Crystal Structure of 2,6-Dioxa-14,18-diazatricyclo-[18.4.0.0^{7,12}]-tetracos-7,9,11,20,22,24(1)-hexsaene-diacetatopalladium(II)

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In the title complex, C₂₄H₃₂N₂O₆Pd, Pd(II) ion, is coordinated bidentately to N atoms of the macroring and monodentately to O atoms of the acetate ligands, in a square-planar geometry. The etheric oxygens of the macroring are not bonded to the metal ion, but are interestingly bonded to each hydrogen of the benzylic CH₂ groups. On the other hand, beside of the intramolecular C-H...O bonds, the strong intramolecular N-H...O hydrogen bonds, between the two acetate oxygens and N atoms of the macroring, also contribute to stabilization of the molecular structure. It belongs to the space group *Pbca* with cell parameters *a* = 14.1507(6), *b* = 16.9866(7), *c* = 20.4128(11) Å.

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In contrast to the metal-ion chemistry of macrocyclic multidentate ligands, incorporating all of the ether-oxygens (crown ethers) or all nitrogen donor atoms (macrocyclic polyamines), the chemistry of mixed oxygen-nitrogen, O_xN_y (*x,y* = 2,3,4,...), donor type macrocycles has received less attention.¹ On the other hand, the incorporation of nitrogen-oxygen donor

atoms in the macrocyclic rings has increased the affinity for transition metal cations. These kinds of applications are of fundamental importance for broad areas of coordination and bio-chemistry.²

Hence, a number of mixed macrocyclic multidentate ligand complexes have been extensively investigated in order to

Fig. 1 Chemical diagram.

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula: C ₂₄ H ₃₂ N ₂ O ₆ Pd
Formula weight: 550.92
Crystal system: orthorhombic
Space group: <i>Pbca</i> Z = 8
<i>a</i> = 14.1507(6) Å
<i>b</i> = 16.9866(7) Å
<i>c</i> = 20.4128(11) Å
<i>V</i> = 4906.7(4) Å ³
<i>D_x</i> = 1.492 g/cm ³
<i>μ</i> (Mo <i>K</i> _α) = 0.797 mm ⁻¹
<i>T</i> = 296 K
Crystal color: yellow
Crystal size: 0.31 × 0.28 × 0.23 mm
<i>λ</i> (Mo <i>K</i> _α) = 0.71073 Å
<i>R</i> = 0.0368 <i>wR</i> = 0.0893
No. of reflections measured = 5369
No. of reflections used = 3083 [<i>I</i> > 2σ(<i>I</i>)]
No. of parameters = 382
Goodness-of-fit = 0.934
(Δ/ <i>σ</i>) _{max} = 0.001
(Δρ) _{max} = 0.568 eÅ ⁻³
(Δρ) _{min} = -0.513 eÅ ⁻³
2θ _{max} = 54.22°
Measurements: STOE IPDS-II diffractometer
Program system: X-Area and X-RED
Structure determination: SHELXS-97
Refinement: full matrix

CCDC 274486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq}
Pd	0.451671(17)	0.187884(14)	0.397043(15)	0.05917(10)
C1	0.4912(3)	-0.0823(2)	0.2698(2)	0.0700(10)
O2	0.5375(2)	-0.09780(16)	0.32654(17)	0.1010(10)
C3	0.6047(5)	-0.1616(3)	0.3280(3)	0.144(3)
C4	0.6283(4)	-0.1857(3)	0.3880(3)	0.129(2)
C5	0.6905(3)	-0.1453(2)	0.4348(3)	0.0780(12)
O6	0.65265(16)	-0.06831(13)	0.44868(14)	0.0709(7)
C7	0.6982(2)	-0.02294(19)	0.49422(19)	0.0576(9)
C8	0.7762(2)	0.0476(2)	0.5297(2)	0.0660(10)
C9	0.8178(3)	0.0028(3)	0.5738(2)	0.0745(11)
C10	0.7844(3)	0.0775(3)	0.5824(2)	0.0787(12)
C11	0.7058(3)	0.1012(2)	0.5477(2)	0.0717(11)
C12	0.6602(2)	0.05227(19)	0.50438(18)	0.0574(8)
C13	0.5708(2)	0.0777(2)	0.4707(2)	0.0598(9)
C14	0.5800(2)	0.15125(18)	0.43111(19)	0.0641(8)
C15	0.6550(3)	0.1485(3)	0.3809(3)	0.0833(15)
C16	0.6325(3)	0.0936(3)	0.3245(3)	0.0846(14)
C17	0.5495(3)	0.1175(3)	0.2838(3)	0.0791(12)
N18	0.4579(2)	0.11311(17)	0.31929(17)	0.0643(8)
C19	0.4215(3)	0.0321(2)	0.3315(2)	0.0623(10)
C20	0.4291(2)	-0.0193(2)	0.2719(2)	0.0618(9)
C21	0.3799(4)	-0.0015(3)	0.2163(3)	0.0910(15)
C22	0.3910(6)	-0.0436(4)	0.1596(3)	0.116(2)
C23	0.4515(5)	-0.1051(4)	0.1579(3)	0.1068(18)
C24	0.5030(4)	-0.1245(3)	0.2121(3)	0.0899(14)
C25	0.4626(3)	0.3714(2)	0.5445(2)	0.0968(15)
C26	0.4987(3)	0.3042(2)	0.5024(2)	0.0698(10)
O27	0.5833(2)	0.28749(17)	0.50297(17)	0.0933(10)
O28	0.43554(17)	0.26924(14)	0.46908(14)	0.0725(7)
C29	0.1837(4)	0.2600(4)	0.3158(3)	0.153(3)
C30	0.2795(3)	0.2235(2)	0.3166(3)	0.0822(13)
O31	0.3097(2)	0.19355(18)	0.26585(16)	0.0929(9)
O32	0.32186(18)	0.22728(16)	0.37113(16)	0.0834(9)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

understand their synthetic, thermo-dynamic, selective-ion binding and structural properties of complex formation.³

