Crown ether complexes of lead(II) nitrate. Crystal structures of the 12-crown-4, 15-crown-5, benzo-15-crown-5 and 18-crown-6 complexes

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Abstract

The straightforward reaction of common crown ethers with $Pb(NO_3)_2$ in CH_3CN and CH_3OH mixtures has produced several crystalline complexes which have been structurally characterized. Crystallographic analysis reveals the following formulations: $[Pb(NO_3)(12\text{-crown-}4)_2][Pb(NO_3)_3(12\text{-crown-}4)]$ (**1**), $[PbL_2][Pb(NO_3)_3L]_2$ (L = 15-crown-5 (**2**) or benzo-15-crown-5 (**3**)), and $[Pb(NO_3)_2(18\text{-crown-}6)]$ (**4**). As anticipated the cavity size of 18-crown-6 matches the ionic radius of Pb^{2+} and the lead ion resides exactly in the center of the crown ether. For all four structures, the Pb–O separations range from 2.645(8)–3.06(1) Å (crown ether) and 2.53(1)–2.809(8) Å (nitrate). Variations in bond distances are noted relating to differences in coordination number, geometry and ionic charge, however, a lone pair effect is not distinguished. The crystallographic parameters are as follows: **1**: monoclinic, $P2_1/c$ with (at 22 °C) $a=8.237(5)$, $b=28.464(9)$, $c=16.331(8)$ Å, $\beta=93.77(7)°$, $D_{calc}=2.07$ g cm^{-3} for $Z=4$ formula units, and $R=0.038$ utilizing 4596 independent observed ($F_o \geqslant 5\sigma(F_o)$) reflections; **2**: orthorhombic, $Pccn$ with (at 22 °C) $a=37.462(5)$, $b=9.586(2)$, $c=17.378(4)$ Å, and $D_{calc}=2.00$ g cm^{-3} for $Z=4$ (severe disorder precluded a complete structure determination); **3**: triclinic, $P\bar{1}$ with (at 22 °C) $a=10.392(2)$, $b=18.799(6)$, $c=21.069(8)$ Å, $\alpha=112.11(3)$, $\beta=98.01(2)$, $\gamma=104.32(2)°$, $D_{calc}=1.92$ g cm^{-3} for $Z=2$, and $R=0.052$ (8505 reflections); **4**: monoclinic, $P2_1/c$ with (at 22 °C) $a=8.171(8)$, $b=15.499(9)$, $c=7.856(8)$ Å, $\beta=105.08(7)°$, $D_{calc}=2.06$ g cm^{-3} for $Z=2$ and $R=0.034$ (1018 reflections).

Introduction

Although crown ethers are noted for their ability to selectively separate Pb^{2+}, and removal of Pb^{2+} is of environmental concern [1–6], structural characterizations of Pb^{2+}/crown ether complexes are limited to $[Pb(NO_3)_2L]$ (L = either *cis-syn-cis* [7] or *cis-anti-cis*-dicyclohexyl-18-crown-6 [8]), $[Pb(NCS)(15\text{-crown-}5)(\mu\text{-}NCS)_2][Pb(NCS)(15\text{-crown-}5)]$ [9] and $[Pb(18\text{-crown-}6)(CCl_3COO)_2]\cdot 2CCl_3OOH$ [10]. Much more attention has been paid to nitrogen macrocycles presumably due to the better match of the softer N donor with the soft Pb^{2+} cation [11–21]. The extremely good match between the ionic radius of Pb^{2+} and 18-membered six donor crown ethers, however, results in very stable complexes and thus the utility of crown ethers in Pb^{2+} separations is receiving renewed attention [5, 22].

Hancock *et al.* have demonstrated [23] that control of the activity of the inert pair of electrons on Pb^{2+} is a useful tool in the control of its complexation chemistry. We have recently structurally characterized over twenty Bi^{3+} halide [24], nitrate [25] and alkoxide [25] structures which suggest that the formation of covalent or partially covalent bonds to Bi^{3+} is responsible for activation of the lone pair. This is in keeping with the suggestion of Hancock *et al.* that increasing the number of nitrogen donors in macrocyclic ligands for Pb^{2+} increases the activity of the lone pair.

With the present work we initially intended to study the effect on structure of decreasing the crown ether cavity size on Pb^{2+} complexes. It became clear early that a dynamic situation obviously existed in solution for the small crowns resulting in overall ion paired structures. It also became evident that some form of disorder or another was the rule rather than the exception in these complexes, making them somewhat difficult to successfully analyze. The structural results obtained do paint a picture of the control steric saturation has on overall structure and also once again demonstrate the perfect fit of Pb^{2+} inside the 18-crown-6 cavity. In the absence of covalent bonds to Pb^{2+} we do not find stereochemical activity of the lone pair as we would predict from our results with Bi^{3+} [24, 25].

Experimental

$Pb(NO_3)_2$, 12-crown-4, 15-crown-5, benzo-15-crown-5 and 18-crown-6 were used as purchased. CH_3CN and

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CH_3OH were of reagent quality and distilled from CaH_2 prior to use. All melting points are uncorrected. All samples were dried *in vacuo* prior to combustion analysis.

[Pb(NO$_3$)(12-crown-4)$_2$][Pb(NO$_3$)$_3$(12-crown-4)]

To $Pb(NO_3)_2$ (0.4102 g, 1.2 mmol) was added a 2:1 CH_3CN:CH_3OH solution (7 ml) followed by stirring at 58 °C for 10 h. 12-Crown-4 (0.22 ml, 1.4 mmol) was added followed by 5 h of stirring at 57 °C. A white precipitate was then centrifuged and the supernatant evaporated to produce a white solid. 2:1 CH_3CN:CH_3OH (7 ml) was added, the solution stirred and slowly concentrated which provided crystals on the wall of the vessel. Melting point 233.5 °C, decomposition. *Anal.* Calc.: C, 24.20; H 4.06; N, 4.70. Found for precipitate: C, 17.98; H, 3.26; N, 4.78. Found for crystals: C, 24.63; H, 4.53; N, 4.05%.

[Pb(15-crown-5)$_2$][Pb(NO$_3$)$_3$(15-crown-5)]$_2$

To $Pb(NO_3)_2$ (0.2043 g, 0.62 mmol) was added 2:1 CH_3CN:CH_3OH (5 ml) followed by 1 h of stirring at 60 °C. 15-Crown-5 (0.26 ml, 1.3 mmol) was then added followed by mixing. Evaporation to dryness, dissolution as described above, and further slow evaporation afforded diffraction quality crystals. Melting range 195–200 °C. *Anal.* Calc.: C, 25.63; H, 4.30; N, 4.48. Found for crystals: C, 26.67; H, 4.60; N, 3.68%.

[Pb(benzo-15-crown-5)$_2$][Pb(NO$_3$)$_3$(benzo-15-crown-5)]$_2$

To $Pb(NO_3)_2$ (0.2000 g, 0.60 mmol) were added 2:1 CH_3CN:CH_3OH (5 ml) and benzo-15-crown-5 (0.2012 g, 0.75 mmol). The solution was then stirred at 50 °C for 0.75 h. Evaporation to dryness and dissolution with more reaction solution (5 ml) followed by slow evaporation provided crystalline material. Melting point 149.5–150.5 °C. *Anal.* Calc.: C, 32.54; H, 3.90; N, 4.07. Found for crystals: C, 32.79; H, 4.40; N, 3.80%.

