# The Crystal and Molecular Structure of Lead(II) Nitrate : 18-Crown-6

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Macrocyclic polyethers (crown ethers) react with a variety of main-group acceptors to give a rich structural chemistry of complex species in solutions that is only partly reflected by the solid-state products that crystallise.[1-12] We can distinguish two kinds of product; those in which the metal atom interacts directly with all or some of the ring oxygen atoms, and those in which the metal atoms are only indirectly linked to the ether via hydrogen bonds from coordinated water molecules.[13-15] A key factor behind the versatility of crown ethers as ligands is the coupling of their fluxional properties to their multidonor properties, i.e. the oxygen atoms. Such a coupling leads to a number of options for complexation because different conformations (albeit small variations) can lead to changes in the numbers of the donor sites that can be effectively presented to a potential acceptor.[16] An appropriate conformation of the crown ether towards a potential acceptor may be able to exploit the so-called macrocylic or entropy effect, which is an expression for the favourable displacement of solvent molecules coordinated to the acceptor. The effect depends on the size of the crown ether (or, more specifically, on the number of oxygen atoms made available), since the process of liberating a greater number of solvent molecules from the coordination sphere of the metal atoms gives more favourable entropy values.

We have previously characterised by means of X-ray crystallography and synchrotron X-ray spectroscopy a number of complexes formed between macrocyclic polyethers and acceptor compounds containing the heavier main-group elements thallium(I), tin(II), lead(II), antimony(III) and bismuth(III).[1-10] In addition, Alcock et al. have recently reported the structures of 12-crown-4 and 18-crown-6 complexes with bismuth(III) chloride and 18-crown-6 with antimony(III) chloride.[11,12] We extend this work by reporting here the crystal and molecular structure

of the lead(II) nitrate complex dinitrato(1,4,7,10,13,16-hexaoxacyclooctadecane)lead(II), $Pb(NO_3)_2(CR)$, where CR denotes 18-crown-6.

## Experimental

*Preparation.* The complex was prepared by adding 18-crown-6 (0.5 g) dropwise to a saturated aqueous solution (5 $cm^3$) of lead(II) nitrate; diffraction quality crystals were obtained after a few hours at room temperature.

*Crystal data.* $C_{12}H_{24}O_{12}N_2Pb$, $M = 595.52$, monoclinic, $a = 7.755(8)$, $b = 15.415(9)$, $c = 8.095(8)$ Å, $\beta = 104.0(1)°$, $V = 938.96$ Å$^3$, $Z = 2$, $F(000) = 576$, $MoK_\alpha$ radiation, $\lambda = 0.710\ 69$ Å, $\mu = 89.2$ cm$^{-1}$. Absent reflections were consistent with space group $P2_1/a$.

*Table 1.* Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses and equivalent isotropic thermal parameters (in $10^3$ Å$^2$).

| Atom | x/a | y/b | z/c | $U_{eq}$[a] |
|------|------|------|------|------|
| Pb | 5000 | 5000 | 0 | 53.4(4) |
| O(1) | 6768(17) | 5035(6) | −2446(14) | 67(6) |
| C(2) | 8465(19) | 4597(13) | −2105(19) | 39(6) |
| C(3) | 8271(21) | 3761(11) | −1312(18) | 64(9) |
| O(4) | 7877(15) | 3936(6) | 267(13) | 75(7) |
| C(5) | 7904(30) | 3191(11) | 1308(23) | 98(14) |
| C(6) | 7479(24) | 3409(12) | 2865(25) | 48(8) |
| O(7) | 5672(15) | 3688(7) | 2408(12) | 65(6) |
| C(8) | 4970(26) | 3817(10) | 3832(17) | 117(15) |
| C(9) | 3163(24) | 4147(10) | 3169(18) | 78(11) |
| N(11) | 7405(26) | 6251(10) | 2481(19) | 102(13) |
| O(12) | 8429(20) | 6759(9) | 3506(19) | 103(12) |
| O(13) | 7266(24) | 5509(10) | 2931(18) | 149(15) |
| O(14) | 6789(34) | 6440(11) | 1068(21) | 298(32) |

