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Structure of (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)lead(II) Eosin Dihydrate

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Abstract. (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-*N*¹,*N*¹⁰,*O*⁴,*O*⁷,*O*¹³,*O*¹⁶,*O*²¹,*O*²⁴)[2-(2,4,6,8-tetrabromo-3,7-dioxo-9-xanthenyl)benzoato-*O*,*O'*]lead dihydrate, [Pb(C₁₈H₃₆N₂O₆)(C₂₀H₆Br₄O₅)]·2H₂O, *M_r* = 1265.60, triclinic, *P* $\bar{1}$, *a* = 12.079 (2), *b* = 12.671 (3), *c* = 18.01 (2) Å, α = 101.46 (5), β = 96.45 (6), γ = 113.60 (3)°, *V* = 2418 (3) Å³, *Z* = 2, *D_x* = 1.74 Mg m⁻³, Mo *K* α radiation (graphite-crystal monochromator), λ = 0.71073 Å, μ = 6.84 mm⁻¹, *F*(000) = 1228, *T* = 293 K, final conventional *R* = 0.078 for 3877 observed reflections and 530 variables. The central Pb²⁺ cation is decahedrally coordinated by one eosin and one cryptand organic ligand. Distances: Pb—O(cryptand) 2.62 (2)–3.09 (2) Å; Pb—O(eosin) 2.50 (2) and 2.57 (2) Å; Pb—N 2.81 (3) and 2.97 (3) Å. The Pb²⁺ cation is coordinated by two N atoms and four O atoms of the cryptand on a plane; the two eosin O atoms are above this plane and the last two cryptand O atoms are below it, forming a nearly tetrahedral arrangement.

Introduction. The diazopolyoxamacrobicycles or cryptands, first synthesized by Lehn (Dietrich, Lehn & Sauvage, 1969), are well known for their ability to form inclusion complexes, called cryptates, with metal ions. Since then, these ligands and related synthetic macrobicyclic compounds have been at the centre of interest to physical, organic, inorganic and biochemists and, to a lesser extent, analytical chemists. From the analytical point of view these host-guest complexes are important because they are readily extractable as colourful ion pairs or fluor-

escent hydrophobic anions into suitable organic solvents and can be used for selective and sensible separation and determination of a variety of metal ions, especially alkali-metal, alkaline-earth-metal and toxic heavy-metal cations.

In an earlier paper we reported a highly sensitive and selective spectrofluorimetric method for the determination of ultratraces of lead, based on solvent extraction with chloroform or 1,2-dichloroethane of the ion pair formed between the positively charged cryptate of lead with cryptand ethers, and the eosinate anion (Blanco-Gomís, Fuente-Alonso & Sanz-Medel, 1985; Blanco-Gomís, Arias-Abrodo, Picinelli-Lobo & Sanz-Medel, 1988). Since the elucidation of the spatial structures of ionophores and their complexes is essential for understanding the detailed mechanisms of selective complex formation and phase transfer of ions, crystallization of a ternary ion-association complex in 1,2-dichloroethane, under the same analytical conditions, has been carried out and an X-ray diffraction single-crystal study has been undertaken. The present paper reports the crystal structure of a new Pb²⁺ complex with cryptand ether and eosin.

Experimental. A red crystal of size 0.20 × 0.17 × 0.10 mm was used for data collection with Mo *K* α radiation and graphite-crystal monochromator on an Enraf-Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections with θ between 6 and 18°. Space group *P* $\bar{1}$ was confirmed from structure determination. The intensity data of 9069 reflections, in *hkl* range $-14, -15, 0$ to $14, 14, 21$

