Synthesis and crystal structure of the 1:1 Pd(II) complex of 1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane

Jonathan L. Sessler*, John W. Sibert and Vincent Lynch
Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712 (USA)

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Abstract

The synthesis and structural characterization of [**1**·Pd]$(PF_6)_2$, complex **3**, where **1** = 1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane, are reported. The palladium atom in the complex is coordinated by the four ligand nitrogen atoms in an essentially square planar structure (average Pd–N bond length = 2.040(1) Å). A further weak apical interaction exists (2.98 Å) to one O atom of the ligand. The pale yellow crystals of $Pd(C_{16}H_{36}N_4O_4)(PF_6)_2$ are monoclinic with unit-cell dimensions a = 15.222(7), b = 20.480(9), c = 8.733(4) Å, β = 91.53(4)°, V = 2722(2) Å^3, space group $P2_1/c$ (No. 14) and Z = 4. Crystals of [**1**·Pd]$(PF_6)_2$ are, thus, isomorphous with those of a $Cu(PF_6)_2$ salt of **1**, complex **2**, reported earlier (J. L. Sessler, J. W. Sibert, J. D. Hugdahl and V. Lynch, *Inorg. Chem., 28* (1989) 1417–1419). The coordination around Cu, however, is better described as square pyramidal with a long Cu–O axial contact (2.47(2)).

Introduction

Oxygen-containing aza-crown ethers have both a rich cation and anion complexation chemistry. As such, they have been the subject of quite extensive study [1]. Because they possess both oxygen and nitrogen donor atoms, they are able to ligate a wider variety of cations than either the purely oxygen-containing or nitrogen-containing crowns.

In an earlier report [2], we discussed the synthesis of a novel aza-crown ether, 1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane (or [24]-aneN_4O_4) (**1**), in which the four nitrogen atoms and four oxygen atoms are situated on opposite sides of the macrocycle. This arrangement of donor atoms was designed to facilitate the simultaneous coordination of two cations that are of quite differing hardness (e.g. a soft transition metal and a hard alkali metal) within the same macrocyclic framework. Little is known about these types of dinuclear metal complexes [3]. They, thus, promise to extend the range of coordination chemistry while, perhaps, finding utility in the binding and activation of small molecules [4] or as models for naturally occurring metalloprotein systems.

We also have reported the structural characterization of the mononuclear complex [**1**·Cu]$(PF_6)_2$ [2]. The copper ion was shown to lie in a square pyramidal geometry, coordinated by the four nitrogen atoms (basal positions) and one oxygen atom (apical position) of ligand **1**. Attempts to coordinate a second metal (e.g. Na^+, K^+, Li^+) to **2** using the polyether moiety, however, have proven to be unsuccessful. In light of the binucleating abilities of the isostructural [24]aneN_8 [5], [24]aneN_6O_2, and [24]aneN_2O_6 macrocycles [6], and the polynucleating abilities of still larger azacrowns [7, 8], the difficulties associated with binding a second metal to **2** may not be a reflection of inadequate ligand size, but, instead, may be the result of axial ligation by the O_{ether} atom. Since macrocycle size and metal-binding ability are interrelated, the Cu–O_{ether} bond, which serves to decrease the size and the denticity of the crown ether portion of **1**, is a highly unfavorable interaction for the purposes of coordinating a second metal ion. We, therefore, sought to synthesize a 1:1 metal complex involving **1** in which all four of the ether oxygen atoms are available for coordination to a second metal ion. We report, here, the synthesis and structural characterization of [**1**·Pd]$(PF_6)_2$ (**3**) and compare it to

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*Author to whom correspondence should be addressed.

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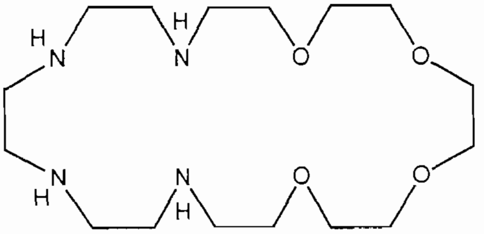
the previously reported complex $[\mathbf{1}\cdot Cu](PF_6)_2$ (**2**).