[a] $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

*Intensity data collection and structure refinement.* A crystal of approximate size 0.3 × 0.2 × 0.35 mm was mounted so as to rotate about the *a*-axis on a Stoe STADI2 diffractometer, and data were collected via a variable-width ω-scan. Background counts were for 20 s, and a scan rate of 0.0333° s⁻¹ was applied to a width of (1.5 + sin μ/tan θ). Lattice constants were obtained from accurate measurements of axial reflections taken at room temperature. The intensities of 2665 independent reflections were measured out to 2θ < 50° using monochromatised MoK$_\alpha$ radiation. Of these, 2160 reflections were classified as observed, i.e. $I_{net}$ > 3.0σ(*I*), and used in the refinement. Lorentz and polarisation corrections were applied, systematic absences rejected and equivalent reflections merged. The crystal was stable under data collection. Scattering factors and dispersion corrections were taken from Ref. 17, lead values being used for lead(II). The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares method using the weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Anisotropic temperature factors were applied to the non-hydrogen atoms and a common isotropic factor to the hydrogen atoms. The positions of the latter were calculated but not refined. The computer programs used were those of the SHELX 76 package,[18] and the calculations were carried out on an Amdahl V7 computer; the final *R* factor is 0.058 ($R_w$ = 0.062). The data were corrected empirically for absorption.[19]

The atomic positions are given in Table 1, and Table 2 shows the interatomic distances and valence angles. Additional material, available from the authors, comprises the thermal parameters, structure factors and hydrogen coordinates.

Table 2. Bond distances (in Å) and angles (in °) with e.s.d.s in parentheses.

**(a) Lead coordination**

| Pb–O(1) | 2.667(12) | Pb–O(4) | 2.735(11) |
|---|---|---|---|
| Pb–O(7) | 2.770(9) | Pb–O(13) | 2.705(15) |
| Pb–O(14) | 2.650(16) | | |

**(b) Nitrate anion**

| N(11)–O(12) | 1.27(2) | O(12)–N(11)–O(13) | 118.2(2) |
|---|---|---|---|
| N(11)–O(14) | 1.17(2) | O(13)–N(11)–O(14) | 119.1(2) |
| N(11)–O(13) | 1.21(2) | O(12)–N(11)–O(14) | 122.0(2) |

**(c) 18-Crown-6**

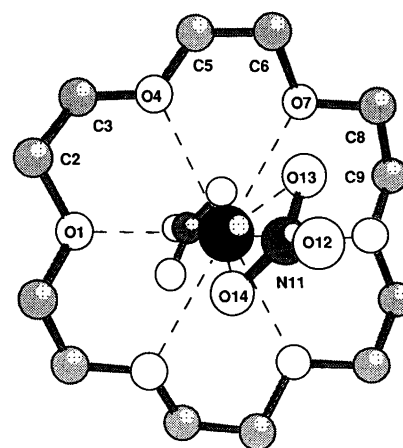| O(1)–C(2) | 1.45(2) | C(2)–O(1)–C(9)ᵃ | 112.1(1) |
|---|---|---|---|
| C(3)–O(4) | 1.41(2) | C(2)–C(3)–O(4) | 107.2(2) |
| C(5)–C(6) | 1.42(2) | O(4)–C(5)–C(6) | 111.3(2) |
| O(7)–C(8) | 1.40(2) | C(6)–O(7)–C(8) | 112.4(2) |
| C(9)–O(1ᵃ) | 1.40(2) | C(8)–C(9)–O(1)ᵃ | 110.6(2) |
| C(2)–C(3) | 1.46(2) | O(1)–C(2)–C(3) | 108.1(2) |
| O(4)–C(5) | 1.42(2) | C(3)–O(4)–C(5) | 114.0(1) |
| C(6)–O(7) | 1.43(2) | C(5)–C(6)–O(7) | 105.4(5) |
| C(8)–C(9) | 1.47(2) | O(7)–C(8)–C(9) | 106.0(2) |

ᵃSymmetry element 1−*x*, 1−*y*, −*z*.