[Pb(NO$_3$)$_2$(18-crown-6)]

Three previous attempts at isolation of this compound were unsuccessful. The solids obtained from 1:1 metal to ligand ratios in 3:1 and 2:1 solutions of CH_3CN:CH_3OH proved to be $Pb(NO_3)_2$. To $Pb(NO_3)_2$ (0.3305 g, 1.0 mmol) were added 3:1 CH_3CN:CH_3OH (5 ml) and 18-crown-6 (0.5292 g, 2.0 mmol). The reaction solution was stirred at 60 °C for 1 h followed immediately by centrifugation to remove a precipitate. The supernatant was stored consecutively at 3 and −10 °C with no crystal formation. Slow concentration of the reaction solution afforded a crystalline mixture of $Pb(NO_3)_2$ and the 18-crown-6 adduct. Melting range 86–92 °C. *Anal.* Calc.: C, 24.20; H, 4.06; N, 4.70. Found for precipitate: C, 13.88; H, 2.32; N, 4.84. Found for crystals: C, 24.74; H, 4.05; N, 4.34%.

X-ray data collection, structure determination and refinement

Each complex was mounted in a thin-walled glass capillary and flushed with argon prior to being transferred to the goniometer. Complexes **1** and **4** were uniquely determined to be $P2_1/c$ from their systematic absences. Complex **2** was uniquely defined as *Pccn*. Complex **3** was either $P1$ or $P\bar{1}$ and was successfully solved and refined in $P\bar{1}$ despite the presence of some ligand disorder. A summary of data collection parameters is given in Table 1.

Disorder was evident for **1** in the crown ether coordinated to $Pb(NO_3)_3^-$ and in one ethylene unit (C(9)–C(10)) of one of the other crown ethers (O(5)–O(8)). Resolution of the disorder was possible by constraining the C–O (1.44(2) Å) and C–C (1.53(2) Å) distances with refinement of the two conformations in alternate least-squares cycles. The C–O and C–C parameters were determined by averaging the remaining such distances in the asymmetric unit. The refinement of the disorder proceeded smoothly and we therefore introduced hydrogen atoms in idealized positions 0.95 Å from the bonded carbon atom. These were allowed to ride on the bonded carbon with B fixed at 5.5 Å^2. The disordered carbon atoms were only refined isotropically. Final fractional coordinates are given in Table 2.

It was not possible to fully solve and refine **2**. The unique $[Pb(NO_3)_3(15\text{-crown-}5)]^-$ anion was easily picked out and refined well. The $[Pb(15\text{-crown-}5)_2]^{2+}$ cation, however, resides on a crystallographic mirror plane and is totally disordered. Considering the symmetrical shape of the cation, the disorder should not be considered unusual. Since we were able to isolate the benzo-15-crown-5 derivative **3** and the formulation of **2** was evident from the crystallographic data, we felt it unnecessary to try to completely sort out the disorder in the cation.

In **3** high thermal motion was noted for the alkyl carbon atoms in one crown ether (C(15)–C(22)) and for two of the ethylene groups in another (C(43)–C(46)). To resolve the two conformations present it was necessary to refine them at 50% occupancy, in alternate least-squares cycles, with the O–C and C–C alkyl distances fixed at 1.44(2) and 1.53(2) Å, respectively. The values chosen reflected the average O–C and C–C alkyl distances in the remainder of the asymmetric unit. Due to the nature of the disorder, the hydrogen atoms were not included in the final refinement. The disordered carbon atoms were refined isotropically only. Final fractional coordinates are given in Table 3.

TABLE 1. Crystal data and summary of intensity data collection and refinement

Compound	$[Pb(NO_3)(12\text{-crown-}4)_2]$- $[Pb(NO_3)_3(12\text{-crown-}4)]$ (**1**)	$[Pb(15\text{-crown-}5)_2]$- $[Pb(NO_3)_3(15\text{-crown-}5)]_2$ (**2**)	$[Pb(benzo\text{-}15\text{-crown-}5)_2]$- $[Pb(NO_3)_3(benzo\text{-}15\text{-crown-}5)]_2$ (**3**)	$[Pb(NO_3)_2(18\text{-crown-}6)]$ (**4**)
Color/shape	colorless/parallelepiped	colorless/parallelepiped	colorless/parallelepiped	colorless/parallelepiped
Formula weight	1191	1875	2067	595.5
Space group	$P2_1/c$	$Pccn$	$P\bar{1}$	$P2_1/c$
Temperature (°C)	22	22	22	22
Cell constants[a]				
a (Å)	8.237(5)	37.462(5)	10.392(2)	8.171(8)
b (Å)	28.464(9)	9.586(2)	18.799(6)	15.499(9)
c (Å)	16.331(8)	17.378(4)	21.069(8)	7.856(8)
α (°)			112.11(3)	
β (°)	93.77(7)		98.01(2)	105.08(7)
γ (°)			104.32(2)	
Cell volume (Å^3)	3821	6240	3568.8	960.6
Formula units/unit cell	4	4	2	2
D_{calc} (g cm^{-3})	2.07	2.00	1.92	2.06
μ_{calc} (cm^{-1})	87.7	80.7	70.5	87.3
Diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ
Range relative transmission factors (%)	61/100	36/98	17/100	82/100
Radiation (Å), graphite monochromator	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Max. crystal dimensions (mm)	$0.10 \times 0.20 \times 0.60$	$0.20 \times 0.25 \times 0.45$	$0.08 \times 0.45 \times 0.65$	$0.15 \times 0.18 \times 0.20$
Scan width	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$
Standard reflections	600; 0, 20, 0; 0, 0, 12	800; 040; 0, 0, 18	700; 0, 10, 0; 0, 0, 14	500; 0, 14, 0; 004
Decay of standards (%)	±5	±2	±2	±2
Reflections measured	7348	6155	13, 499	1881
2θ range (°)	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	$+9, +33, \pm 19$	$+44, +11, -20$	$+12, \pm 22, \pm 25$	$+9, +18, \pm 9$
Reflections observed ($F_o \geqslant 5\sigma(F_o)$)[b]	4596		8505	1018
Computer programs[c]	SHELX [26]		SHELX	SHELX
Structure solution	SHELXS [27]		SHELXS	SHELXS
No. parameters varied	477		916	124
Weights	$(\sigma(F_o)^2 + 0.002F_o^2)^{-1}$		$(\sigma(F_o)^2 + 0.0008F_o^2)^{-1}$	$(\sigma(F_o)^2 + 0.0004F_o^2)^{-1}$
GOF	0.69		1.78	0.85
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.038		0.052	0.034
R_w	0.053		0.065	0.040
Largest feature final difference map (e$^-$ Å^{-3})	0.8		1.3 near Pb(1)	1.0 within 1.4 Å of Pb

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[a] Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 24 reflections $\theta > 20°$. [b] Corrections: Lorentz–polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 28.

