A conoscopic examination between two crossed polarizers on a Zeiss Photomicroscope II confirmed the optical quality and nature of the crystal. Due to a most satisfactory refinement, it was deemed unnecessary to continue further iterations [see $(\Delta/\sigma)_{\max}$ under refinement]. The structure was checked for additional symmetry by the *MISSYM* program (Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual.* Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989) (heavy-atom Patterson method). Program(s) used to refine structure: *SHELXTL-Plus.* Molecular graphics: *SHELXTL-Plus* and *XP* (Siemens, 1994). Software used to prepare material for publication: local *CIFGEN* program.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Benzyl *sym*-dibenzo-16-crown-5 ether)-lead(II) Dinitrate

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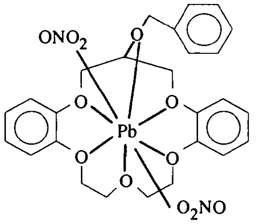
Abstract

The title complex, (17-benzyloxy-2,5,8,15,19-pentaoxatricyclo[18.4.0.0^{9,14}]tetracosa-9,11,13,20,22,24-hexaene-κ^6O)bis(nitrato-O,O')lead(II), [$Pb(NO_3)_2(C_{26}H_{28}O_6)$], prepared from benzyl *sym*-dibenzo-16-crown-5 ether and $Pb(NO_3)_2$ in aqueous $CHCl_3$/MeOH at room temperature, has decacoordinate geometry for the Pb^{2+} ion, with bonds to the five ring O atoms, the side-arm ether O atom and two O atoms of each of the two coordinated nitrate ions. The four Pb—O bond lengths for the nitrate ligands are considerably shorter than those for the crown ether.

Comment

While crystal structures of metal complexes of simple crown and cryptand lariat ethers are well documented (Vögtle & Weber, 1989), corresponding complexes with C-pivot lariat ethers remained unknown until the recent report (Liu, Lin, Young, Shgu & Ueng, 1996) that C-pivot hydroxy- and 2′-methoxyethyl benzyl *sym*-dibenzo-16-crown-5 ethers form complexes with Na^+ and Pb^{2+} ions, respectively. These results provide concrete evidence of side-arm participation in C-pivot lariat crown–metal complexation.

The structure of the title complex, (I), formed from benzyl *sym*-dibenzo-16-crown-5 ether and $Pb(NO_3)_2$, is shown in Fig. 1. Of the six lariat donor atoms, the side-arm O6 atom is the closest to the metal [2.658 (5) Å]. The lengths of the other five Pb—O bonds in the macrocycle are in the range 2.725 (6)–2.901 (5) Å. That the Pb—O bond for the side-arm is significantly shorter than those for the ring may be attributed to the flexibility of the side-arm. Two nitrate anions also serve as bidentate donors, making Pb^{2+} decacoordinate, and the four nitrate Pb—O bond lengths are considerably shorter than the others. The coordination geometry may be described as two superimposed trigonal bipyramids. The first is formed by atoms O3, O6 and O13 in equatorial sites, and O5 and O11 in axial sites; the second has O2, O4 and O14 equatorial, and O1 and O10 axial. The structure is similar to that of the pentanitratocerate(III) ion (Al-Karaghouli & Wood, 1970), but more distorted.



(I)

The two benzo groups of the macrocyclic ligand form a V-shape with a dihedral angle of 128.4 (4)°. Fig. 1 shows that the crown provides a large enough cavity to immerse the lead cation and the benzyl side-arm cradles the metal ion towards the ring. The present structural study helps to explain why benzyl *sym*-dibenzo-16-crown-5 ether is better than the other lariat crown ethers in binding heavy metal ions. As demonstrated by our results, the side-arm of the crown ether cooperates with the ring fully in cation binding by pushing the metal ion into the ring cavity.

