried out. The average lengths obtained for different types of H bonds are compared with those obtained by other authors and with the van der Waals radii of the atoms forming H bonds. It is shown that the H-bond length is determined just by the van der Waals contact between *X* and *Y* atoms, as if the H atom were absent.

The length of the H bond $XH\cdots Y$ is usually considered as a distance *R* between atoms *X* and *Y* or as a distance *d* between atoms H and *Y*. We shall use the former description. The distance *d* is known only if the H atom is located. Its position can only be determined with sufficient accuracy by neutron diffraction, whereas the distance *R* is available from normal X-ray analysis. However, as will be shown in this paper, the *R* values are in some respects more informative than the *d* values.

We have carried out a statistical analysis of X-ray data on the intermolecular H bond in organic homo-

0567-7408/81/071363-04$01.00