TABLE 2. Final fractional coordinates for $[Pb(NO_3)(12\text{-crown-}4)_2][Pb(NO_3)_3(12\text{-crown-}4)]$

Atom	x/a	y/b	z/c	B_{eq}[a]
Pb(1)	0.33160(5)	0.20262(1)	0.02178(2)	2.40
O(1)	0.267(1)	0.1165(3)	−0.0465(4)	3.46
O(2)	0.0187(9)	0.1649(3)	0.0224(5)	3.60
O(3)	0.212(1)	0.1758(3)	0.1683(4)	3.55
O(4)	0.4618(9)	0.1261(3)	0.0992(5)	4.05
O(5)	0.141(1)	0.2785(3)	0.0183(5)	4.30
O(6)	0.451(1)	0.2850(3)	−0.0387(5)	4.77
O(7)	0.475(1)	0.1990(3)	−0.1184(4)	3.73
O(8)	0.153(1)	0.2260(3)	−0.1263(4)	3.49
C(1)	0.110(2)	0.0955(4)	−0.0446(7)	3.83
C(2)	−0.012(2)	0.1348(4)	−0.0451(7)	3.72
C(3)	−0.037(2)	0.1483(4)	0.0976(6)	3.79
C(4)	0.035(1)	0.1791(4)	0.1643(7)	3.69
C(5)	0.277(2)	0.1337(5)	0.2076(6)	4.22
C(6)	0.450(2)	0.1289(5)	0.1872(7)	4.29
C(7)	0.423(2)	0.0791(4)	0.0670(9)	4.44
C(8)	0.397(2)	0.0852(5)	−0.0236(8)	4.67
C(9)	0.232(2)	0.3190(6)	0.041(1)	5.4(4)[b]
C(10)	0.339(2)	0.3260(6)	−0.033(1)	5.8(4)[b]
C(9)′	0.216(3)	0.3230(7)	−0.005(2)	9.5(7)[b]
C(10)′	0.402(3)	0.3258(8)	0.000(2)	13(1)[b]
C(11)	0.522(2)	0.2846(5)	−0.1154(8)	4.86
C(12)	0.585(2)	0.2367(5)	−0.1304(8)	4.77
C(13)	0.370(1)	0.1872(4)	−0.1910(6)	3.59
C(14)	0.227(1)	0.2202(4)	−0.2030(6)	3.59
C(15)	0.048(2)	0.2661(5)	−0.1271(7)	4.23
C(16)	0.003(2)	0.2758(4)	−0.0383(9)	4.69
O(9)	0.648(1)	0.2181(3)	0.0686(6)	4.54
O(10)	0.480(1)	0.2490(3)	0.1462(5)	4.35
O(11)	0.738(1)	0.2648(4)	0.1645(7)	6.78
N(1)	0.623(1)	0.2456(4)	0.1262(6)	3.70
Pb(2)	0.03790(4)	0.49378(1)	0.21759(2)	2.21
O(12)	−0.1753(9)	0.4985(2)	0.0802(4)	3.70
O(13)	−0.2821(9)	0.5151(3)	0.2369(5)	5.25
O(14)	−0.1604(9)	0.4243(3)	0.2826(4)	5.06
O(15)	−0.0607(9)	0.4098(2)	0.1249(5)	3.93
C(17)	−0.343(2)	0.5076(8)	0.072(1)	5.2(5)[b]
C(18)	−0.342(2)	0.5382(6)	0.1517(8)	3.5(4)[b]
C(19)	−0.406(2)	0.4878(7)	0.260(1)	5.2(5)[b]
C(20)	−0.292(3)	0.4554(8)	0.316(1)	6.2(6)[b]
C(21)	−0.238(3)	0.3848(8)	0.251(2)	8.0(8)[b]
C(22)	−0.102(3)	0.3765(9)	0.193(1)	6.5(6)[b]
C(23)	−0.185(3)	0.4091(7)	0.067(1)	5.8(5)[b]
C(24)	−0.152(3)	0.4563(6)	0.027(1)	4.4(4)[b]
C(17)′	−0.309(2)	0.5301(7)	0.106(1)	4.5(4)[b]
C(18)′	−0.409(2)	0.5109(9)	0.179(1)	6.0(6)[b]
C(19)′	−0.329(2)	0.4803(5)	0.3099(9)	3.2(3)[b]
C(20)′	−0.324(2)	0.4274(7)	0.291(2)	6.0(6)[b]
C(21)′	−0.125(2)	0.3770(5)	0.2375(9)	2.9(3)[b]
C(22)′	−0.169(2)	0.3763(7)	0.145(1)	4.5(4)[b]
C(23)′	−0.109(2)	0.4283(6)	0.0377(8)	3.2(3)[b]
C(24)′	−0.252(2)	0.4627(6)	0.035(1)	4.5(4)[b]
O(16)	0.256(1)	0.4621(3)	0.1199(5)	4.12
O(17)	0.251(1)	0.4223(3)	0.2325(5)	4.34
O(18)	0.397(1)	0.3981(4)	0.1344(6)	6.43
N(2)	0.301(1)	0.4263(4)	0.1621(7)	3.85
O(19)	0.244(1)	0.5056(3)	0.3474(5)	4.56
O(20)	0.0072(9)	0.5283(3)	0.3675(5)	4.54
O(21)	0.197(1)	0.5349(3)	0.4630(5)	4.51
N(3)	0.150(1)	0.5238(3)	0.3944(5)	2.97
O(22)	0.241(1)	0.5639(3)	0.1857(7)	6.19
O(23)	0.007(1)	0.5884(3)	0.1813(8)	6.73
O(24)	0.194(1)	0.6361(3)	0.1608(7)	6.50
N(4)	0.148(1)	0.5969(3)	0.1760(5)	3.00

[a] $B_{eq}=4/3[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. [b] Isotropic refinement.

Refinement of **4** proceeded smoothly although high thermal motion was noted for O(4). It was not possible to resolve a disorder model for this atom. Hydrogen atoms were included as indicated for **1**. Final fractional coordinates are given in Table 4.

Results and discussion

The reaction of 1:1 stoichiometries of crown ethers and $Pb(NO_3)_2$ does not produce crystalline compounds of 1:1 stoichiometry in all cases, rather the size of the crown ether and the resulting steric saturation or unsaturation of the Pb^{2+} coordination sphere control the final crystalline form. The smallest of the crowns used, 12-crown-4, can form a sandwich ion with Pb^{2+} but it is only eight-coordinate and the resulting steric unsaturation allows bidentate coordination of a nitrate anion increasing the coordination number to 10. The charge is balanced by a $[Pb(NO_3)_3(12\text{-crown-}4)]^-$ anion and a 3:2 12-crown-4:Pb^{2+} stoichiometry is realized in the crystalline form as $[Pb(NO_3)(12\text{-crown-}4)_2][Pb(NO_3)_3(12\text{-crown-}4)]$ (**1**).

Both 15-crown-5 and benzo-15-crown-5 are 15-membered, 5-donor macrocycles. Pb^{2+} is still too large to fit within a macrocycle of this size, however, the sandwich ion is now sterically saturated and has a coordination number of 10. Two $[Pb(NO_3)_3L]^-$ counterions are needed to balance this charge and an overall 4:3 crown ether:Pb^{2+} stoichiometry is observed in $[PbL_2][Pb(NO_3)_3L]_2$ (L = 15-crown-5 (**2**) or benzo-15-crown-5 (**3**)).