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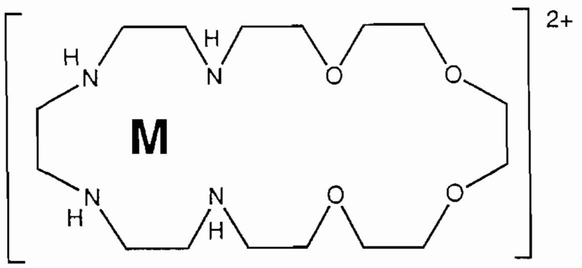

2 M = Cu
3 M = Pd

Experimental

Preparation of $[Pd(C_{16}H_{36}N_4O_4)](PF_6)_2$ (3)

Ligand **1** was prepared as described previously [2]. A solution containing bis(acetonitrile)dichloropalladium(II) (Strem Chemical Co., 140 mg; 0.540 mmol), **1** (196 mg; 0.563 mmol) and NH_4PF_6 (177 mg; 1.08 mmol) in chloroform (100 ml) was stirred and heated at reflux for 6 h. The chloroform was removed from the reaction mixture on a rotary evaporator. The residue was then taken up in ethanol which caused the immediate formation of $[Pd(C_{16}H_{36}N_4O_4)](PF_6)_2$ (**3**) as a yellow precipitate. An X-ray quality crystal of **3** was grown by slow evaporation of a chloroform solution. HR FAB-MS *m/e*: 454.1737 (M^+) (calc. for $C_{16}H_{36}N_4O_4Pd$, *m/e* 454.1771). *Anal.* Calc. for $C_{16}H_{36}N_4O_4PdP_2F_{12}$: C, 25.80; H, 4.87; N, 7.52. Found: C, 24.91; H, 4.86; N, 7.39%. The complex was further characterized by X-ray crystallography.

TABLE 1. Crystallographic data for $Pd(C_{16}H_{36}N_4O_4)$ $(PF_6)_2$ (**3**)

Chemical formula	$PdC_{16}H_{36}N_4O_4P_2F_{12}$
M_r	744.81
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	15.222(7)
b (Å)	20.480(9)
c (Å)	8.733(4)
β (°)	91.53(4)
V (Å^3)	2722(2)
Z	4
T (°C)	−100
λ (Mo Kα) (Å)	0.7107
ρ_{calc} (g/cc)(−100 °C)	1.82
Data collected	9838
Unique data	4773
R for merging equivalent data	0.020
Data with $F > 4(\sigma)F$	4091
μ (cm^{-1})	8.982
Transmission factor range	0.7960–0.8373
$R(F)$	0.0278
$R_w(F)$	0.0395
No. parameters refined	532
Min., max. peaks in final ΔF map (e$^-$/Å^3)	−0.44, 0.68

X-ray experimental

The data crystal was a pale yellow needle of approximate dimensions 0.26×0.26×0.64 mm. The data were collected at 173 K on a Nicolet R3 diffractometer, with a graphite monochromator using Mo Kα radiation ($\lambda = 0.7107$ Å) and equipped with a Nicolet LT-2 low-temperature delivery system. Details of crystal data and refinement are listed in Table 1. The lattice parameters were obtained from least-squares refinement of 42 reflections with $18.6 < 2\theta < 23.8°$. The data were collected using the ω scan technique from 4.0–50.0° in 2θ with a 1.2° ω scan at 3–6°/min. ($h = -17 \rightarrow 17$, $k = 0 \rightarrow 24$, $l = -10 \rightarrow 10$). Four reflections (2,−8,−1; 3,4,3; −3,7,−1; −4,−3,−2) were remeasured every 96 reflections to monitor instrument and crystal stability. The maximum decay correction was <1.0%. The data were also corrected for Lp effects and absorption. The absorption correction was based on crystal shape measurements. Reflections having $F_o < 4(\sigma(F_o))$ were considered unobserved (682 reflections). The structure was solved by direct methods and refined by full-matrix least-squares procedures [9] with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were obtained from a ΔF map and refined with isotropic temperature factors. One of the PF_6^- groups was disordered by rotation about an F–P–F axis. The F atoms of the minor component of the disorder (43.6(4)%) are labeled with an A. A total of 532 parameters was refined. The function, $\Sigma w(|F_o| - |F_c|)^2$, was minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$. The intensity, I, is given by $(I_{peak} - I_{background}) \times$ (scan rate), 0.02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times$ (scan rate)]. Final $R = 0.0278$ for 4091 reflections, $R_w = 0.0395$ (R for all reflections = 0.0355, R_w for all reflections = 0.0429) and a goodness of fit = 1.524. The maximum |shift/e.s.d.| < 0.1 in the final refinement cycle and the minimum and maximum peaks in the final difference electron density map were −0.44 and 0.68 e$^-$/Å^3, respectively. The scattering factors for the non-H atoms were taken from Cromer and Mann [10], with anomalous-dispersion corrections taken from Cromer and Liberman [11], while scattering factors for the H atoms were obtained from Stewart *et al.* [12]. The linear absorption coefficient was obtained from values found in the International Tables for X-ray Crystallography (1974) [13]. Other computer programs are listed in ref. 11 of Gadol and Davis [14].