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Table 1. Fractional positional parameters and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	U_{eq}
Pb(1)	0.4051 (1)	0.2751 (1)	0.17620 (8)	3.44 (5)
N(1)	0.472 (2)	0.246 (2)	0.022 (2)	4. (1)
C(2)	0.604 (3)	0.325 (3)	0.040 (2)	5. (2)
C(3)	0.636 (3)	0.447 (3)	0.084 (2)	4. (2)
O(4)	0.620 (2)	0.443 (2)	0.161 (1)	5. (1)
C(5)	0.645 (3)	0.558 (3)	0.209 (2)	5. (2)
C(6)	0.659 (3)	0.548 (3)	0.294 (2)	6. (2)
O(7)	0.556 (2)	0.444 (2)	0.298 (1)	5. (1)
C(8)	0.536 (3)	0.449 (3)	0.375 (2)	6. (2)
C(9)	0.423 (3)	0.334 (3)	0.369 (2)	5. (2)
N(10)	0.320 (3)	0.314 (2)	0.314 (2)	5. (1)
C(11)	0.273 (4)	0.408 (3)	0.327 (2)	6. (2)
C(12)	0.306 (4)	0.486 (3)	0.273 (2)	6. (2)
O(13)	0.273 (2)	0.419 (2)	0.197 (1)	6. (1)
C(14)	0.256 (4)	0.479 (3)	0.144 (2)	5. (2)
C(15)	0.217 (4)	0.394 (3)	0.065 (2)	6. (2)
O(16)	0.320 (2)	0.373 (2)	0.048 (1)	6. (1)
C(17)	0.287 (3)	0.278 (3)	-0.018 (2)	5. (2)
C(18)	0.404 (3)	0.277 (3)	-0.037 (2)	4. (2)
C(19)	0.451 (3)	0.119 (3)	0.000 (2)	5. (2)
C(20)	0.319 (3)	0.032 (3)	-0.008 (2)	5. (2)
O(21)	0.283 (2)	0.056 (2)	0.065 (1)	6. (1)
C(22)	0.154 (3)	-0.021 (3)	0.062 (2)	6. (2)
C(23)	0.135 (4)	0.010 (4)	0.141 (3)	7. (2)
O(24)	0.154 (2)	0.124 (2)	0.166 (2)	6. (1)
C(25)	0.118 (3)	0.152 (4)	0.235 (3)	7. (2)
C(26)	0.211 (4)	0.192 (4)	0.302 (3)	8. (3)
C(31)	0.346 (4)	0.108 (4)	0.486 (2)	6. (2)
Br(31)	0.2093 (4)	0.1093 (4)	0.5277 (2)	6.8 (2)
C(32)	0.469 (3)	0.203 (3)	0.531 (2)	4. (2)
O(32)	0.481 (2)	0.281 (2)	0.590 (1)	5. (1)
C(33)	0.571 (3)	0.192 (3)	0.498 (2)	5. (2)
Br(33)	0.7310 (4)	0.2989 (4)	0.5572 (3)	7.9 (2)
C(34)	0.554 (3)	0.110 (3)	0.429 (2)	3. (1)
C(35)	0.252 (3)	-0.199 (3)	0.199 (2)	3. (1)
C(36)	0.131 (3)	-0.266 (3)	0.163 (2)	4. (1)
Br(36)	0.0926 (4)	-0.3586 (3)	0.0592 (2)	6.0 (2)
C(37)	0.033 (3)	-0.262 (3)	0.196 (2)	5. (2)
O(37)	-0.079 (2)	-0.323 (2)	0.160 (1)	7. (1)
C(38)	0.075 (3)	-0.182 (3)	0.276 (2)	5. (2)
Br(38)	-0.0558 (3)	-0.1706 (4)	0.3230 (2)	7.1 (2)
O(39)	0.215 (2)	-0.049 (2)	0.382 (1)	4. (1)
C(40)	0.410 (3)	-0.046 (3)	0.316 (2)	3. (1)
C(41)	0.287 (3)	-0.122 (3)	0.274 (2)	3. (1)
C(42)	0.186 (3)	-0.119 (3)	0.312 (2)	4. (1)
C(43)	0.330 (3)	0.028 (2)	0.422 (2)	3. (1)
C(44)	0.433 (3)	0.030 (3)	0.387 (2)	4. (1)
C(51)	0.519 (3)	-0.042 (2)	0.277 (2)	3. (1)
C(52)	0.565 (3)	-0.120 (3)	0.285 (2)	4. (1)
C(53)	0.666 (3)	-0.119 (3)	0.259 (2)	5. (2)
C(54)	0.724 (3)	-0.034 (3)	0.226 (2)	5. (2)
C(55)	0.677 (3)	0.048 (3)	0.211 (2)	5. (2)
C(56)	0.573 (2)	0.044 (3)	0.238 (2)	3. (1)
C(57)	0.521 (3)	0.129 (3)	0.219 (2)	4. (1)
O(58)	0.576 (2)	0.203 (2)	0.184 (2)	6. (1)
O(59)	0.425 (2)	0.124 (2)	0.241 (1)	4. (1)
O(60)	0.101 (2)	0.384 (2)	0.502 (1)	8. (1)
O(61)	0.016 (2)	0.515 (3)	0.708 (1)	7. (1)

and θ limits 0–25°, were measured using the ω -2 θ -scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift correction factors were between 0.99 and 1.07. On all reflections, profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); a semi-empirical absorption correction was applied using ψ scans (North, Phillips & Mathews, 1968), $\mu(\text{Mo } K\alpha) = 6.84 \text{ mm}^{-1}$ (correction factors were in the range 0.86–1.00). Some double-measured reflections were averaged, $R_{\text{int}} =$