The perfect fit of Pb^{2+} in the 18-membered cavity of 18-crown-6 results in the 1:1 stoichiometry observed in $[Pb(NO_3)_2(18\text{-crown-}6)]$ (**4**). Similar results have been obtained for the *cis-syn-cis* and *cis-anti-cis* isomers of dicyclohexyl-18-crown-6 [7, 8] and for $[Pb(18\text{-crown-}6)(CCl_3COO)_2]\cdot 2CCl_3COOH$ [10].

The structures of **1**, **3** and **4** are represented in Figs. 1–3, respectively. The bonding parameters for the Pb^{2+} coordination spheres are averaged in Table 5. It is interesting to note that rather severe disorder problems are noted for each structure with the smaller crown

TABLE 3. Final fractional coordinates for $[\text{Pb(benzo-15-crown-5)}_2][\text{Pb(NO}_3)_3\text{(benzo-15-crown-5)}]_2$

Atom	x/a	y/b	z/c	B_{eq}[a]
Pb(1)	0.22324(4)	0.23550(2)	0.97770(2)	2.61
O(1)	0.4221(9)	0.3404(5)	0.9518(5)	4.64
O(2)	0.202(1)	0.2272(6)	0.8422(5)	5.30
O(3)	−0.0175(8)	0.2285(5)	0.9039(5)	4.20
O(4)	0.0893(7)	0.3331(5)	1.0478(4)	3.49
O(5)	0.3725(8)	0.3915(5)	1.0749(5)	3.90
C(1)	0.421(2)	0.328(1)	0.8796(9)	5.78
C(2)	0.281(2)	0.296(1)	0.8360(9)	6.58
C(3)	0.060(1)	0.191(1)	0.7993(7)	5.30
C(4)	−0.030(1)	0.2345(9)	0.8369(7)	4.83
C(5)	−0.098(1)	0.2691(9)	0.9455(8)	4.84
C(6)	−0.015(2)	0.346(1)	1.002(1)	5.93
C(7)	0.169(1)	0.4058(8)	1.1061(9)	5.39
C(8)	0.300(1)	0.4474(7)	1.0990(8)	4.36
C(9)	0.506(1)	0.4237(7)	1.0716(7)	3.48
C(10)	0.533(1)	0.3953(7)	1.0063(7)	3.66
C(11)	0.665(1)	0.4174(8)	0.996(1)	5.55
C(12)	0.768(1)	0.4759(9)	1.061(1)	5.68
C(13)	0.743(1)	0.5065(9)	1.129(1)	5.34
C(14)	0.610(1)	0.4796(8)	1.1345(8)	4.60
O(6)	0.0115(9)	0.1409(5)	1.0034(4)	4.30
O(7)	0.239(1)	0.2364(7)	1.1054(6)	7.15
O(8)	0.4665(9)	0.2376(7)	1.0492(6)	6.59
O(9)	0.3675(9)	0.1402(5)	0.9052(5)	6.01
O(10)	0.0928(9)	0.0741(5)	0.8921(5)	4.55
C(15)	0.032(2)	0.126(1)	1.065(1)	5.2(5)[b]
C(16)	0.114(2)	0.208(1)	1.124(1)	5.5(6)[b]
C(17)	0.364(3)	0.236(3)	1.143(2)	11(1)[b]
C(18)	0.497(3)	0.257(2)	1.122(1)	7.9(8)[b]
C(19)	0.523(3)	0.176(2)	1.009(1)	8.5(9)[b]
C(20)	0.515(2)	0.177(2)	0.936(1)	6.2(6)[b]
C(21)	0.308(2)	0.053(1)	0.877(2)	6.8(7)[b]
C(22)	0.158(2)	0.034(2)	0.839(1)	6.0(6)[b]
C(15)′	0.003(3)	0.161(2)	1.075(1)	6.9(7)[b]
C(16)′	0.142(2)	0.182(2)	1.122(1)	6.0(6)[b]
C(17)′	0.375(2)	0.275(2)	1.155(1)	7.2(8)[b]
C(18)′	0.451(3)	0.222(2)	1.112(1)	5.2(5)[b]
C(19)′	0.561(3)	0.208(2)	1.011(2)	6.7(7)[b]
C(20)′	0.472(3)	0.128(2)	0.950(2)	11(1)[b]
C(21)′	0.291(3)	0.059(1)	0.852(1)	8.5(9)[b]
C(22)′	0.162(3)	0.017(1)	0.865(2)	6.5(7)[b]
C(23)	−0.044(2)	0.0415(8)	0.8865(8)	4.72
C(24)	−0.085(1)	0.0758(8)	0.9454(9)	4.44
C(25)	−0.225(2)	0.053(1)	0.951(1)	8.66
C(26)	−0.314(2)	−0.015(1)	0.879(1)	7.39
C(27)	−0.277(3)	−0.048(1)	0.823(1)	9.15
C(28)	−0.130(2)	−0.022(1)	0.823(1)	7.32
Pb(2)	0.89471(5)	0.25657(3)	1.31463(3)	3.40
O(11)	1.1210(8)	0.4137(5)	1.3945(4)	4.18
O(12)	1.0064(9)	0.3725(5)	1.2554(5)	4.45
O(13)	0.7342(9)	0.3509(6)	1.2764(5)	4.73
O(14)	0.6840(8)	0.3018(5)	1.3863(5)	3.87
O(15)	0.9529(7)	0.3756(5)	1.4599(4)	3.97
C(29)	1.207(1)	0.4360(9)	1.3516(8)	4.87
C(30)	1.117(1)	0.4493(8)	1.2986(8)	4.72
C(31)	0.896(1)	0.385(1)	1.2129(9)	6.26
C(32)	0.802(1)	0.414(1)	1.254(1)	6.30
C(33)	0.642(1)	0.3774(9)	1.3189(9)	5.57
C(34)	0.581(1)	0.311(1)	1.3377(9)	5.30
C(35)	0.723(1)	0.3653(8)	1.4568(7)	4.19
C(36)	0.849(1)	0.3594(8)	1.4977(7)	4.04
C(37)	1.089(1)	0.3930(7)	1.4936(7)	3.62
C(38)	1.181(1)	0.4134(7)	1.4564(7)	3.44
C(39)	1.323(1)	0.4316(7)	1.4845(7)	3.98
C(40)	1.367(1)	0.4286(8)	1.5489(8)	4.73
C(41)	1.273(1)	0.4091(8)	1.5862(8)	4.60
C(42)	1.131(1)	0.3898(8)	1.5568(7)	4.36
O(16)	1.105(1)	0.225(1)	1.2775(8)	10.50
O(17)	1.115(1)	0.2318(8)	1.3799(7)	7.65
O(18)	1.264(1)	0.193(1)	1.3241(9)	9.66
N(1)	1.160(1)	0.216(1)	1.3248(9)	6.48
O(19)	0.831(1)	0.1830(6)	1.1785(6)	5.57
O(20)	0.647(1)	0.1528(6)	1.2125(6)	5.71
O(21)	0.647(1)	0.0951(6)	1.1012(6)	6.22
N(2)	0.708(1)	0.1435(7)	1.1631(7)	4.74
O(22)	0.858(1)	0.1050(7)	1.2902(8)	7.69
O(23)	0.820(2)	0.1713(8)	1.3846(8)	10.74
O(24)	0.830(2)	0.0536(8)	1.365(1)	11.90
N(3)	0.834(2)	0.1114(8)	1.348(1)	6.82
Pb(3)	0.36100(4)	0.72552(3)	0.32950(2)	3.11
O(25)	0.370(1)	0.8851(6)	0.3200(6)	6.41
O(26)	0.5904(9)	0.8219(6)	0.3000(5)	5.77
O(27)	0.6411(9)	0.7687(7)	0.4064(6)	5.99
O(28)	0.4329(9)	0.7723(5)	0.4774(5)	4.19
O(29)	0.333(1)	0.8745(5)	0.4366(5)	5.10
C(43)	0.510(2)	0.930(2)	0.327(2)	8.8(9)[b]
C(44)	0.605(4)	0.893(2)	0.287(2)	11(1)[b]
C(45)	0.726(2)	0.843(2)	0.343(2)	7.5(8)[b]
C(46)	0.745(3)	0.781(2)	0.369(2)	6.2(6)[b]
C(43)′	0.477(2)	0.929(1)	0.300(1)	5.5(6)[b]
C(44)′	0.541(2)	0.866(1)	0.263(1)	4.9(5)[b]
C(45)′	0.712(2)	0.872(1)	0.355(1)	7.2(7)[b]
C(46)′	0.745(2)	0.813(2)	0.384(2)	6.2(6)[b]
C(47)	0.679(1)	0.798(1)	0.4806(9)	5.88
C(48)	0.554(1)	0.753(1)	0.5002(8)	5.20
C(49)	0.430(2)	0.8475(9)	0.5290(7)	5.39
C(50)	0.308(2)	0.8655(9)	0.4990(7)	4.96
C(51)	0.260(1)	0.9167(8)	0.4111(8)	4.53
C(52)	0.288(1)	0.9258(8)	0.3530(7)	4.37
C(53)	0.226(2)	0.9711(9)	0.3250(9)	5.73
C(54)	0.130(2)	1.002(1)	0.357(1)	6.09
C(55)	0.099(2)	0.9898(9)	0.415(1)	5.68
C(56)	0.160(2)	0.9453(8)	0.4412(9)	5.00
O(30)	0.4840(9)	0.6165(5)	0.2617(5)	4.69
O(31)	0.3830(8)	0.6002(5)	0.3420(5)	3.94
O(32)	0.450(1)	0.5036(6)	0.2747(6)	5.52
N(4)	0.440(1)	0.5725(6)	0.2931(6)	3.80
O(33)	0.1898(9)	0.5960(5)	0.2162(4)	4.10
O(34)	0.2916(8)	0.6867(5)	0.1850(5)	4.16
O(35)	0.1294(9)	0.5812(6)	0.1081(5)	4.81
N(5)	0.203(1)	0.6209(6)	0.1691(6)	3.49
O(36)	0.106(1)	0.7336(6)	0.2933(6)	5.55
O(37)	0.1325(9)	0.6678(6)	0.3565(5)	4.86
O(38)	−0.073(1)	0.6521(9)	0.3019(7)	7.85
N(6)	0.052(1)	0.6840(8)	0.3182(6)	4.87