Fractional coordinates are given in Table 2; bond lengths and angles in Table 3.

Results and discussion

The crystal structure determination of **3** confirms the stoichiometry of the compound as [**1**·Pd](PF$_6$)$_2$. As shown in Fig. 1, the palladium(II) ion, coordinated by the four nitrogen donor atoms of the macrocycle, lies in an essentially square planar geometry, as would be expected based on earlier literature precedent [7,15,16]. A small distortion from ideal square planar geometry, due to the restricted bite angles of the ethylenediamine-like chelate rings (N1–Pd–N2 = 84.62(11); N2–Pd–N3 = 86.25(11); N3–Pd–N4 = 84.24(10)), is shown by the

TABLE 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms of 3

Atom	*x*	*y*	*z*	*U*
Pd1	0.249030(10)	0.068750(10)	0.03506(2)	0.02466(8)
N1	0.1316(2)	0.08688(14)	−0.0834(3)	0.0343(8)
N2	0.2858(2)	0.15552(12)	−0.0478(3)	0.0339(8)
N3	0.3632(2)	0.06958(12)	0.1548(3)	0.0339(8)
N4	0.23560(15)	−0.02385(11)	0.1265(3)	0.0238(7)
O1	0.22401(13)	−0.02635(11)	−0.2206(2)	0.0342(6)
O2	0.35481(14)	−0.11709(11)	−0.1144(2)	0.0344(6)
O3	0.25585(14)	−0.20160(11)	0.0794(2)	0.0375(7)
O4	0.09763(14)	−0.12582(10)	0.1112(2)	0.0346(6)
C1	0.1431(2)	0.1509(2)	−0.1675(4)	0.0425(11)
C2	0.2039(3)	0.1944(2)	−0.0755(5)	0.0494(13)
C3	0.3580(3)	0.1799(2)	0.0548(5)	0.0493(13)
C4	0.4173(3)	0.1234(2)	0.0918(5)	0.0471(12)
C5	0.3953(2)	0.0015(2)	0.1541(4)	0.0376(10)
C6	0.3219(2)	−0.04109(15)	0.2069(3)	0.0313(9)
C7	0.1592(2)	−0.03299(15)	0.2273(3)	0.0291(9)
C8	0.1363(2)	−0.10399(15)	0.2519(3)	0.0307(9)
C9	0.0993(2)	−0.19519(15)	0.0917(4)	0.0376(10)
C10	0.1753(2)	−0.2162(2)	−0.0021(4)	0.0417(11)
C11	0.3325(2)	−0.2211(2)	0.0011(4)	0.0442(12)
C12	0.3465(3)	−0.1850(2)	−0.1462(4)	0.0412(11)
C13	0.3622(2)	−0.0787(2)	−0.2489(4)	0.0403(11)
C14	0.2760(3)	−0.0617(2)	−0.3239(4)	0.0440(12)
C15	0.1522(2)	0.0058(2)	−0.2966(4)	0.0385(10)
C16	0.0923(2)	0.0342(2)	−0.1806(4)	0.0395(11)
P1	0.04583(5)	0.14160(4)	0.34606(8)	0.0291(2)
F1	0.02749(13)	0.09683(9)	0.1967(2)	0.0436(6)
F2	−0.05808(12)	0.15306(9)	0.3577(2)	0.0457(7)
F3	0.0642(2)	0.18608(11)	0.4924(2)	0.0582(8)
F4	0.14883(13)	0.12846(11)	0.3311(3)	0.0589(8)
F5	0.0538(2)	0.20417(10)	0.2383(2)	0.0570(8)
F6	0.0374(2)	0.07829(10)	0.4507(2)	0.0532(7)
P2	0.43070(7)	0.12827(5)	−0.41281(10)	0.0434(3)
F7	0.4172(8)	0.1892(3)	−0.3046(8)	0.113(4)
F8	0.3413(5)	0.1356(5)	−0.465(2)	0.229(8)
F9	0.4464(8)	0.0707(3)	−0.5217(8)	0.101(4)
F10	0.5292(6)	0.1244(5)	−0.360(2)	0.159(5)
F11	0.4123(2)	0.08244(12)	−0.2697(3)	0.0853(12)
F12	0.4477(3)	0.17293(14)	−0.5539(3)	0.114(2)
F7A	0.3362(4)	0.1620(3)	−0.3825(7)	0.059(2)
F8A	0.3707(11)	0.0747(5)	−0.5086(8)	0.125(5)
F9A	0.5131(9)	0.0893(7)	−0.4418(13)	0.136(6)
F10A	0.4728(6)	0.1802(6)	−0.3181(10)	0.092(4)