Fig. 1. Structure of the Pb(18-crown-6) cation and 2 NO₃⁻ anions viewed almost perpendicularly to the least-squares plane through the 18-crown-6 molecule. The atom labels for the asymmetric part of the centrosymmetric structure are shown.

## Results and discussion

A stereoview of the structure (Fig. 1) shows that the Pb ion (in the centre of symmetry) is linked to six crown oxygen atoms. Several complexes with crown ethers lead to complexes in which the crystal structure is built up from two independent metal sites and several crystallographically distinct crown molecules. Thus, in the salt formed by reacting lead(II) nitrate with 12-crown-4, there are three different conformers of the 12-crown-4 (designated CR′) molecules incorporated in the structure, which consists of a PbNO₃CR′₂⁺ cation and a Pb(NO₃)₃CR′⁻ anion.[16] A similar situation pertains to the 1:1 bismuth(III) chloride:18-crown-6 system that produces a solid, the crystal structure of which also contains two discrete units(molecules), i.e. BiCl₃O · H₂ · CR and BiCl₃ · CR,[4] and a 2:1 complex that, like the lead(ii) nitrate:12-crown-4 complex, is ionic and contains two [BiCl₂ · CR]⁺ cations and a [Bi₂Cl₈]²⁻ anion.[11] These observations are consistent with the statement that the fluxional nature of crown ligands can lead to a range of complexes in solution. However, the present complex is simpler because only a single conformer of the crown is present, cf. Fig. 1.

*Lead coordination.* A feature that the present structure has in common with the other complexes is that the lead atom interacts with all of the crown oxygen atoms (the O₆ grouping). A similar situation has been observed in the complex formed between thallium(I) nitrate and 18-crown-8. In this the complex emulates the 12-crown-4 complexes with antimony(III) chloride,[1] lead(II) nitrate[16] and bismuth(III) chloride,[11] the 15-crown-5 complexes with tin(II) chloride,[6] antimony(III) chloride[7,12] and bismuth(III) chloride,[4] and the 18-crown-6 complexes with bismuth(III) chloride[11] and thallium nitrate.[2]

As is also the case with the thallium atom in the latter

complex, there is no significant expression of stereochemical activity on the part of the lead lone pair. In common with all crown [12-crown-4 $(O)_4$, 15-crown-5 $(O)_5$, 18-crown-6 $(O)_6$] complexes coordinated to main-group metals, the metal–$(O)_6$ distances are long [2.667(12), 2.735(11) and 2.770(9) Å], cf. Table 2.

*The 18-crown-6 molecule.* The C–C and C–O bond distances in the 18-crown-6 ligand are comparable, within the standard deviations, with those reported for other cyclic polyether complexes.[2-4,6-9] The conformation of the crown ether is such that all six ring oxygens are directed towards the lead atoms and is similar to that observed in the thallium(I) and tin(II) complexes.[2,9]

*The nitrate anion.* The nitrate anion retains its structural integrity, the bond angles in the nitrate anion being 120° within experimental error. Also the same within experimental error are the three N–O bond lengths, as is also the case in lead nitrate itself.[20] This indicates that interaction with the lead atom is weak and that the complex may be regarded as a complex cation. The high thermal parameters for the nitrate indicate that the anion is weakly bound to the complex cation.

*Some considerations on the properties of the lone pair on the lead atom.* In order to analyse the stereochemical implications of the lead lone pair in the $PbCR^{2+}$ cation it is necessary to place its behaviour in context with the other complexes in the series (see above); the background for our description for this series of complexes has been expounded upon in some detail in the recent literature.[6] With this in mind, it is clear that the influences of the crown ethers on the lone pairs on the lead atoms are central when discussing the stereochemistries of the complexes. It is a trivial matter to establish that the lead lone pair in the present complex is non-sterically active (since the lead atom lies on a centre of symmetry, see Ref. 6), as is also the case with the tin and lead lone pairs in the centrosymmetric $SnCR'_2{}^{2+}$ (see above) and $PbCR''^{2+}$ cations.[6,16] Suffice it to state that the metal lone pair in the present complex can be identified with contributions from the 6s and 6p orbitals and is explicitly represented by the sum of antibonding molecular orbitals with their varying lead or ligand character. The geometry adopted reflects the desire of the system to attain a lower total energy through maximum population of the lead lower 6s valence orbital. This end is achieved through distortions which are appropriate in the context of all the other energies that are germane to the system as a whole.