[a,b] As defined in Table 2.

TABLE 4. Final fractional coordinates for [Pb$(NO_3)_2$(18-crown-6)]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}[a]
Pb	1.0000	0.5000	0.5000	2.12
O(1)	0.757(1)	0.4969(6)	0.680(1)	2.92
O(2)	1.028(1)	0.6062(5)	0.790(1)	2.94
O(3)	1.2406(9)	0.6303(5)	0.567(1)	2.67
O(4)	0.889(2)	0.6424(9)	0.323(3)	11.24
O(5)	0.712(2)	0.5518(8)	0.263(2)	6.30
O(6)	0.646(1)	0.6757(7)	0.161(1)	4.74
N	0.750(2)	0.6268(8)	0.260(2)	4.23
C(1)	0.787(2)	0.5430(9)	0.846(2)	3.19
C(2)	0.870(2)	0.6250(8)	0.828(2)	3.21
C(3)	1.127(2)	0.6832(8)	0.798(2)	3.68
C(4)	1.285(2)	0.6585(8)	0.749(2)	2.81
C(5)	1.382(1)	0.6174(8)	0.496(2)	3.13
C(6)	1.318(1)	0.5862(7)	0.315(2)	3.09

[a] As defined in Table 2.

ethers. This may be at least partially attributed to the large size of the complex ions and the insensitivity of the overall packing to the conformation of the crown ethers. The only more or less spherical complex ion, $[Pb(15\text{-crown-}5)_2]^{2+}$, is totally disordered, again reflecting the lack of a preferred orientation in the unit cell packing.

The structure of **1** consists of one ten-coordinate $[Pb(NO_3)(12\text{-crown-}4)_2]^+$ cation (Fig. 1(a)) and one ten-coordinate $[Pb(NO_3)_3(12\text{-crown-}4)]^-$ anion (Fig. 1(b)) in the asymmetric unit. Each Pb^{2+} ion has a 6A, 4B-expanded dodecahedral coordination geometry. One crown ether coordinated to Pb(1) (O(1)–O(4)) and the ether coordinated to Pb(2) can be planar in this geometry and the maximum oxygen atom deviation from planarity for these ethers is only 0.008 Å. The second 12-crown-4 molecule coordinated to Pb(1) (O(5)–O(8)) is required to be bent by the constraints of the 6A, 4B-expanded dodecahedron with O(5) and O(7) bending out of the four oxygen atom plane towards Pb(1), and O(6) and O(8) bending away. (The maximum deviation from planarity is 0.36 Å.) As a result, the Pb–O(1–4) distances have a 0.089 Å range while a 0.18 Å range is observed for Pb–O(5–8). (O(6) and O(8) have the largest separations for this ether.)

The nitrate anion coordinated to Pb(1) is asymmetrically coordinated although the difference is only 6.5σ. The average Pb(1)–ONO_2 separation is 2.68(3) Å (Table 5).

The $[Pb(NO_3)_3(12\text{-crown-}4)]^-$ anion is also a ten-coordinate, 6A, 4B-expanded dodecahedron. The Pb(2)–O(ether) separations average 2.81(7) Å, slightly longer than the 2.73(6) Å average observed for the cation. Considering the range of the Pb–O distances, the difference is actually quite small. The nitrate anions are again asymmetrically coordinated to Pb(2) and have a larger range (0.13 Å) than found for Pb(1). The average Pb(2)–ONO_2 separation of 2.68(4) Å is identical to that observed for the cation.