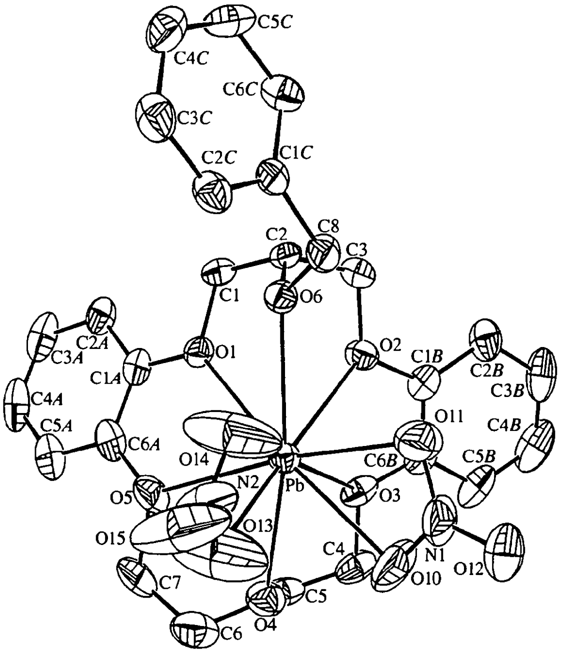


Fig. 1. The molecular structure of the title compound with H atoms omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

Experimental

To a stirred solution of $Pb(NO_3)_2$ (0.662 g, 2 mmol) in 4 ml $MeOH/H_2O$ (4:1) at room temperature, benzyl *sym*-dibenzo-16-crown-5 ether (0.436 g, 1 mmol) (Niu, Wu & Qu, 1989) in 1 ml $CHCl_3$ was added and the reaction mixture was stirred for 10 min. Crystals of the product complex suitable for X-ray diffraction were grown by slow diffusion of hexane into the reaction mixture in a desiccator. Analysis calculated (found) for $C_{26}H_{28}N_2O_{12}Pb$: C 40.68 (40.53), H 3.68 (3.70), N 3.65% (3.73%).

Crystal data

$[Pb(NO_3)_2(C_{26}H_{28}O_6)]$
$M_r = 767.70$
Monoclinic
$P2_1/c$
$a = 14.224\,(2)$ Å
$b = 8.882\,(2)$ Å
$c = 22.885\,(5)$ Å
$\beta = 101.47\,(1)°$
$V = 2833\,(9)$ Å^3
$Z = 4$
$D_x = 1.80$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11.15–15.72°$
$\mu = 6.06$ mm^{-1}
$T = 298$ K
Prismatic
0.30 × 0.20 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical from ψ scans (Larson *et al.*, 1990)
$T_{min} = 0.188$, $T_{max} = 0.408$
5114 measured reflections
4975 independent reflections

3252 reflections with $I > 2.5\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 24.9°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 27$
3 standard reflections frequency: 120 min intensity decay: 5%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.026$
$S = 2.05$
3252 reflections
371 parameters
H atoms fixed with U_{iso} set 0.01 Å^2 > U_{eq}(C)
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.095$

$\Delta\rho_{max} = 1.070$ e Å^{-3}
$\Delta\rho_{min} = -0.800$ e Å^{-3}
Extinction correction: Larson *et al.* (1990)
Extinction coefficient: 0.73 (4)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Pb—O1	2.812 (5)	Pb—O6	2.658 (5)
Pb—O2	2.792 (5)	Pb—O10	2.533 (7)
Pb—O3	2.901 (5)	Pb—O11	2.531 (7)
Pb—O4	2.725 (6)	Pb—O13	2.537 (9)
Pb—O5	2.839 (6)	Pb—O14	2.574 (9)
O1—Pb—O2	65.6 (2)	O2—Pb—O6	62.4 (2)
O1—Pb—O5	55.0 (2)	O4—Pb—O5	58.6 (2)
O1—Pb—O6	59.4 (2)	O10—Pb—O11	47.4 (3)
O2—Pb—O3	52.9 (2)	O13—Pb—O14	42.2 (3)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Larson *et al.*, 1990). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *NRCVAX*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(μ-2,2,6,6,10,10-hexamethyl-4,8-dioxaundecanedioato-$O^1,O^{11}:O^{1'},O^{11'}$)bis(pyridine-$N$)dirhodium(II)($Rh$—$Rh$)

