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Structural Chemistry of Poly(ethylene glycol) Complexes of Lead(II) Nitrate and Lead(II) Bromide

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The reaction of 1:1 stoichiometries (1:1.5 for the nitrate/tetraethylene glycol (EO4) and pentaethylene glycol (EO5) complexes) of PbX_2 (X = NO_3, Br) with five- to eight-donor poly(ethylene glycols) (PEGs) in 3:1 CH_3CN/CH_3OH (CH_3CN only for the nitrate/EO5 complex) followed by solvent evaporation resulted in six crystalline materials upon which X-ray structural analyses were carried out: $[Pb(NO_3)_2(EO4)]_n$, $[Pb(NO_3)_2(EO5)]$, $[Pb(NO_3)_2(EO6)]$, $[PbBr(EO5)(\mu\text{-Br})PbBr_2]\cdot H_2O$, $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$, and $[PbBr(EO7)][PbBr_3]$. The nitrates crystallize as tight ion pairs with the PEG ligands coordinating in an equatorial plane around the Pb^{2+} ions. Because EO4 has only five oxygen donors, this complex exhibits steric unsaturation which is overcome by a monodentate interaction with a third nitrate anion that is also coordinated to a neighboring Pb^{2+} ion. The six donors of EO5 coordinate in an equatorial plane resulting in a 10-coordinate complex with *trans*, twisted, bidentate nitrate anions. The seven-donor hexaethylene glycol (EO6) only uses six of its oxygen donors to coordinate Pb^{2+}. $[Pb(NO_3)_2(EO4)]_n$ is monoclinic, $P2_1/c$, with $a = 7.902(3)$ Å, $b = 22.136(6)$ Å, $c = 8.910(2)$ Å, $\beta = 90.96(3)°$, and $Z = 4$. $[Pb(NO_3)_2(EO5)]$ is triclinic $P\bar{1}$, with $a = 9.332(3)$ Å, $b = 10.025(3)$ Å, $c = 11.688(4)$ Å, $\alpha = 68.41(3)°$, $\beta = 68.39(3)°$, $\gamma = 68.58(3)°$, and $Z = 2$. $[Pb(NO_3)_2(EO6)]$ is monoclinic $P2_1/c$, with $a = 16.289(4)$ Å, $b = 10.773(4)$ Å, $c = 12.329(4)$ Å, $\beta = 106.77(2)°$, and $Z = 4$. Lead(II) bromide complexes with PEGs tend to crystallize as PEG complexed cations with polymeric lead(II) bromide anions. In the EO5 complex, bromide anions in the polymer also coordinate to the PEG-wrapped Pb^{2+} cations. The hexa- and heptaethylene glycol (EO6 and EO7, respectively) complexes contain discreet ions. In these halide complexes, EO7 is the only PEG to expand the Pb^{2+} coordination number from eight to nine. $[PbBr(EO5)(\mu\text{-Br})PbBr_2]\cdot H_2O$ is triclinic $P\bar{1}$, with $a = 7.922(6)$ Å, $b = 15.802(9)$ Å, $c = 19.001(9)$ Å, $\alpha = 73.19(8)°$, $\beta = 88.91(9)°$, $\gamma = 87.22(9)°$, and $Z = 4$. $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$ is monoclinic $P2_1/c$, with $a = 14.389(4)$ Å, $b = 31.931(9)$ Å, $c = 8.029(2)$ Å, $\beta = 97.76(3)°$, and $Z = 2$. $[PbBr(EO7)][PbBr_3]$ is monoclinic Cc, with $a = 13.165(3)$ Å, $b = 24.732(5)$ Å, $c = 8.007(1)$ Å, $\beta = 94.58(2)°$, and $Z = 4$.

Introduction

Crown ethers, especially the 18-membered six-donor macrocycles, are noted for the stability of their Pb^{2+} complexes.[1,2] Separation processes based on crown ether complexes of Pb^{2+} have been reported and are often quite selective.[3−6] Despite the success of the oxygen-based crown ether separation processes, considerably more attention has been paid to nitrogen-containing macrocyclic complexes of Pb^{2+} due to a better match of the softer Lewis base nitrogen donor with lead.[7−14] Hancock has suggested, however, that the use of nitrogen donor macrocycles may introduce another variable into the complexation chemistry.[15] Increasing the number of nitrogen donors for Pb^{2+} increases the potential stereochemical activity of the lone pair which could influence the complexation, and in turn, the separation chemistry of Pb^{2+}.

We have published the crystal structures of several $Pb(NO_3)_2$ complexes of crown ethers[16] and have also begun a systematic investigation of Pb^{2+} partitioning in poly(ethylene glycol) (PEG)-based aqueous biphasic systems.[17−19] Such systems are prepared using high molecular weight PEGs and consist of two largely aqueous phases. PEG-based aqueous biphasic systems may prove useful in removing lead from high ionic strength solutions, yet little is known about how PEGs, acyclic crown ether analogs, influence the Pb^{2+} coordination sphere. Crown

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(1) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.

(2) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721.

(3) Izatt, R. M.; Clark, G. A.; Christensen, J. J. *Sep. Sci. Technol.* **1986**, *21*, 865.

(4) Izatt, R. M.; Bruening, R. L.; Clark, G. A.; Lamb, J. D.; Christensen, J. J. *Sep. Sci. Technol.* **1987**, *22*, 661.

(5) Izatt, R. M.; Eblerhardt, L.; Clark, G. A.; Bruening, R. L.; Bradshaw, J. S.; Cho, M. H.; Christensen, J. J. *Sep. Sci. Technol.* **1987**, *22*, 701.

(6) Horwitz, E. P.; Chiarizia, R.; Dietz, M. L. *Solvent Extr. Ion Exch.* **1992**, *10*, 313.