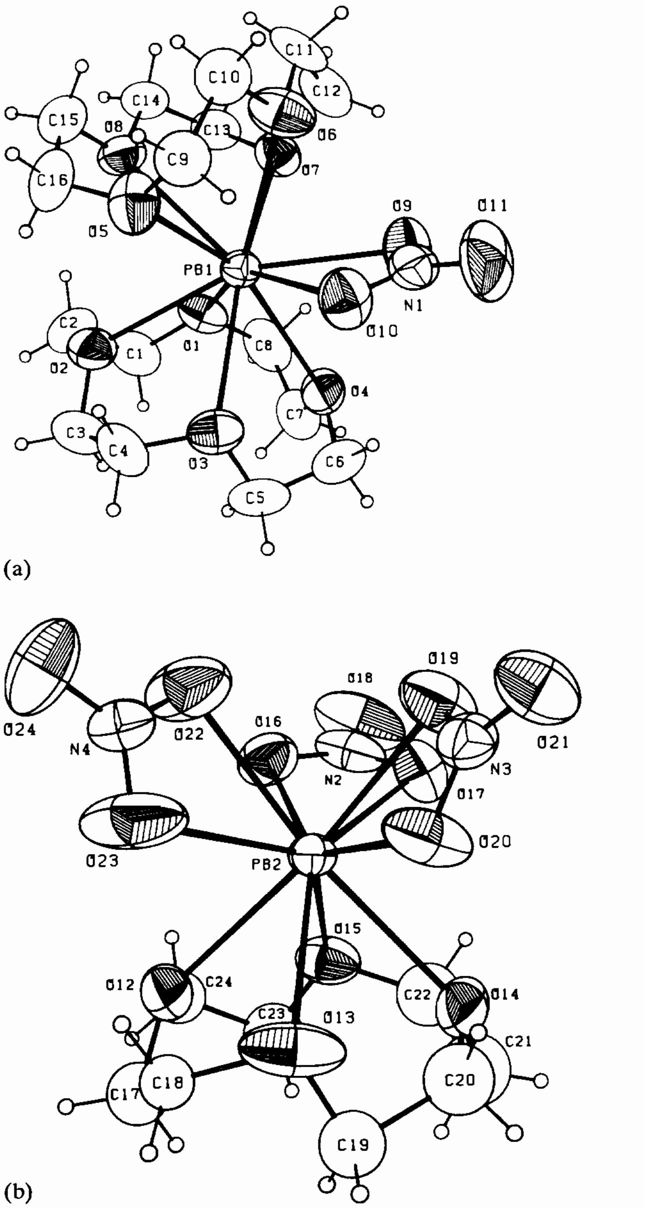

Fig. 1. (a) $[Pb(NO_3)(12\text{-crown-}4)_2]^+$ cation in **1** represented with 50% probability ellipsoids for thermal motion. Hydrogen atoms have arbitrarily reduced radii. The ethylene linkage C(9)–C(10) is disordered. (b) $[Pb(NO_3)_3(12\text{-crown-}4)]^-$ anion. All ethylene linkages are disordered.

The crystalline form of the 15-crown-5 and benzo-15-crown-5 complexes are quite similar, however, the rigid benzo substituent and its preferred packing orientation are necessary for a well ordered structure. Unlike the 12-crown-4 complex, a 2:1 complex of these five donor macrocycles leaves no room for nitrate ion coordination and leads instead to the observed formulation $[PbL_2][Pb(NO_3)_3L]_2$. There are one cation

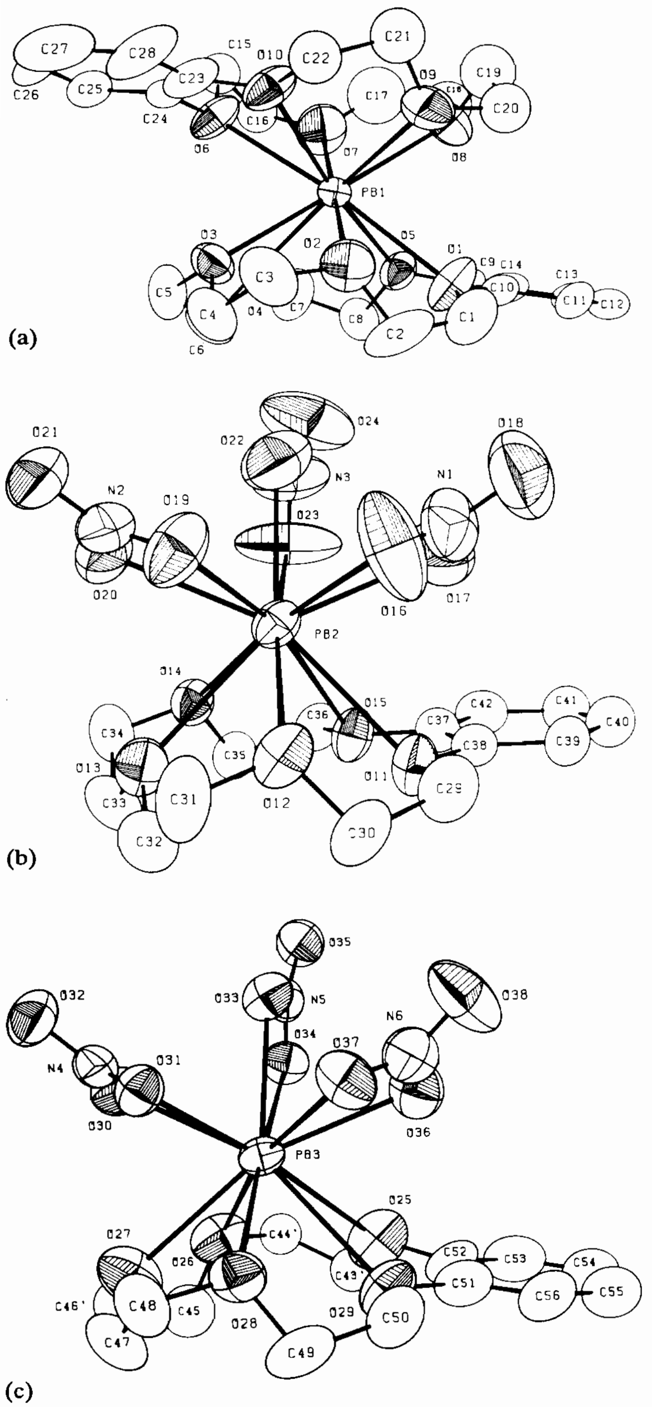

Fig. 2. (a) [Pb(benzo-15-crown-5)$_2$]$^{2+}$ cation in **3**. Hydrogen atoms were not included in the refinement. The ethylene units in the O(6)–O(10) crown ether are disordered. (b) One of two unique [Pb(NO$_3$)$_3$(benzo-15-crown-5)]$^-$ anions. (c) The second unique anion. The C(43)–C(44) and C(45)–C(46) ethylene groups are disordered.