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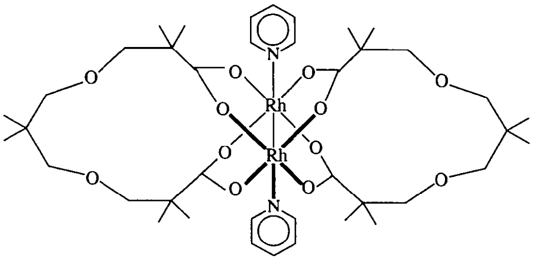
Abstract

The title compound, [$Rh_2(C_{15}H_{26}O_6)_2(C_5H_5N)_2$], lies about an inversion centre which is at the midpoint of the Rh—Rh bond. The polyether dicarboxylate ligands bridge the Rh atoms and function as macrocyclic chelates to the Rh—Rh unit. A pyridine molecule is axially coordinated to each Rh atom completing the octahedral coordination. Main dimensions are Rh—Rh 2.4017 (2), Rh—O 2.0367 (9)–2.0405 (9), Rh—N 2.2540 (11) Å and Rh—Rh—N 178.59 (3)°.

Comment

The chemistry of metal–metal bonded complexes has been extensively studied over the past thirty years with the main emphasis largely on individual dinuclear M_2 species (Cotton & Walton, 1994). Recent developments have concentrated on the macromolecular chemistry of M_2 compounds due to the interesting physical properties which may arise from co-operative interaction between the metal centres (Cayton, Chisholm, Huffman & Lobkovsky, 1991; Mashima, Nakano & Nakamura, 1996). Studies on dirhodium(II) complexes have focused on catalysis (Doyle, Kalinin & Ene, 1996; Kennedy, McKervey, Maguire & Roos, 1990) and on rhodium-binding modes in DNA studies (Dunbar, Matonic, Saharan, Crawford & Christou, 1994). We are currently studying dicarboxylic acids (Ferguson, Gallagher & McAlees, 1995) and their reactivity towards metal complexes with a view to exploring applications in catalysis and antitumour chemistry, and report here on the structure and stereochemistry of the title compound, (I).



(I)

Molecule (I) resides on an inversion centre which is at the midpoint of the Rh—Rh bond. The relatively flexible dicarboxylate ligand functions as a macrocyclic chelate to the Rh—Rh unit and adopts two conformations [occupancies 0.943 (3) and 0.057 (3)] in the crystal (see details in the *Experimental* section). The Rh—Rh bond is 2.4017 (2) Å and the carboxylate groups of each dicarboxylate ligand bridge the Rh_2 unit in an orthogonal fashion; the angle between the Rh1, Rh1$^{\rm i}$, O11, O12, C1 and Rh1, Rh1$^{\rm i}$, O21, O22, C11 planes is 87.36 (3)° [symmetry code: (i) $1-x, -y, -z$]. The Rh—O distances are in the range 2.0367 (9)–2.0405 (9) Å and the *cis*-O—Rh—O angles 87.73 (4)–92.59 (4)°, with Rh—Rh—O 86.82 (3)–88.92 (3)°. A pyridine molecule is axially coordinated to each Rh atom completing the octahedral coordination [Rh—N 2.2540 (11) Å and Rh—Rh—N 178.59 (3)°]. The pyridine ring is bent away from the Rh—Rh—N axis such that atom Rh1 lies 0.282 (3) Å from the plane of the pyridine ring.

In (I), the overall dicarboxylate ligand conformation is determined primarily by the *cis* arrangement of the carboxylate groups. The C—C—C—O torsion angles of the major component of the macrocycle chain (Table 2) all have values close to *gauche* and three of the C—C—O—C torsion angles are close to fully *trans* values;