For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

TABLE 3. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of **3**

1	2	3	1–2	1–2–3
N1	Pd1	N2	2.075(3)	84.62(11)
N1	Pd1	N3		169.16(11)
N2	Pd1	N3	2.004(3)	86.25(11)
N2	Pd1	N4		169.47(10)
N3	Pd1	N4	2.004(3)	84.24(10)
N4	Pd1	N1	2.070(2)	105.28(10)
C1	N1	C16	1.514(5)	113.6(3)
C1	N1	Pd1		106.7(2)
C16	N1	Pd1	1.488(5)	118.8(2)
C2	N2	C3	1.493(5)	121.3(3)
C2	N2	Pd1		107.0(2)
C3	N2	Pd1	1.486(5)	106.8(2)
C4	N3	C5	1.490(5)	120.6(3)
C4	N3	Pd1		107.1(2)
C5	N3	Pd1	1.477(4)	105.8(2)
C6	N4	C7	1.515(4)	112.2(2)
C6	N4	Pd1		107.4(2)
C7	N4	Pd1	1.490(4)	115.5(2)
C14	O1	C15	1.415(4)	112.0(2)
C15	O1		1.425(4)	
C12	O2	C13	1.423(4)	112.9(2)
C13	O2		1.421(4)	
C10	O3	C11	1.433(4)	113.8(3)
C11	O3		1.425(4)	
C8	O4	C9	1.420(4)	114.0(2)
C9	O4		1.431(4)	
C2	C1	N1	1.502(5)	109.4(3)
N2	C2	C1		105.7(3)
C4	C3	N2	1.497(6)	107.7(3)
N3	C4	C3		108.3(3)
C6	C5	N3	1.500(4)	107.3(3)
N4	C6	C5		111.5(2)
C8	C7	N4	1.512(4)	113.0(2)
O4	C8	C7		105.8(2)
C10	C9	O4	1.498(5)	111.6(3)
O3	C10	C9		109.3(3)
C12	C11	O3	1.504(5)	114.2(3)
O2	C12	C11		109.1(3)
C14	C13	O2	1.491(5)	113.8(3)
O1	C14	C13		109.8(3)
C16	C15	O1	1.499(5)	109.7(3)
N1	C16	C15		115.2(3)

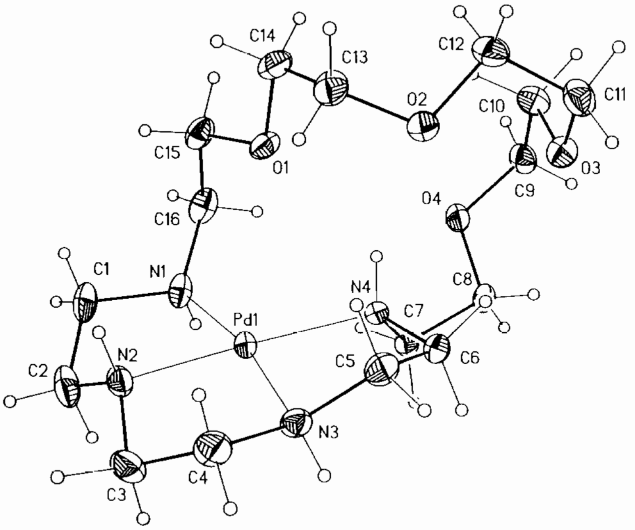

Fig. 1. Atom-labeling scheme for the cation in **3** depicting the coordination to Pd. H atoms and PF_6^- anions have been omitted for clarity. Ellipsoids are scaled to the 30% probability level.