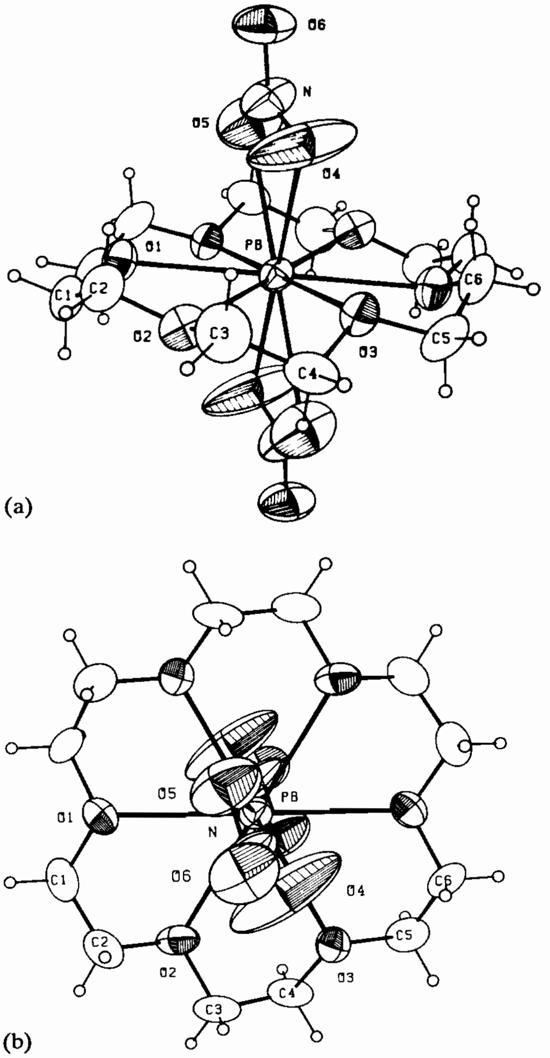

Fig. 3. (a) [Pb(NO$_3$)$_2$(18-crown-6)] (**4**). (b) Top view.

(Fig. 2(a)) and two anions (Fig. 2(b) and (c)) in the asymmetric unit.

The [Pb(benzo-15-crown-5)$_2$]$^{2+}$ cation is ten-coordinate with Pb^{2+} in an approximate pentagonal anti-prismatic geometry. The Pb–O separations have only a 0.10 Å range and average 2.73(3) Å, exactly the same as observed for [Pb(NO$_3$)(12-crown-4)$_2$]$^+$. The ethylene linkages in the O(6)–O(10) crown ether are disordered and the benzo substituents are approximately *trans* to one another and nearly parallel ($\delta = 10°$). In sandwich complexes of this ether and the dual action NH$_4^+$ cation, hydrogen bonding considerations result in more nearly eclipsed benzo substituents [31].

A lone pair effect for this cation is not immediately obvious. One would expect that if there were a non-spherical contribution to the lone pair density through one of the ether rings that some difference in coordination for that ether would be observed. In fact the coordination is nearly identical. The average Pb–O separations are identical and each five-membered pentagonal plane is planar to within 0.12 Å. The dihedral angle between these planes is 2°.

TABLE 5. Comparison of bonding parameters

Compound	*CN*	IR[a]	M–O(etheric) (Å)			M–ONO$_2$ (Å)			Reference
			Range	Δ	Av.	Range	Δ	Av.	
[Pb(NO$_3$)(12-crown-4)$_2$]-	10	1.40	2.645(8)–2.827(7)	0.18	2.73(6)	2.653(8)–2.705(8)	0.052	2.68(3)	this study
[Pb(NO$_3$)$_3$(12-crown-4)]	10	1.40	2.743(8)–2.916(7)	0.17	2.81(7)	2.638(8)–2.77(1)	0.13	2.68(4)	
[Pb(benzo-15-crown-5)$_2$]-	10	1.40	2.67(1)–2.77(1)	0.10	2.73(3)				
[Pb(NO$_3$)$_3$(benzo-15-crown-5)]$_2$	11	1.45	2.899(8)–2.98(1)[b] 2.829(9)–3.06(1)	0.081 0.23	2.95(3) 2.93(8)	2.55(2)–2.809(8) 2.53(1)–2.79(1)	0.26 0.26	2.65(9) 2.67(9)	this study
[Pb(NO$_3$)$_2$(18-crown-6)]	10	1.40	2.724(8)–2.772(7)	0.048	2.76(2)	2.64(1)–2.72(1)	0.08	2.68(4)	this study
[Pb(NO$_3$)$_2$(dicyclohexyl-18-crown-6)] (*cis-syn-cis*)	10	1.40	2.72(3)–2.88(3)	0.16	2.79(7)			2.71(4)	7
[Pb(NO$_3$)$_2$(dicyclohexyl-18-crown-6)] (*cis-anti-cis*)	10	1.40	2.69(2)–2.89(1)	0.20	2.78(8)	2.68–2.75	0.07	2.72(4)	8
[Pb(NCS)(15-crown-5)(μ-NCS)$_2$]-	8	1.29	2.74(1)–2.85(1)	0.11	2.81(5)				9
[Pb(NCS)(15-crown-5)]	8	1.29	2.53(1)–2.82(1)	0.29	2.7(1)				
[Pb(18-crown-6)(CCl$_3$COO)$_2$]·2CCl$_3$COOH	10	1.40	2.75(1)–2.79(1)	0.04	2.76(2)				10
[Cd(NO$_3$)$_2$(15-crown-5)]	9		2.401(5)–2.646(5)	0.24	2.49(9)	2.348(5)–2.709(6)	0.36	2.5(1)	30
[Cd(NO$_3$)$_2$(18-crown-6)]	10		2.513(8)–2.78(1)	0.27	2.6(1)	2.299(8)–2.58(1)	0.28	2.4(1)	30

[a]From ref. 29. [b]The values given are for the two unique anions, Pb(2) and Pb(3), respectively.

The two unique [Pb(NO$_3$)$_3$(benzo-15-crown-5)]$^-$ anions are eleven-coordinate approximately capped pentagonal antiprisms. The five crown ether donors form one pentagonal plane (to within 0.34 Å) and five nitrate donors a second pentagonal plane (to within 0.19 Å) capped by a sixth nitrate donor (O(22), O(33)). Distortions of the coordination sphere geometry are greater than observed in the cation probably due to the bidentate nature of the NO$_3$$^-$ anions.

In keeping with the higher coordination number, the average Pb–O(crown ether) distances of 2.95(3) (Pb(2)) and 2.93(8) (Pb(3)) Å are longer than the 2.73(3) Å found for the cations in this structure or in **1**, and longer than the 2.81(7) Å observed for the anion in **1**. Despite this, the Pb–ONO$_2$ distances (2.65(9), Pb(2); 2.67(9), Pb(3) Å) are statistically identical to those observed for both the cation and anion in **1**.

The bidentate nitrate anions are again asymmetrically coordinated to Pb^{2+}. The range in Pb–ONO$_2$ separations for the two anions is the largest observed for the title complexes (0.26 Å). It does not appear that the differences in these values can be attributed to either coordination polyhedron location or to a localized lone pair affect. We have observed similar asymmetric nitrate coordination in [Cd(NO$_3$)$_2$(15-crown-5)] [30] and [Cd(NO$_3$)$_2$(18-crown-6)] [30].

The structure of the final complex, [Pb(NO$_3$)$_2$(18-crown-6)], is depicted in Fig. 3(a). The 18-crown-6 cavity is perfectly suited to Pb^{2+} and the cation resides exactly in the mean plane of the six oxygen atoms. The crown ether adopts its normal coordinated D_{3d} conformation. The Pb–O(crown ether) separations have the narrowest range of the structurally characterized Pb^{2+} crown ether complexes (0.048 Å) and average 2.76(2) Å. This value is consistent with the 2.73 Å found for the cations in **1** and **3** and the observations for the neutral complexes [Pb(NO$_3$)$_2$(dicyclohexyl-18-crown-6)] (*cis-syn-cis*: Pb–O(ether) = 2.79(7) Å; *cis-anti-cis*: Pb–O(ether) = 2.78(8) Å) and [Pb(18-crown-6)(CCl$_3$COO)$_2$]·2CCl$_3$COOH (Pb–O(ether) = 2.76(2) Å).