(7) Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *29*, 1088.

(8) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1486.

(9) Alcock, N. W.; Curzon, E. H.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2813.

(10) Alcock, N. W.; Curzon, E. H.; Moore, P.; Pierpoint, C. *J. Chem. Soc., Dalton Trans.* **1984**, 605.

(11) Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J.; Zsolnai, L.; Huttner, G. *Inorg. Chem.* **1986**, *25*, 1647.

(12) Buschmann, H. J. *Thermochim. Acta* **1986**, *107*, 219.

(13) Bhula, R.; Osvath, P.; Weatherburn, D. C. *Coord. Chem. Rev.* **1988**, *91*, 89.

(14) Tadokoro, M.; Okawa, H.; Matsumoto, N.; Koikawa, M.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1991**, 1657.

(15) Hancock, R. D.; Shaikjee, M. S.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1988**, *154*, 229.

(16) Rogers, R. D.; Bond, A. H. *Inorg. Chim. Acta* **1992**, *192*, 163.

(17) Rogers, R. D.; Bond, A. H.; Bauer, C. B.; Zhang, J.; Jezl, M. L.; Roden, D. M.; Rein, S. D.; Chomko, R. R. In *Aqueous Biphasic Separations: Biomolecules to Metal Ions*; Rogers, R. D., Eiteman, M. A., Eds.; Plenum: New York, 1995; pp 1−20.

(18) Bond, A. H. Ph.D. Thesis, Northern Illinois University, DeKalb, IL, 1995.

(19) Rogers, R. D.; Bond, A. H.; Bauer, C. B.; Zhang, J.; Griffin, S. T. *J. Chromatogr., B: Biomed. Appl.* **1995**, *680*, 221.

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ethers and PEGs provide similar five-membered chelate rings when complexed to a metal ion, and Hancock has proposed that the chelate ring size is more important than cavity size in determining selectivity.[20,21]

This paper reports the synthesis, isolation, and structural characterization of six new complexes of small-chain PEGs with $Pb(NO_3)_2$ and $PbBr_2$. The nitrate anion was chosen because (a) of the solubility of its lead salt, (b) it provides an example of ionic coordination, and (c) it is used in the nuclear processing industry.[6,22,23] Previous work by our group studying halide complexes of Hg^{2+},[24] Cd^{2+},[25-27] and Bi^{3+} [28,29] with PEGs has shown that the halides exert a greater influence than nitrate anions on PEG coordination modes, and we have chosen Br^- as an intermediate halide for comparative studies with Pb^{2+}. The resulting PEG/Pb^{2+} complexes are compared with Pb^{2+}/crown ether complexes and PEG complexes of Hg^{2+}, Cd^{2+}, Sr^{2+}, and Ba^{2+}.

Experimental Section

$Pb(NO_3)_2$, $PbBr_2$, EO4, EO5, EO6, EO7, and Cs_2CO_3 were used as purchased without purification. CH_3CN and CH_3OH were distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. The colorless crystalline materials appeared to be air stable and were not hygroscopic, although no detailed studies of their stabilities were performed. All samples were dried in vacuo prior to combustion analyses, which was carried out at Northern Illinois University. Some crystalline samples were isolated from viscous oils containing the PEG ligands, which were not removed in the drying procedure. Consequently, poor agreement for some analyses is observed. All melting points are uncorrected.

[Pb(NO$_3$)$_2$(EO4)]$_n$. $Pb(NO_3)_2$ (0.1555 g, 0.47 mmol) and EO4 (0.13 mL, 0.75 mmol) were combined with 5 mL of 3:1 CH_3CN/CH_3OH and stirred at 60 °C for 1 h. The clear solution was stored at 5 °C for 25 h and −10 °C for 24 h. Slow evaporation at ambient temperature combined with volume reduction in vacuo produced crystalline material, mp 125−126 °C. Anal. Calcd: C, 18.29; H, 3.45; N, 5.33. Found for crystals: C, 18.30; H, 3.61; N, 5.01.

[Pb(NO$_3$)$_2$(EO5)]. Cs_2CO_3 (0.1626 g, 0.50 mmol) (present in the reaction to assess the effects of weak bases on the reaction products) and EO5 (0.16 mL, 0.75 mmol) were combined with 5 mL of CH_3CN and stirred at 23 °C for 10 min. $Pb(NO_3)_2$ (0.1649 g, 0.50 mmol) was added and the resulting clear solution stirred at 60 °C for 2 h. The solution was then stored at 3 °C for 12 h. Slow evaporation at room temperature produced crystalline material, mp 113−115 °C (dec). Anal. Calcd: C, 21.09; H, 3.89; N, 4.92. Found for crystals: C, 21.38; H, 4.28; N, 4.56.

[Pb(NO$_3$)$_2$(EO6)]. $Pb(NO_3)_2$ (0.1652 g, 0.50 mmol) and EO6 (0.13 mL, 0.52 mmol) were combined with 5 mL of 3:1 CH_3CN/CH_3OH and stirred at 60 °C for 1 h. The clear solution was stored at 5 °C for ~36 h and −10 °C for ~24 h. Slow evaporation at ambient temperature combined with volume reduction in vacuo produced crystalline material, mp 120−123 °C. Anal. Calcd: C, 23.49; H, 4.27; N, 4.57. Found for crystals: C, 23.58; H, 4.64; N, 4.00.

[PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O. $PbBr_2$ (0.18 g, 0.49 mmol) was weighed under an Ar atmosphere and then taken into the air. Five milliliters of 3:1 CH_3CN/CH_3OH was added along with EO5 (100 μL, 0.47 mmol) and the resulting solution stirred at 60 °C for 1 h. A small quantity of a white precipitate was centrifuged and the supernatant decanted and stored at 3 °C for ~25 h and at −10 °C for ~24 h. Slow evaporation at room temperature produced diffraction-quality crystalline material, mp 126−130 °C (dec). Anal. Calcd: C, 12.13; H, 2.44. Found for precipitate: C, 0.55; H, 0.04. Found for crystals: C, 15.68; H, 3.48. The crystals were removed from an oily residue, and the discrepancy in these values may be due to a surface coating of EO5 on the crystals submitted for combustion analysis.