The title compound was prepared from the reaction of [2,6-Dioxo-14,18-diazatricyclo-[18.4.0.0^{7,12}]-tetracos-7,9,11,20,22,24(1)-hexaene (0.87 g, 2.69 mmol) and Pd(CH₃CO₂)₂ (0.60 g, 2.69 mmol) in CH₂Cl₂ (150 ml). The mixture was refluxed for 3 h and then the solution was cooled and filtered. The pale-yellow product was crystallized from a CHCl₃/hexane mixture (3:1), (yield 0.55 g, 63%, decompose point 583 K).

The X-ray analysis results are given in Tables 1–4. The H3A, H3B, H4A, H4B, H8, H25A, H25B, H25C, H29A, H29B and H29C atoms were positioned geometrically and refined by using a riding model; the remaining H atoms were located by a difference synthesis and refined isotropically.

The molecular structure of the title compound is shown in Fig. 2. The Pd(II) ion is at a distance of –0.0062(2) Å to the best plane of the N14, N18, O28, O32 atoms, and the coordination geometry of Pd(II) is square planar, which can be compared with the corresponding value of –0.1060(3) Å in [2,5-dioxo-13,16,19-triazatricyclo[19.4.0.0^{6,11}]-pentacos-6,8,10,21,23,25(1)-hexaenediacetato}palladium(II)-trihydrate.⁴ The average valence bond angle around Pd(II) is 90.02(13)°. The acetate ligands are bonded monodentately to the Pd(II) ion. On the other hand, the oxygen atoms of the acetate ligands are hydrogen bonded (Table 4) to the nitrogens of the 16-membered macrocyclic ring (Fig. 2). The acetate ligands are in the *cis*-configuration. The nitrogens of the 16-membered macrocyclic ring are bonded bidentately to the Pd(II) ion. The nitrogen atoms in the 16-membered macro-cyclic ring are bonded bidentately, while no etheric oxygen atom is coordinated. This phenomenon has been found in several related complexes.⁴ The etheric oxygens are interestingly hydrogen bonded to each hydrogen of the benzylic CH₂ groups (Fig. 2).

The molecule is made up of one bicyclic ring fused by a

Table 3 Selected bond distances (Å) and angles (°)

Pd	N18	2.035(3)	N18	C17	1.487(5)
Pd	N14	2.041(3)	N18	C19	1.490(5)
O2	C1	1.356(5)	C26	O27	1.229(5)
O2	C3	1.442(6)	O28	C26	1.270(4)
O6	C7	1.369(4)	O28	Pd	2.031(3)
O6	C5	1.441(4)	O31	C30	1.231(5)
N14	C13	1.493(5)	O32	C30	1.266(5)
C15	N14	1.476(6)	O32	Pd	2.025(3)
O32-Pd-O28	82.08(10)	C13-N14-Pd	111.2(2)		
O32-Pd-N18	92.41(13)	C15-N14-Pd	114.4(3)		
O32-Pd-N14	175.11(14)	C17-N18-Pd	112.8(3)		
O28-Pd-N18	173.98(13)	C19-N18-Pd	115.5(2)		
O28-Pd-N14	93.49(13)	C26-O28-Pd	128.8(3)		
N18-Pd-N14	92.10(15)	C30-O32-Pd	130.0(3)		
C1-O2-C3-C4	-163.5(5)	C16-C15-N14-C13	70.1(5)		
C5-C4-C3-O2	-74.5(9)	N14-C15-C16-C17	64.9(5)		
C3-C4-C5-O6	58.8(8)	N18-C17-C16-C15	-67.1(5)		
C7-O6-C5-C4	176.6(4)	C19-N18-C17-C16	-72.9(5)		
C5-O6-C7-C12	178.1(4)	C17-N18-C19-C20	-45.1(5)		
C13-C12-C7-O6	4.5(5)	C1-C20-C19-N18	111.7(4)		
N14-C13-C12-C7	-123.9(4)	C19-C20-C1-O2	5.4(5)		
C15-N14-C13-C12	55.7(5)	C3-O2-C1-C20	-178.8(5)		

Table 4 Hydrogen bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N14-H141 ... O27	0.87(4)	1.90(4)	2.738(5)	162(4)
N18-H181 ... O31	0.80(3)	1.95(3)	2.731(4)	163(3)
C13-H132 ... O6	0.99(3)	2.29(3)	2.774(4)	108.7(2)
C19-H191 ... O2	0.91(3)	2.32(3)	2.753(5)	109(3)

NpN fragment and two acetate ligands. The 6-membered ring A(Pd/N14/C15/C16/C17/N18) is in a slightly distorted chair conformation, as evidenced by the puckering parameters:⁵ $\Phi_2 = 152.8(5.5)$, $\theta_2 = 176.2(4)^\circ$, and $Q_T = 0.639(4)$ Å. The torsion angles of the 16-membered macrocycle (Table 3) have the sequence +sp, –ap, –ap, –sc, +sc, +ap, +ap, +sp, –ac, +sc, +sc, +sc, –sc, –sc, –ap, +ac (ap denotes antiperiplanar, sc synclinal, ac anticlinal and sp synperiplanar), corresponding to the C20–C1,...,C19–C20 bond sequence. The conformations of the 6-membered and 16-membered macrocyclic rings are conditioned by the four hydrogen bonds (Fig. 2) and by the planarity of the two benzo-fused O–C–C–C system.

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