Table 2. Selected bond lengths (\AA) and bond angles ($^\circ$)

Pb(1)—N(1)	2.97 (3)	Pb(1)—O(4)	2.70 (2)
Pb(1)—O(7)	2.62 (2)	Pb(1)—N(10)	2.81 (3)
Pb(1)—O(13)	2.86 (2)	Pb(1)—O(16)	3.09 (2)
Pb(1)—O(21)	2.78 (2)	Pb(1)—O(24)	2.82 (2)
Pb(1)—O(58)	2.57 (2)	Pb(1)—O(59)	2.50 (2)
O(4)—Pb(1)—N(1)	62.1 (7)	O(7)—Pb(1)—N(1)	122.0 (7)
O(7)—Pb(1)—O(4)	60.2 (7)	N(10)—Pb(1)—N(1)	172.2 (7)
N(10)—Pb(1)—O(4)	119.1 (8)	N(10)—Pb(1)—O(7)	60.6 (8)
O(13)—Pb(1)—N(1)	113.1 (7)	O(13)—Pb(1)—O(4)	98.2 (7)
O(13)—Pb(1)—O(7)	80.6 (7)	O(13)—Pb(1)—N(10)	59.4 (7)
O(16)—Pb(1)—N(1)	57.2 (7)	O(16)—Pb(1)—O(4)	76.9 (7)
O(16)—Pb(1)—O(7)	112.9 (7)	O(16)—Pb(1)—N(10)	115.1 (7)
O(16)—Pb(1)—O(13)	56.1 (6)	O(21)—Pb(1)—N(1)	60.3 (7)
O(21)—Pb(1)—O(4)	120.6 (7)	O(21)—Pb(1)—O(7)	161.5 (7)
O(21)—Pb(1)—N(10)	119.9 (8)	O(21)—Pb(1)—O(13)	116.3 (7)
O(21)—Pb(1)—O(16)	84.2 (7)	O(24)—Pb(1)—N(1)	111.4 (8)
O(24)—Pb(1)—O(4)	165.3 (7)	O(24)—Pb(1)—O(7)	126.0 (7)
O(24)—Pb(1)—N(10)	65.4 (8)	O(24)—Pb(1)—O(13)	71.6 (7)
O(24)—Pb(1)—O(16)	88.5 (7)	O(24)—Pb(1)—O(21)	58.6 (7)
O(58)—Pb(1)—N(1)	72.3 (7)	O(58)—Pb(1)—O(4)	69.3 (7)
O(58)—Pb(1)—O(7)	83.0 (8)	O(58)—Pb(1)—N(10)	115.5 (8)
O(58)—Pb(1)—O(13)	162.9 (8)	O(58)—Pb(1)—O(16)	128.1 (7)
O(58)—Pb(1)—O(21)	80.6 (8)	O(58)—Pb(1)—O(24)	122.8 (7)
O(59)—Pb(1)—N(1)	110.9 (7)	O(59)—Pb(1)—O(4)	115.5 (7)
O(59)—Pb(1)—O(7)	89.1 (7)	O(59)—Pb(1)—N(10)	75.9 (7)
O(59)—Pb(1)—O(13)	133.4 (7)	O(59)—Pb(1)—O(16)	158.1 (7)
O(59)—Pb(1)—O(21)	73.9 (7)	O(59)—Pb(1)—O(24)	78.9 (7)
O(59)—Pb(1)—O(58)	50.5 (7)		

$\sum(I - \langle I \rangle) / \sum I = 0.035$, resulting in 8451 unique reflections of which only 3877 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by direct methods using the programs *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens *et al.*, 1982). Isotropic least-squares refinement, using a local version of the program *SHELX76* (Sheldrick, 1976), converged to $R = 0.10$. At this stage an additional empirical absorption correction was performed using *DIFABS* (Walker & Stuart, 1983); correction factors were 0.82 and 1.30. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of some of the H atoms; the rest were geometrically placed and all were refined riding on their parent atoms. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. All the H-atoms were refined with a common isotropic thermal parameter. The final conventional agreement factor was $R = 0.078$ for the 3877 observed reflections and 530 variables. No weights were applied. The maximum shift to e.s.d. ratio in the final full-matrix least-squares cycle was less than 0.06. The final difference Fourier map showed no peaks higher than 1.3 e \AA^{-3} or deeper than -0.84 e \AA^{-3} . The slightly high R factor found may be assigned to crystal quality, absorption effects and slight disorder of the water molecules. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The plots were made with *PLUTO* (Motherwell & Clegg, 1978). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were performed on

a MicroVAX 3400 computer at the Scientific Computer Centre of the University of Oviedo.