[PbBr(NCMe)(EO6)]$_2$[PbBr$_2$(EO6)][PbBr$_3$]$_2$. $PbBr_2$ (0.18 g, 0.49 mmol) was weighed under an Ar atmosphere and then taken into the air. Five milliliters of 3:1 CH_3CN/CH_3OH was added along with EO6 (125 μL, 0.50 mmol) and the resulting solution stirred at 60 °C for 1 h. A small quantity of a white precipitate was centrifuged and the supernatant decanted and stored at 3 °C for ~25 h and at −10 °C for ~24 h. Slow evaporation at room temperature produced crystalline material, mp 105 °C (dec). Anal. Calcd: C, 17.38; H, 3.06; N, 1.01. Found for precipitate: C, 0.69; H, 0.00; N, 0.00. Found for crystals: C, 25.11; H, 5.05; N, 0.00. It is likely that the crystals submitted for analysis had a coating of EO6 on the surface and that the drying in vacuo removed the lattice solvate.

[PbBr(EO7)][PbBr$_3$]. $PbBr_2$ (0.18 g, 0.49 mmol) was weighed under an Ar atmosphere and then taken into the air. Five milliliters of 3:1 CH_3CN/CH_3OH was added along with EO7 (145 μL, 0.50 mmol) and the resulting solution stirred at 60 °C for 1 h. A small quantity of a white precipitate was centrifuged and the supernatant decanted and stored at 3 °C for ~25 h and at −10 °C for ~24 h. Slow evaporation at ambient temperature produced crystalline material, mp 220−251 °C (dec). Anal. Calcd: C, 15.86; H, 2.85. Found for precipitate: C, 0.95; H, 0.00. Found for crystals: C, 18.78; H, 3.72. It is likely that the crystals submitted for analysis had a coating of EO7 on the surface.

X-ray Data Collection, Structure Determination, and Refinement. A single crystal of each complex was mounted in a thin-walled glass capillary flushed with Ar and transferred to an Enraf-Nonius CAD-4 diffractometer. A summary of data collection parameters is given in Table 1. For those space groups not uniquely determined by the systematic absences, the higher symmetry centrosymmetric alternative was found to be the correct choice for [Pb(NO$_3$)$_2$(EO5)] and [PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O, while [PbBr(EO7)][PbBr$_3$] was successfully refined in the acentric space group *Cc*.

The structures were solved by utilizing SHELXS[30] and refined with SHELX76.[31] Neutral scattering factors and anomalous dispersion corrections were from ref 32. Except as noted below, geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. It was possible to locate the alcoholic hydrogen atoms for [Pb(NO$_3$)$_2$(EO5)], and these were included in the final refinements with fixed contributions ($B = 5.5$ Å^2). Unless otherwise noted, all non-hydrogen atoms were refined anisotropically. No decay or extinction corrections were applied. The fractional coordinates for each structure are available in the Supporting Information. Considerations unique to each crystallographic study are discussed below.

[Pb(NO$_3$)$_2$(EO4)]$_n$. High thermal motion was observed, but there was no resolvable disorder. Due to the high thermal motion, the hydrogen atoms were not included in the final refinement.

[PbBr(NCMe)(EO6)]$_2$[PbBr$_2$(EO6)][PbBr$_3$]$_2$. Refinement of this structure was complicated by high thermal motion and disorder. Pb(1) resides on a crystallographic center of inversion and this requires that the coordinated EO6 ligand be disordered. This disorder was resolved with 50% occupancy of an ethylene linkage (C(5), C(6)) and 50% occupancy by a dangling CH_2CH_2OH unit (C(5)′, C(6)′, O(4)). High thermal motion was noted in the second EO6 molecule as well; however, a disorder model could not be resolved. To improve the data/

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(20) Hancock, R. D.; Wade, P. W.; Ngwenya, M. P.; de Sousa, A. S.; Damu, K. V. *Inorg. Chem.* **1990**, *29*, 1968.

(21) Hancock, R. D. *J. Chem. Educ.* **1992**, *69*, 615.

(22) *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C., Choppin, G. R., Eds.; Marcel Dekker: New York, 1992.

(23) *Chemical Pretreatment of Nuclear Waste for Disposal*; Schulz, W. W., Horwitz, E. P., Eds.; Plenum Press: New York, 1994.

(24) Rogers, R. D.; Bond, A. H.; Wolff, J. L. *J. Coord. Chem.* **1993**, *29*, 187.

(25) Rogers, R. D.; Bond, A. H.; Aguinaga, S. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 857.

(26) Rogers, R. D.; Bond, A. H.; Aguinaga, S.; Reyes, A. *Inorg. Chim. Acta* **1993**, *212*, 225.

(27) Rogers, R. D.; Bond, A. H. *Inorg. Chim. Acta*, in press.

(28) Rogers, R. D.; Bond, A. H.; Aguinaga, S. *J. Am. Chem. Soc.* **1992**, *114*, 2960.

(29) Rogers, R. D.; Bond, A. H.; Aguinaga, S.; Reyes, A. *J. Am. Chem. Soc.* **1992**, *114*, 2967.

(30) Sheldrick, G. M. SHELXS. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(31) Sheldrick, G. M. *SHELX76 a system of computer programs as locally modified*; University of Cambridge: Cambridge, England, 1976.

(32) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974; Vol. IV, p 72.