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# Thermodynamics of Ionization of Benzoic Acid and Some Substituted Benzoic Acids in 1,4-Dioxane–Water Mixtures

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Thermodynamic parameters, $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$, for the dissociation of aromatic carboxylic acids and phenols have frequently been used to explain the effect of substituents on the ionization of functional groups.[1,2] The fundamental measurements of this type were mainly carried out in aqueous solutions. More recently the effect of solvent on proto-lytic equilibria has become a subject of considerable interest, and thermodynamic data in mixtures of water and organic solvents have been determined.[3,4] These data have also been used to obtain values for the thermodynamic functions of transfer from the aqueous to an aqueous-organic solvent.[3-5]

Table 1. Standard Gibbs energy, enthalpy and entropy of ionization of benzoic acids in dioxane–water mixtures at 298.2 K.

| Comp. | $\varepsilon_r$ | $x_D{}^a$ | $\Delta G^{\ominus\,b}$ kJ mol$^{-1}$ | $\Delta H^\ominus$ kJ mol$^{-1}$ | $T\Delta S^\ominus$ kJ mol$^{-1}$ | $\Delta S^\ominus$ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Benzoic acid | 78.2 | 0 | 24.20 | 0.65$^c$ | −23.6 | −79 |
| | 60.2 | 0.050 | 27.83 | 0.67 | −27.2 | −91 |
| | 41.5 | 0.112 | 32.73 | 0.88 | −31.9 | −107 |
| | 25.9 | 0.234 | 41.07 | 1.00 | −40.1 | −134 |
| | 10.7 | 0.455 | 53.17 | 1.42 | −51.8 | −174 |
| | 8.2 | 0.551 | 42.68 | 1.13 | −41.6 | −140 |
| | 5.6 | 0.648 | 32.90 | 0.75 | −32.2 | −108 |
| 4-Chlorobenzoic acid | | 0 | 23.07 | 0.92$^d$ | −22.2 | −74 |
| | | 0.050 | 25.87 | 2.96 | −22.9 | −77 |
| | | 0.112 | 29.88 | 5.43 | −24.5 | −82 |
| | | 0.234 | 38.41 | 8.78 | −29.6 | −99 |
| | | 0.455 | 51.24 | 7.85 | −43.4 | −146 |
| | | 0.551 | 41.84 | 5.85 | −36.0 | −121 |
| | | 0.648 | 28.88 | 3.34 | −25.5 | −86 |
| 3-Nitrobenzoic acid | | 0 | 19.89 | 0.29 | −19.6 | −66 |
| | | 0.050 | 23.74 | 0.42 | −23.3 | −78 |
| | | 0.112 | 26.75 | 1.71 | −25.0 | −84 |
| | | 0.234 | 34.69 | 3.26 | −31.4 | −105 |
| | | 0.455 | 46.82 | 2.72 | −44.1 | −148 |
| | | 0.551 | 43.28 | 2.48 | −40.8 | −137 |
| | | 0.648 | 40.96 | 2.17 | −38.8 | −130 |
| 4-Nitrobenzoic acid | | 0 | 18.47 | 0.21$^e$ | −18.3 | −61 |
| | | 0.050 | 23.28 | 0.42 | −22.9 | −77 |
| | | 0.112 | 26.88 | 1.37 | −25.5 | −86 |
| | | 0.234 | 34.56 | 2.42 | −32.1 | −108 |
| | | 0.455 | 46.82 | 1.50 | −45.3 | −152 |
| | | 0.551 | 43.92 | 0.72 | −43.2 | −145 |
| | | 0.648 | 40.96 | 0.04 | −40.9 | −137 |

[a] Mole fraction of dioxane. [b] Calculated from p$K_a$ values reported in Ref. 6. [c] Lit. 0.62 kJ mol$^{-1}$.[1] [d] Lit. 0.96 kJ mol$^{-1}$.[1] [e] Lit. 0.13 kJ mol$^{-1}$.[1]