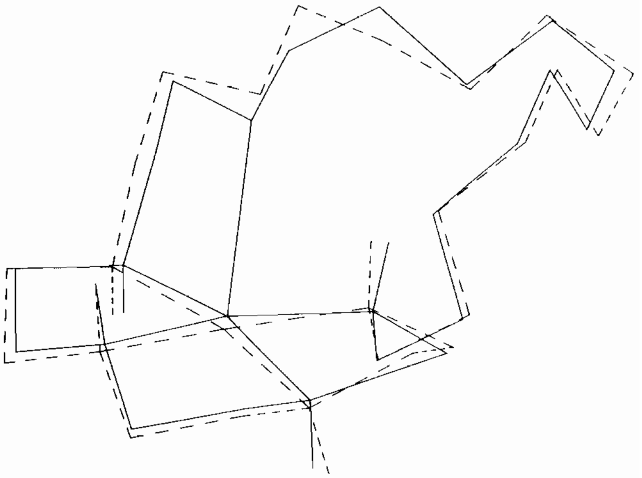

Fig. 2. Comparison of complex cations **2** and **3**. The Pd(II) complex, **3**, (shown by dotted line) is fitted by least-squares to the equivalent atoms in the Cu(II) complex, [2] **2** (solid line), highlighting the nearly identical conformations of the macrocycle.

wide N1–Pd–N4 angle (105.28(10)°). The Pd–N bond lengths to N1 and N4 (2.075(3) and 2.070(2) Å, respectively) are slightly longer than those to N2 and N3 (2.004(3) Å). The average Pd–N bond length (2.040(1) Å) is typical for secondary amines [7,15,16]. A very weak apical interaction (2.980(3) Å) to a ligand ether atom (O1) results in the Pd(II) ion being slightly out of the plane of the four nitrogen atoms (by 0.013 Å).

A comparison of **3** to the copper(II)-containing complex **2** reveals several similarities. Both metal ions reside in the polyaza portion of the macrocycle. Furthermore, both metal ions organize the large, flexible macrocycle in a nearly identical fashion. In fact, the only significant difference in the two structures is the metal–O1 bond (*vide infra*). This similarity in ligand conformation is illustrated by Fig. 2, which provides an overlay view of the two complex cations. This Figure thus helps highlight the fact that the major difference between complex cations **2** and **3** lies in the region near O1 of the chelating macrocycle.

The metal environment in **3**, however, differs significantly from that in **2**. The Cu(II) ion in **2** interacts more strongly with a ligand O_{ether} atom (Cu–O1 = 2.47(2) Å) to form a five-coordinate, square pyramidal structure. This axial ligation causes the copper ion to be considerably farther out of the plane of the four nitrogen atoms than the palladium ion (Cu(II), 0.10 Å out of plane; Pd(II), 0.013 Å). Thus, the degree of interaction between the crown ether moiety of ligand **1** and the metal center is reduced in the Pd(II) complex. As a consequence, complex **3** should be more ideally suited for the ligation of a second metal ion.

Conclusions

We have synthesized a Pd(II) complex of [24]aneN_4O_4 and compared its structure to the previously described Cu(II) complex, **2**. Despite some general similarities in structure between the two complexes, the immediate ligand environment was found to be significantly different in **3** (square planar) as compared to that in **2** (square pyramidal). As shown by X-ray diffraction studies, the Pd(II) ion lies approximately in the plane of the four nitrogen atoms of ligand **1**, and unlike the copper(II) ion in **2**, is essentially non-interacting with the crown ether moiety. We, thus, consider complex **3** to be a more viable candidate than **2** for the coordination of a second metal ion and should, therefore, be capable of forming bimetallic complexes with cations such as Na^+ and K^+. We are currently exploring this possibility.

Supplementary material

Full details of the X-ray structure of complex **3**, including atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

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