Table 1. Crystallographic Data

chem formula	$[Pb(NO_3)_2(EO4)]_n$	$[Pb(NO_3)_2(EO5)]$	$[Pb(NO_3)_2(EO6)]$	$[PbBr(EO5)$-$(\mu$-$Br)PbBr_2]\cdot H_2O$	$[PbBr(NCMe)(EO6)]_2$-$[PbBr_2(EO6)][PbBr_3]_2$	$[PbBr(EO7)]$-$[PbBr_3]$
formula wt	525.44	569.49	613.54	990.31	2764.15	1060.4
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	Cc (No. 9)
T, °C	22	21	22	20	20	20
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a, Å	7.902(3)	9.332(3)	16.289(4)	7.922(6)	14.389(4)	13.165(3)
b, Å	22.136(6)	10.025(3)	10.773(4)	15.802(9)	31.931(9)	24.732(5)
c, Å	8.910(2)	11.688(4)	12.329(4)	19.001(9)	8.029(2)	8.007(1)
α, deg		68.41(3)		73.19(8)		
β, deg	90.96(3)	68.39(3)	106.77(2)	88.91(9)	97.76(3)	94.58(2)
γ, deg		68.58(3)		87.22(9)		
V, Å^3	1558	911.3	2072	2274	3655	2599
Z	4	2	4	4	2	4
ρ_{calcd}, g cm^{-3}	2.24	2.08	1.97	2.89	2.51	2.71
μ, cm^{-1}	107.4	91.9	81.1	220.4	171.6	193.0
$R\ (F_o)^a$	0.042	0.028	0.039	0.054	0.072	0.039
$R_w\ (F_o)^b$	0.049	0.028	0.043	0.059	0.080	0.048

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(||F_o| - |F_c||)^2/\Sigma(F_o)^2]^{1/2}$.

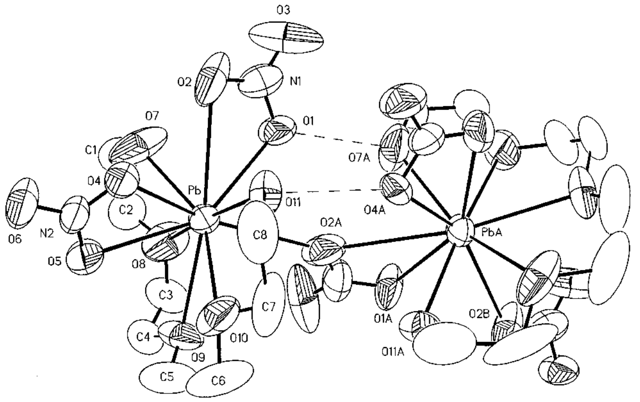

Figure 1. ORTEP illustration (50% probability ellipsoids) showing a portion of the polymeric chain in $[Pb(NO_3)_2(EO4)]_n$. The symmetry codes are $A = x, 0.5 - y, 0.5 + z$ and $B = x, y, 1 + z$.

parameter ratio and because of the disorder and high thermal motion, carbon atoms were only refined isotropically and hydrogen atoms were not included.

[PbBr(EO7)][PbBr₃]. The crystals obtained for this complex were weakly diffracting, and the correction for absorption was very large (range of relative transmission factors 19−100%), making it difficult to account for all of the absorption effects. The carbon atoms were the most affected with elongated ellipsoids typical of absorption problems. C(9) and C(14) could not be anisotropically refined.

Results

$[Pb(NO_3)_2(EO4)]_n$. An ORTEP illustration of this complex is presented in Figure 1. Bond distances within each Pb^{2+} coordination sphere are given in Table 2, and average bonding contacts for each complex along with comparative data from the literature are presented in Table 3. This structure is strongly influenced by the inability of the five donors of the EO4 ligand to complete the Pb^{2+} coordination sphere. EO4 wraps Pb^{2+} in an equatorial girdle reminiscent of crown ether coordination of this metal ion, but even with two bidentate nitrate anions, steric saturation has not been achieved. The Pb^{2+} ion achieves a coordination number of 10 by additional monodentate nitrate coordination to O(2)a, an oxygen atom that is part of a bidentate interaction to a neighboring Pb^{2+} ion. The N(1)-containing nitrate anion is thus tridentate, and O(2) bridges Pb^{2+} ions in a polymeric zigzag chain which propagates along *c*.

Due to the bridging nature of O(2), the μ-NO_3^- anion exhibits an asymmetric bidentate coordination with Pb−O(1) = 2.67(1) Å and Pb−O(2) = 3.13(2) Å. The bridging distances are also asymmetric with the shorter interaction to the monodentate side (Pb−O(2)A = 2.83(1) Å, Pb−O(2) = 3.13(2) Å).

The Pb^{2+} coordination geometry is a very distorted bicapped square antiprism with O(2) and the etheric O(9) in capping positions (O(2)−Pb−O(9) = 170.4(4)°). Both of the capping atoms exhibit the longest Pb−O separations for each type (NO_3^- or EO4) of interaction. Major distortions of the coordination geometry are a result of the nitrate containing N(1) attempting to occupy both capping and prismatic sites.

The terminal bidentate nitrate anion (N(2)) is also asymmetrically coordinated to Pb^{2+}. Despite accepting a hydrogen bond from O(11), O(4) exhibits the shortest of all $Pb-ONO_2$ distances (2.55(1) Å). The Pb−O(5) separation of 2.79(1) Å is the longest of the terminal $Pb-ONO_2$ interactions.