Discussion. Final positional and thermal parameters are given in Table 1.* Selected molecular geometry data are collected in Table 2. The plot in Fig. 1 shows the Pb coordination and the atomic numbering scheme; H atoms, water molecules and C-atom labels have been removed for clarity. The central Pb²⁺ cation is decahedrally coordinated by

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles including those involving H atoms, least-squares-planes data and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55692 (65 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0410]

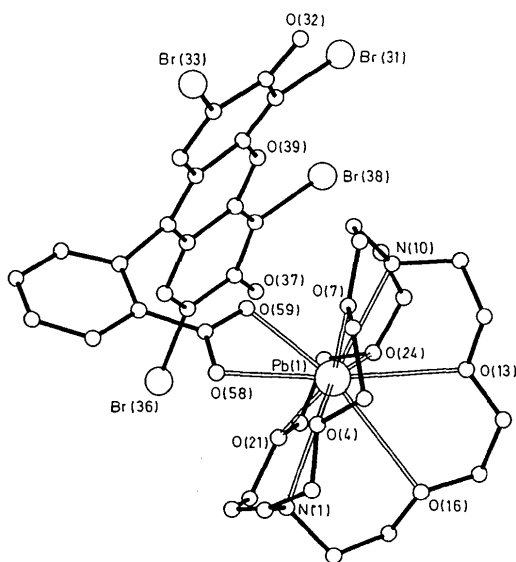


Fig. 1. PLUTO (Motherwell & Clegg, 1978) diagram showing a view of the compound and the atomic numbering scheme.

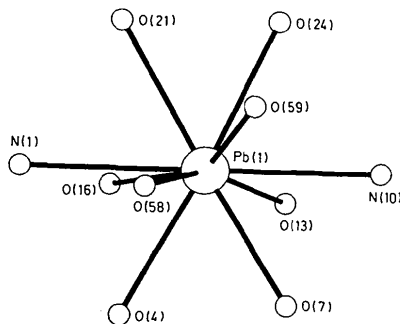


Fig. 2. PLUTO (Motherwell & Clegg, 1978) schematic plot showing details of the Pb²⁺ coordination.

the cryptand ether (eight coordination positions) and eosin (two coordination positions). Distances Pb—O(cryptand) range from 2.62 (2) to 3.09 (2) Å, distances Pb—O(eosin) are 2.50 (2) and 2.57 (2) Å and distances Pb—N are 2.81 (3) and 2.97 (3) Å, corresponding to the *in-in* conformation. All the distances are similar to those found in analogous thiocyanate compounds (Metz & Weis, 1974) while the coordination geometry is rather different.

The coordination distances of the chelating O atoms of the eosin are shorter than the rest, indicating the covalent character of these bonds; this fact may explain the very high selectivity of this system for Pb²⁺ extraction. The decahedral coordination may be seen schematically in Fig. 2; the Pb²⁺ is coordinated by two N atoms and four O atoms of the cryptand on a plane; the two eosin O atoms are above this plane and the last two cryptand O atoms are below it, forming a nearly tetrahedral arrangement. The dihedral angles between the least-squares planes through Pb(1)—N(1)—N(10)—O(4)—O(7)—O(21)—O(24) with those through Pb(1)—O(13)—O(16) and Pb(1)—C(57)—O(58)—O(59) are close to 90° [91.4 (5) and 86.9 (7)°, respectively]. In the eosin ligand, the two main planes form a dihedral angle of 84.2 (8)°.

The distance of the plane C(31)—C(32)—C(33)—C(34)—C(35)—C(36)—C(37)—C(38)—O(3)—C(40)—C(41)—C(42)—C(43)—C(44) to the central cation is 5.137 (3) Å giving a highly polar character to our molecule, which explains the impossibility of performing the extraction process in non-polar solvents.

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