O1···Hg—C1—C2	18.8 (4)	O1—C8—C9—O2	−70.6 (6)
O1···Hg—C1—C6	−159.9 (4)	O2—C10—C11—O3	−70.4 (6)
C3—C2—C7—O1	141.2 (5)	O3—C12—C13—O4	75.1 (6)
C1—C2—C7—O1	−39.1 (7)	O4—C14—C15—O5	−70.6 (6)

Symmetry code: (i) $\frac{1}{2} + x, 1 - y, z$.

X-ray data were collected on a larger-than-usual needle using a sufficiently large collimator tube to ensure a homogeneous X-ray beam at the crystal. The adaptation of the collimator to the crystal size is possible here in view of the use of a β-filter as opposed to a graphite monochromator (Alexander & Smith, 1962).

Data collection: locally modified CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: SET4 (de Boer & Duisenberg, 1984). Data reduction: HELENA (Spek, 1997). Program(s) used to solve structure: DIRDIF96 (Beurskens et al., 1996). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: PLATON (Spek, 1990). Software used to prepare material for publication: PLATON.

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Organization of the Cavity in a Bipyridyl Crown Ether Through Coordination with PdCl2

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Abstract

In the crystal structure of dichloro[3,6,9,12,15,18-hexaoxa-24,27-diazatricyclo[24.4.0.0^{20,25}]triaconta-1(26),20,22,24,27,29-hexaene-N,N']palladium(II), [PdCl$_2$-(C$_{22}$H$_{30}$N$_2$O$_6$)], the Pd atom is tetracoordinated by the two pyridyl N atoms and two Cl atoms. The planes formed by atoms Pd1, N21, N31 and atoms Pd1, Cl1, Cl2 make an angle of 12.12 (9)° with one another. The twist of the two pyridyl rings of 31.59 (9)° is associated with the ortho substitution, and the complexation of PdCl$_2$ seems to alter the shape of the crown ether cavity, so that it is less suitable for complexing metal cations.

Comment

Allosteric effects represent an important mechanism for the regulation of the activity of important biomolecules. In this respect, much effort has been devoted to the development and study of simple synthetic models, e.g. bipyridyl crown ethers, that are able to mimic such a behaviour (Rebek, 1984).

Formation of transition metal complexes with bipyridyl crown ethers seems to pre-organize them in such a way as to selectively favour interaction with some specific alkali metal cations. In a different way, the pre-organization provided to the receptor (I) by interaction with the transition metal has been used as a molecular on–off switch for the uptake or release of Hg(CF$_3$)$_2$ (Rebek & Marshall, 1983), the very dramatic

effect in this case being related to the rotaxane-like structure of complexes between crown ethers and HgX_2 species (Luis *et al.*, 1991).

In this respect, it was of interest to study the X-ray structures of the transition metal complexes of crowns (I) and to analyse whether the complexation is really reflected in the pre-organization suggested by solution studies.

(I)
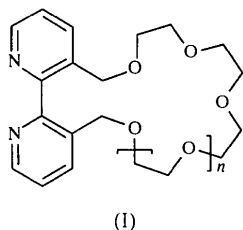
The Pd atom in the title compound, (II), is tetracoordinated by the two pyridyl N atoms and two Cl atoms. The plane formed by atoms Pd1, N21 and N31 forms an angle of 12.12 (9)° with the plane formed by atoms Pd1, Cl1 and Cl2. The two pyridyl rings are twisted by 31.59 (9)° relative to each other. This angle is presumably caused by the *ortho* substitution at C23 and C33, because the torsion angle N21—C22—C32—N31 of 26.2 (3)° lies in the range observed for similar complexes, for example, (2,2′-bipyridyl-3,3′-dicarboxylic acid-*N,N*′)dichlorocopper(II) (30.03°; Goddard *et al.*, 1990), [3,3′-bis(methoxycarbonyl)-2,2′-bipyridyl-*N,N*′]-dichloroplatinum(II) (21.33°; Miskowski *et al.*, 1993) and [3,3′-bis(methoxycarbonyl)-2,2′-bipyridyl-*N,N*′]di-chloropalladium (25.07°; Klein *et al.*, 1997). Thus, it can be inferred that it is not the complexation of the Pd atom which causes the twist between the two pyridyl rings, but rather the substituents in the *ortho* positions.

(II)
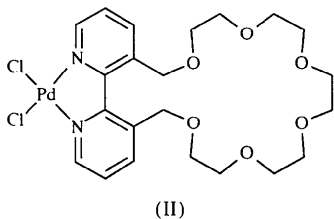
As predicted by Rebek, coordination of the two N atoms to the Pd cation pre-organizes the crown ether cavity in such a way as to render difficult the simultaneous coordination of both benzylic O atoms (O2 and O17) to a guest located in the crown ether cavity.

In a comparable structure, [3,6,9,12,15,18-hexaoxa-tricyclo[24.4.0.0²⁰,²⁵]triaconta-1(26),20,22,24,27,29-hexaene]bis(trifluoromethyl)mercury (Onan *et al.*, 1983; Rebek *et al.*, 1985), in which the pyridyl moiety is replaced by a 2,2′-dimethylbiphenyl moiety, all six O atoms coordinate a $Pd(CF_3)_2$ moiety and the two phenyl rings are twisted by 89.4° relative to each other. Thus, it can be concluded that the complexation of $PdCl_2$ by

the bipyridyl moiety has a great influence on the shape of the cavity formed by the crown ether part of the molecule.