The glycol ligand exhibits relatively high thermal motion which may be indicative of ±gauche disorder in the O−C−C−O linkages. The torsion angles starting at O(7)−C(1)−C(2)−O(8) have the sequence $(g^-)ag^-(g^-)aa(g^+)aa(g^-)$. (In this and subsequent torsion angle sequences, the O−C−C−O torsion angles are given in parens.) In D_{3d} 18-crown-6 (e.g., the conformation of the ether in $[Pb(NO_3)_2(18\text{-crown-}6)]$[16,33]), the O−C−C−O torsion angles alternate ±g and the C−O−C−C torsion angles are all anti. In $[Pb(NO_3)_2(EO4)]_n$, the first two O−C−C−O torsion angles have like sign, which forces one of the C−O−C−C torsion angles between them toward gauche (C(2)−O(8)−C(3)−C(4) = −107.6°).

The two alcoholic termini in the EO4 chain donate hydrogen bonds to oxygens in the polymeric chain. Both O(7) and O(11) donate to coordinated nitrate oxygen atoms (O(1)B and O(4)A, respectively) in different Pb^{2+} coordination spheres.

The $Pb-O_{alc}$ distances, 2.60(1) Å (O(11)) and 2.64(1) Å (O(7)), are expectedly shorter than the average $Pb-O_{eth}$ separations of 2.80(2) Å. The longest $Pb-O_{eth}$ separation, Pb−O(9) = 2.82(l) Å, involves a capping position and occurs in the middle of the glycol chain.

$[Pb(NO_3)_2(EO5)]$. This 10-coordinate complex is depicted in Figure 2. The Pb^{2+} ion is coordinated to an EO5 ligand, which forms an equatorial girdle, and two *trans*, bidentate nitrate anions complete the coordination sphere. The metal ion geometry is roughly a bicapped square antiprism with O(2) and O(5) in capping positions (O(2)−Pb−O(5) = 174.1(2)°), although it is easier to describe the geometry as a hexagonal bipyramid by assuming each nitrate anion occupies a single axial position.

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(33) Drew, M. G. B.; Nicholson, D. G.; Sylte, I.; Vasudevan, A. K. *Acta Chem. Scand.* **1992**, *46*, 396.

Table 2. Bond Distances (Å) within Each Pb^{2+} Coordination Sphere

$[Pb(NO_3)_2(EO4)]_n$		$[Pb(NO_3)_2(EO5)]$		$[Pb(NO_3)_2(EO6)]$	
atoms	distance	atoms	distance	atoms	distance
		Nitrate			
Pb−O(1)	2.67(1)	Pb−O(7)	2.685(5)	Pb−O(1)	2.681(8)
Pb−O(2)	3.13(2)	Pb−O(8)	2.678(5)	Pb−O(2)	2.565(8)
Pb−O(4)	2.55(1)	Pb−O(10)	2.712(5)	Pb−O(4)	2.823(8)
Pb−O(5)	2.79(1)	Pb−O(11)	2.709(5)	Pb−O(5)	2.766(9)
Pb−O(2)*A*[a]	2.83(1)				
		PEG			
Pb−O(7)$_{alc}$	2.64(1)	Pb−O(1)$_{alc}$	2.650(5)	Pb−O(7)$_{alc}$	2.604(8)
Pb−O(8)	2.80(1)	Pb−O(2)	2.750(5)	Pb−O(8)	2.673(6)
Pb−O(9)	2.82(1)	Pb−O(3)	2.847(5)	Pb−O(9)	2.721(7)
Pb−O(10)	2.77(1)	Pb−O(4)	2.834(5)	Pb−O(10)	2.708(8)
Pb−O(11)$_{alc}$	2.60(1)	Pb−O(5)	2.719(5)	Pb−O(11)	2.795(7)
		Pb−O(6)$_{alc}$	2.674(4)	Pb−O(12)	2.780(8)
				Pb···O(13)$_{alc}$	4.564(8)

$[PbBr(EO5)(\mu\text{-}Br)PbBr_2]\cdot H_2O$				$[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$				$[PbBr(EO7)][PbBr_3]$	
atoms	distance	atoms	distance	atoms	distance	atoms	distance	atoms	distance
				Bromide					
Pb(1)−Br(1)	2.715(5)	Pb(2)−Br(3)	2.703(5)	Pb(1)−Br(1)	2.982(6)	Pb(3)−Br(5)	2.741(5)	Pb(1)−Br(1)	2.926(4)
Pb(1)−Br(2)$_{\mu}$	3.365(4)	Pb(2)−Br(4)$_{\mu}$	3.434(4)			Pb(3)−N	3.09(4)		
				PEG					
Pb(1)−O(1)$_{alc}$	2.47(3)	Pb(2)−O(7)$_{alc}$	2.60(2)	Pb(1)−O(1)	2.84(3)	Pb(3)−O(5)$_{alc}$	2.57(3)	Pb(1)−O(1)$_{alc}$	2.69(3)
Pb(1)−O(2)	2.76(2)	Pb(2)−O(8)	2.72(2)	Pb(1)−O(2)	2.67(2)	Pb(3)−O(6)	2.63(3)	Pb(1)−O(2)	2.85(2)
Pb(1)−O(3)	2.86(2)	Pb(2)−O(9)	2.84(2)	Pb(1)−O(3)[b]	2.70(3)	Pb(3)−O(7)	2.60(3)	Pb(1)−O(3)	2.80(3)
Pb(1)−O(4)	2.92(2)	Pb(2)−O(10)	2.82(3)	Pb(1)···O(4)$_{alc}$	4.393(3)	Pb(3)−O(8)	2.74(3)	Pb(1)−O(4)	2.74(2)
Pb(1)−O(5)	2.77(2)	Pb(2)−O(11)	2.72(3)			Pb(3)−O(9)	2.77(4)	Pb(1)−O(5)	2.66(3)
Pb(1)−O(6)$_{alc}$	2.58(2)	Pb(2)−O(12)$_{alc}$	2.70(3)			Pb(3)−O(10)	2.74(3)	Pb(1)−O(6)	2.71(3)
						Pb(3)···O(11)$_{alc}$	4.352(3)	Pb(1)−O(7)	2.68(3)
								Pb(1)−O(8)$_{alc}$	2.70(3)

[a] Symmetry code $A = x, 0.5 - y, 0.5 + z$. [b] etheric 50%; alcoholic 50%.