The unique nitrate ion is asymmetrically coordinated, Pb–ONO$_2$ = 2.72(1) (O(5)) and 2.64(1) (O(4)) Å. The 2.68(4) Å average is nearly identical to the values found in all structurally characterized Pb(NO$_3$)$_2$/crown ether complexes (Table 5). The Pb^{2+} ion resides on a center of inversion and thus the nitrate anions are parallel. In addition, the nitrate ions eclipse the O(3)–Pb–O(3)^a bonds (Fig. 3(b)). The nitrate ions are also parallel in [Pb(NO$_3$)$_2$(*cis-anti-cis*-dicyclohexyl-18-crown-6)] and [M(NO$_3$)$_2$(Me$_2$-18-crown-6)] (M = Sr^{2+}, Ba^{2+}) [32] although they do not eclipse any *trans* O–M–O(crown ether) bonds. In the *cis-syn-cis* isomer complex the nitrates are staggered (δ = 68°), as they are in [Cd(NO$_3$)$_2$(18-crown-6)] (δ = 90°) and such complexes as $[Ca(NO_3)_2(Me_2\text{-18-crown-6})]$ [32], $[Ca(NO_3)_2(Ph_4\text{-18-crown-6})]$ [33], and $[Pb(NO_3)_3L]$ (L = a diimino macrocycle with an N_3O_3 donor core) [11].

A review of Table 5 reveals that the average Pb–O(crown ether) separations have only a 0.25 Å range despite various coordination numbers, coordination geometries, anion and ionic charge. The range in average Pb–ONO_2 distance is even narrower at only 0.07 Å. Much longer Pb–ONO_2 values are observed when the macrocyclic oxygen donors are changed to softer nitrogen donors [11, 12].

The standard deviations in all of the $Pb(NO_3)_2$ crown ether structures are relatively high, yet one would expect some observable trend if a stereochemically active lone pair were present on Pb^{2+}. We find no evidence in these structures for such an active lone pair consistent with the findings of Hancock *et al.* that the lone pair is activated by nitrogen donors but not oxygen donors and with our Bi^{3+} results indicating lone pair activation by covalent bond formation.

Supplementary material

Tables of distances and angles, hydrogen atom coordinates, thermal parameters, and observed and calculated structure factors for all three compounds (48 pages) are available from the authors on request.

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References

1 R. M. Izatt, L. Eblerhardt, G. A. Clark, R. L. Bruening, J. S. Bradshaw, M. H. Cho and J. J. Christensen, *Sep. Sci. Tech., 22* (1987) 701.
2 R. M. Izatt, R. L. Bruening, G. A. Clark, J. D. Lamb and J. J. Christensen, *Sep. Sci. Tech., 22* (1987) 661.
3 R. M. Izatt, G. A. Clark and J. J. Christensen, *Sep. Sci. Tech., 21* (1986) 865.
4 A. Yu. Nazarenko, O. I. Kronikovskii and V. V. Sukhan, *Zh. Neorg. Khim., 32* (1987) 2233.
5 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Anal. Chem., 63* (1991) 522.
6 K. Abu-Dari, F. E. Hahn and K. N. Raymond, *J. Am. Chem. Soc., 112* (1990) 1519.
7 N. F. Krasnova, Yu. A. Simonov, A. A. Dvorkin, M. B. Korshunov, V. V. Yakshin and T. I. Malinovskii, *Izv. Akad. Mold SSR, Ser. Fiz.-Tekh.,* (1984) 63.
8 N. I. Krasnova, Yu. A. Simonov, M. B. Korshunov and V. V. Yakshin, *Kristallografiya, 32* (1987) 499.
9 H. J. Brügge, R. Fölsing, A. Knöchel and W. Dreissig, *Polyhedron, 4* (1985) 1493.
10 S. T. Malinovskii, Yu. A. Simonov and A. Yu. Nazarenko, *Kristallografiya, 35* (1990) 1410.
11 A. Bashall, M. McPartlin, B. P. Murphy, D. E. Fenton, S. J. Kitchen and P. A. Tasker, *J. Chem. Soc., Dalton Trans.,* (1990) 505.
12 N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.,* (1979) 1486.
13 N. W. Alcock, E. H. Curzon and P. Moore, *J. Chem. Soc., Dalton Trans.,* (1984) 2813.
14 R. Bhula, P. Osvath and D. C. Weatherburn, *Coord. Chem. Rev., 91* (1988) 89.
15 N. W. Alcock, E. H. Curzon, P. Moore and C. Pierpoint, *J. Chem. Soc., Dalton Trans.,* (1984) 605.
16 K. Wieghardt, M. Kleine-Boymann, B. Nuber, J. Weiss, L. Zsolnai and G. Huttner, *Inorg. Chem., 25* (1986) 1647.
17 H.-J. Buschmann, *Thermochim. Acta, 107* (1986) 219.
18 B. Metz and R. Weiss, *Acta Crystallogr., Sect. B, 29* (1973) 1088.
19 L. F. Lindoy, in Y. Inoue and G. W. Gokel (eds.), *Cation Binding by Macrocycles,* Marcel Dekker, New York, 1990, pp. 599–629.
20 M. Takagi, in Y. Inoue and G. W. Gokel (eds.), *Cation Binding by Macrocycles,* Marcel Dekker, New York, 1990, pp. 465–495.
21 M. Tadokoro, H. Okawa, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1991) 1657.
22 D. B. Gomis and E. A. Garcia, *Analyst, 115* (1990) 89.
23 R. D. Hancock, M. S. Shaikjee, S. M. Dobson and J. C. A. Boeyens, *Inorg. Chim. Acta, 154* (1988) 229.
24 R. D. Rogers, A. H. Bond, S. Aguinaga and A. Reyes, *J. Am. Chem. Soc.,* (1992) in press.
25 R. D. Rogers, A. H. Bond and S. Aguinaga, *J. Am. Chem. Soc.,* (1992) in press.
26 G. M. Sheldrick, *SHELX76,* a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, UK, 1976.
27 G. M. Sheldrick, *SHELXS, Acta Crystalllogr., Sect. A, 46* (1990) 467.
28 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 72, 99, 149. (Present distributor: Kluwer, Dordrecht, Netherlands.)
29 R. D. Shannon, *Acta Crystallogr., Sect. A, 32* (1976) 751.
30 R. D. Rogers and A. H. Bond, 1991, unpublished results.
31 R. D. Rogers, L. K. Kurihara and M. M. Benning, *Inorg. Chem., 26* (1987) 4346.
32 R. B. Dyer, D. H. Metcalf, R. G. Ghirardelli, R. A. Palmer and E. M. Holt, *J. Am. Chem. Soc., 108* (1986) 3621.
33 J. Crosby, M. E. Fakley, C. Gemmell, K. Martin, A. Quick, A. M. Z. Slawin, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *Tetrahedron Lett., 30* (1989) 3849.