The polyether chain is disordered in two parts; two different sites can be found for C9 [occupation factor 0.866 (8)], and O11 and C12 [occupation factor 0.577 (7)].
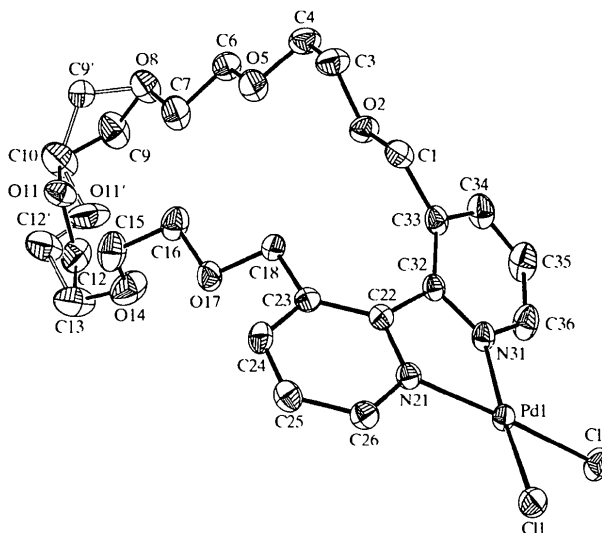

Fig. 1. Perspective view of (II) with the atom numbering; displacement ellipsoids are at the 50% probability level and H atoms have been omitted for clarity. The major conformer is drawn with solid bonds and the minor conformer with open bonds.

Experimental

The bipyridyl crown ether and the palladium complex were prepared according to Rebek *et al.* (1979). Single crystals (m.p. 463 K) were obtained from a methanol solution. Calculated for $C_{22}H_{30}Cl_2N_2O_6Pd$: C 44.3, H 5.1, N 4.7%; found: C 42.5, H 4.8, N 4.6%.

Crystal data

[PdCl₂(C₂₂H₃₀N₂O₆)]	Mo *Kα* radiation
$M_r = 595.78$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 7965
$P2_1/c$	reflections
$a = 15.1015(1)$ Å	$\theta = 1-25°$
$b = 9.9128(1)$ Å	$\mu = 1.019$ mm⁻¹
$c = 16.3279(2)$ Å	$T = 173$ K
$\beta = 92.359(1)°$	Block
$V = 2442.18(4)$ Å³	$0.43 \times 0.25 \times 0.15$ mm
$Z = 4$	Transparent red
$D_x = 1.620$ Mg m⁻³	
D_m not measured	

Data collection

Siemens CCD three-circle diffractometer	4362 reflections with $I > 2\sigma(I)$

ω scans
Absorption correction:
  empirical (*SADABS*;
  Sheldrick, 1996)
  T_{min} = 0.680, T_{max} = 0.858
21 436 measured reflections
4893 independent reflections

R_{int} = 0.026
θ_{max} = 26.32°
$h = -18 \rightarrow 18$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 20$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.067
S = 1.138
4893 reflections
322 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2$
  $+ 1.8145P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.794 e Å^{-3}
$\Delta\rho_{min}$ = −0.699 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—N21	2.031 (2)	Pd1—Cl2	2.3107 (6)
Pd1—N31	2.0416 (19)	Pd1—Cl1	2.3110 (6)
N21—Pd1—N31	79.90 (8)	N21—Pd1—Cl1	95.77 (5)
N21—Pd1—Cl2	170.98 (5)	N31—Pd1—Cl1	169.39 (6)
N31—Pd1—Cl2	94.74 (6)	Cl2—Pd1—Cl1	90.70 (2)

The data collection nominally covered over a sphere of reciprocal space, by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All non-H atoms, except for C9′, were refined anisotropically. Due to disorder, the bond lengths O8—C9, O8—C9′, O11—C10, O11—C12, O11′—C10 and O11′—C12′ were restrained to 1.430 (3) Å, and C9—C10, C9′—C10, C12—C13 and C12′—C13 to 1.510 (3) Å. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.2U_{eq}(C)] using a riding model with C—H(secondary) = 0.99 or C—H(aromatic) = 0.95 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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[(1,2,5,6-η)-Cyclooctatetraene](η⁵-cyclopentadienyl)cobalt

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Abstract

In the title complex, [Co(C₅H₅)(C₈H₈)], the cycooctatetraene ligand coordinates to the Co atom through two non-adjacent C=C double bonds. A tub-like shape is adopted by the polyolefin ligand.

Comment

For a η^4-bonded C_8H_8 ligand, two coordination geometries are possible (Deganello, 1979). In the cyclooctadiene-like 1,2,5,6-η coordination mode, the polyolefin is bonded to the metal through two non-adjacent C=C double bonds ('1,5-isomer'). The second coordination isomer has a 1–4-η-coordinated butadiene-like substructure, where bonding to the metal occurs through two adjacent double bonds ('1,3-isomer'). Several complexes are known in which both isomers have been observed in solution (Deganello, 1979).