The overall structure is similar to that observed in $[Pb(NO_3)_2(18\text{-crown-6})]$.[16,33] The major differences occur in distortions of O(4) (0.91 Å) and O(6) (−0.87 Å) out of the mean plane defined by O(1), O(2), O(3), and O(5). These deviations are allowed by the flexibility of the acyclic EO5 compared to 18-crown-6. Despite the differences, the glycol adopts essentially the same conformation as D_{3d} 18-crown-6: the O−C−C−O torsion angles alternate ±g and the C−O−C−C torsion angles are all anti.

The Pb−O$_{alc}$ distances average 2.66(1) Å, while the Pb−O$_{eth}$ separations average 2.79(5) Å. As observed for $[Pb(NO_3)_2(EO4)]_n$, the two longest of the latter type occur in the middle of the chain, Pb−O(3) = 2.847(5) Å, Pb−O(4) = 2.834(5) Å. Subtle differences in the O−C−C−O torsion angles and the *cis* O−Pb−O angles are observed for this portion of the polyether. The *cis* O−Pb−O angles involving O(3) and O(4) are all less than 60°, averaging 59.3(3)°. The remaining such angles are over 60° and average 63.1(6)°. The O(3)−C(5)−C(6)−O(4) torsion angle (67.7°) is the largest in this complex with the remaining four O−C−C−O angles averaging 63.9(9)°.

The two *trans* nitrate anions exhibit a dihedral angle of 95.2°. Each bidentate interaction is symmetric despite one coordinated oxygen of each anion accepting a hydrogen bond. All four Pb−ONO_2 distances average 2.70(1) Å. The Pb−O(7), O(8) separations average 2.682(4) Å, while the Pb−O(10), O(11) contacts are longer, averaging 2.710(2) Å. The unique nitrate of $[Pb(NO_3)_2(18\text{-crown-6})]$ was asymmetrically bound with distances of 2.64(1) and 2.72(1) Å.[16,33]

As in $[Pb(NO_3)_2(EO4)]_n$, the hydrogen bonding in this EO5 complex involves alcoholic donor interactions to coordinated nitrate oxygen atoms in neighboring asymmetric units. In this case, the hydrogen bonding creates zigzag chains which propagate along *a*.

$[Pb(NO_3)_2(EO6)]$. As can be seen from Figure 3, there are many similarities between this complex, $[Pb(NO_3)_2(EO5)]$, and $[Pb(NO_3)_2(18\text{-crown-6})]$.[16,33] The Pb^{2+} ion is 10-coordinate, wrapped equatorially by six of the seven potential donors from the PEG and possesses two *trans*, twisted bidentate nitrate anions. The EO6 ligand pseudocyclizes by hydrogen bonding from coordinated O(7) to the uncoordinated terminus O(13). The coordination geometry is again very distorted, somewhere between bicapped square antiprismatic and bicapped dodecahedral (O(8)−Pb−O(11) = 175.7(2)°). As with $[Pb(NO_3)_2(EO5)]$ and $[Pb(NO_3)_2(18\text{-crown-6})]$,[16,33] the geometry can be simplified to a distorted hexagonal bipyramid by assuming that the nitrates occupy single axial locations.

The coordination parameters of the nitrate anions in $[Pb(NO_3)_2(EO6)]$ differ from those found in $[Pb(NO_3)_2(EO5)]$, although the average Pb−O separations are the same at 2.7(1) Å. In $[Pb(NO_3)_2(EO6)]$, the N(1)···Pb···N(2) angle is only 170.5(3)° and the dihedral angle between the N(1) and N(2) nitrates is 59.9°, versus 168.3(2)° and $\delta = 95.2°$ in $[Pb(NO_3)_2(EO5)]$. As described for the EO5 complex, one nitrate ion exhibits longer average Pb−O contacts than the other: Pb−O(1), O(2) = 2.62(6) Å, Pb−O(4), O(5) = 2.79(3) Å. Unlike $[Pb(NO_3)_2(EO5)]$, however, the individual nitrate interactions are more asymmetric with the longest such contact (Pb−O(4) = 2.823(8) Å) involved in a hydrogen-bonding interaction.

The EO6 ligand exhibits a conformation similar to D_{3d} 18-crown-6 up to O(12), where one angle is forced toward gauche (C(10)−O(12)−C(11)−C(12) = 78.7°) to accommodate the hydrogen bonding between O(7) and O(13). The overall torsion angle sequence starting at O(7)−C(1)−C(2)−O(8) is $(g^-)aa(g^+)aa(g^-)aa(g^+)aa(g^-)ag^+(g^+)$. The O−C−C−O torsion angles involving coordinated oxygen atoms show no definite trend, ranging from 56.6 to 67.5° and averaging 61(4)°.

The Pb−O(7)$_{alc}$ distance is 2.604(8) Å and there is a 0.122 Å range in Pb−O$_{eth}$ separations (2.673(6)−2.795(7) Å, 2.74(5)

Table 3. Average Bonding Parameters in Related Metal/Polyether Complexes

compound	CN	av M−X, Å	X−M−X, deg	M−ONO$_2$, Å		M−O$_{alc}$, Å		M−O$_{eth}$, Å		ref
				range	av	range	av	range	av	
$[Pb(NO_3)_2(EO4)]_n$	10			2.55(1)−2.79(1)	2.7(1)	2.60(1)−2.64(1)	2.62(2)	2.77(1)−2.82(1)	2.80(2)	
				$2.83(1)−3.13(2)_\mu$						*d*
$[Pb(NO_3)_2(EO5)]$	10			2.678(5)−2.712(5)	2.70(1)	2.650(5)−2.674(4)	2.66(1)	2.719(5)−2.847(5)	2.79(5)	*d*
$[Pb(NO_3)_2(EO6)]$	10			2.565(8)−2.823(8)	2.7(1)	2.604(8)		2.673(6)−2.795(7)	2.74(5)	*d*
$[PbBr(EO5)(\mu\text{-}Br)\text{-}$	8	2.709(6)				2.47(3)−2.70(3)	2.59(8)	2.72(3)−2.92(2)	2.80(7)	
		$3.40(3)_\mu$	159(2)							
$PbBr_2]\cdot H_2O$	6	$3.0(1)_\mu$								*d*
$[PbBr(NCMe)(EO6)]_2\text{-}$	8	2.741(5)				2.57(3)		2.60(3)−2.77(4)	2.70(7)	
		3.09(4) (N)	158.8(8)							
$[PbBr_2(EO6)]^a\text{-}$	8	2.982(6)	180			2.70(3) (O(3))^b		2.67(2)−2.84(3)	2.74(7)	
$[PbBr_3]_2$	6	$3.05(6)_\mu$								*d*
$[PbBr(EO7)]\text{-}$	9	2.926(4)				2.69(3)−2.70(3)	2.695(5)	2.66(3)−2.85(3)	2.74(7)	
$[PbBr_3]$	6	$3.1(1)_\mu$								*d*
$[Pb(NO_3)(12\text{-crown-}4)_2]\text{-}$	10			2.653(8)−2.705(8)	2.68(3)			2.645(8)−2.827(7)	2.73(6)	16
				2.638(6)−2.716(6)	2.68(4)			2.628(6)−2.817(6)	2.72(6)	46
$[Pb(NO_3)_3(12\text{-crown-}4)]$	10			2.638(8)−2.77(1)	2.68(4)			2.743(8)−2.916(7)	2.81(7)	16
				2.641(6)−2.722(8)	2.67(2)			2.735(7)−2.883(6)	2.79(6)	46
$[PbI_2(12\text{-crown-}4)]_2$	8	3.350(2)						2.74(1)		36
$[PbBr_2(benzo\text{-}12\text{-crown-}4)]_n$	8	3.04(5)						2.741(5)−3.118(5)	2.9(2)	36
$[Pb(15\text{-crown-}5)_2][SbCl_6]_2$	10							2.61(3)−2.87(3)	2.76(7)	34
$[Pb(15\text{-crown-}5)_2][SbCl_6]_2\cdot[SbCl_3(15\text{-crown-}5)]$	10							2.67(1)−2.91(2)	2.80(8)	48
$[Pb(CCl_3CO_2)_2(15\text{-crown-}5)(OH_2)]$	10							2.62−3.02	2.9(2)	38
$[Pb(NCS)(15\text{-crown-}5)(\mu\text{-}NCS)_2]\text{-}$	8							2.74(1)−2.85(1)	2.81(5)	
$[Pb(NCS)(15\text{-crown-}5)]$	8							2.53(1)−2.82(2)	2.7(1)	42
$[Pb(benzo\text{-}15\text{-crown-}5)_2]\text{-}$	10							2.67(1)−2.77(1)	2.73(3)	
$[Pb(NO_3)_3(benzo\text{-}15\text{-crown-}5)]_2$	11			2.53(2)−2.809(8)	2.66(9)			2.829(8)−3.06(1)	2.94(3)	16
$[Pb(NO_3)_2(18\text{-crown-}6)]$	10			2.64(1)−2.72(1)	2.68(4)			2.724(8)−2.772(7)	2.76(2)	16
				2.65(2)−2.70(2)	2.68(2)			2.67(1)−2.770(9)	2.73(4)	33
$[PbI_2(18\text{-crown-}6)]$	8	3.17(1)	180					2.69(2)−2.81(2)	2.75(5)	45
$[PbCl(18\text{-crown-}6)][SbCl_6]$	7	2.504(1)						2.65(3)−2.83(3)	2.74(5)	34
$[Pb(NCS)(SCN)(18\text{-crown-}6)]$	8	2.987(3) (S)						2.687(7)−2.822(6)	2.74(5)	
		2.44(2) (N)	158.0(3)							47
$[Pb(18\text{-crown-}6)(NCCH_3)_3][SbCl_6]_2$	9	2.70(3) (N)						2.54(2)−2.79(3)	2.70(8)	34
$[Pb(CH_3CO_2)_2(18\text{-crown-}6)]\cdot 3H_2O$	10							2.867(7)−3.148(7)	3.00(9)	39
$[Pb(CCl_3CO_2)_2(18\text{-crown-}6)]\cdot 2CCl_3CO_2H$	10							2.75(1)−2.79(1)	2.76(2)	43
$[PbI_2(benzo\text{-}18\text{-crown-}6)]$	8	3.16(6)	174.24(2)					2.608(5)−2.759(5)	2.70(5)	36
[Pb(NO$_3$)$_2$(*cis*-*syn*-*cis*-dicyclohexyl-18-crown-6)]·CCl$_4$	10			2.57−2.83	2.70(9)			2.712−2.883	2.79(7)	40
[Pb(NO$_3$)$_2$(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)]·CHCl$_3$	10			2.68−2.75	2.72(4)			2.69(2)−2.89(1)	2.78(8)	41
[PbCl$_2$(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)]	8	2.776(2)	180					2.715(4)−2.876(4)	2.79(7)	44
[Pb(SCN)$_2$(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)]	8	2.925(3) (S)	180					2.662(4)−2.819(5)	2.73(7)	47
[Pb(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)(OH$_2$)$_2$][ClO$_4$]$_2$	8	2.522(6) (OH$_2$)	180					2.694(4)−2.743(4)	2.72(2)	36
$[HgX_2(EO4)]$										
X = Br	7	2.427(1)	167.02(7)			2.72(1)		2.69(1)−2.95(1)	2.8(1)	24
X = I	7	2.602(2)	166.06(4)			2.76(1)		2.770(9)−3.060(9)	2.9(1)	24
$[HgCl_2(EO5)]$	7	2.287(1)	171.2(2)			3.06(4)		2.74(1)−2.90(1)	2.80(7)	24
$[HgBr_2(EO5)HgBr_2]_2$										
Hg(1)	7	2.45(1)	170.2(1)			$2.88(2)_\mu$		2.69(2)−2.88(2)	2.76(7)	
Hg(2)	5	2.441(9)	153.4(1)			$2.70(2)_\mu$				24

$[HgCl_2(EO4R_2)]$										
R = Me	7	2.30(1)	174.2					2.78−2.96	2.84(7)	49
R = Et[c]	7	2.35	180					2.80−2.91	2.86(4)	50
$[HgBr_2(EO4R_2)]$										
R = $CH_2C_6H_4Br$	7	2.40(1)	174.4(1)					2.72(2)−3.06(1)	2.9(1)	51
$[(HgCl_2)_2(EO6R_2)]$										
R = Et	7	2.31(1)	175.9					2.66−2.91	2.8(1)	52
$[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4\cdot 2H_2O$	6					2.339(5)−2.377(4)	2.35(2)	2.400(5)−2.460(5)	2.43(2)	26
$[Cd_2Br_4(EO3)_2]$	7	2.59(2)				2.43(2)−2.62(2)	2.52(7)	2.44(2)−2.54(2)	2.50(4)	
		$2.72(4)_{\mu}$	171(1)							26
$[Cd(EO3)_2][CdI_4]$	8					2.306(8)−2.370(9)	2.34(2)	2.398(8)−2.472(8)	2.43(3)	26
$[Ba(NO_3)_2(EO5)]\cdot H_2O$	10			2.834(8)−2.884(7)	2.86(2)	2.771(6)−2.760(6)	2.766(6)	2.828(9)−2.852(8)	2.84(1)	36, 37
$[Ba(NO_3)_2(EO6)]$	11			2.843(5)−2.958(6)	2.89(5)	2.769(5)−2.887(6)	2.83(6)	2.854(5)−2.887(5)	2.87(1)	36, 37
$[Sr(EO3)_2]Cl_2$	8					2.523(7)−2.531(7)	2.526(6)	2.602(7)−2.605(7)	2.603(1)	35
$[Sr(EO4)_2]Cl_2\cdot 3H_2O$	10					2.626(4)−2.690(4)	2.67(3)	2.674(4)−2.767(4)	2.73(3)	35
$[Sr(EO4)_2]Cl_2$	10					2.625(4)−2.629(4)	2.627(2)	2.720(4)−2.763(4)	2.74(2)	35
$[Sr(OH_2)_3(EO5)]Cl_2$	9					2.626(5)−2.680(5)	2.65(3)	2.680(5)−2.740(5)	2.71(2)	35
$[Sr(OH_2)_2(EO6)]Cl_2\cdot H_2O$	9					2.572(6)−2.608(6)	2.59(2)	2.716(6)−2.741(6)	2.729(9)	35
$[Sr(NO_3)(EO3)_2][NO_3]$	10			2.699(7)−2.701(7)	2.70(1)	2.464(6)−2.692(7)	2.67(2)	2.663(7)−2.702(7)	2.69(2)	35
$[Sr(NO_3)_2(OH_2)(EO4)]$	10			2.652(7)−2.785(7)	2.71(5)	2.647(6)−2.672(6)	2.66(1)	2.655(6)−2.699(6)	2.67(2)	35
$[Sr(NO_3)_2(EO5)]$	10			2.654(6)−2.680(6)	2.67(1)	2.655(6)−2.679(5)	2.67(1)	2.676(5)−2.800(5)	2.74(5)	35
$[Sr(NO_3)_2(EO6)]$	10			2.615(7)−2.748(7)	2.67(5)		2.556(7)	2.678(7)−2.735(7)	2.71(2)	35

[a] This moiety resides on a center of inversion and the EO6 ligand is thus disordered. [b] O(3) is an alcoholic position in one disorder model and etheric in the other. [c] This structure is severely disordered. [d] This study.

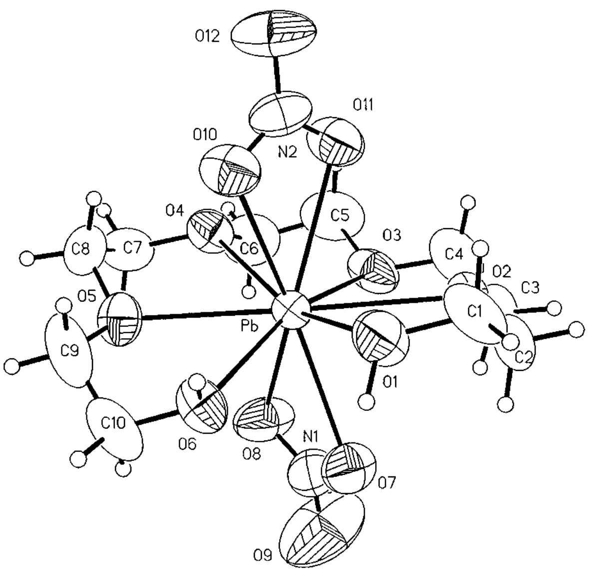

Figure 2. Side view of the $[Pb(NO_3)_2(EO5)]$ complex.

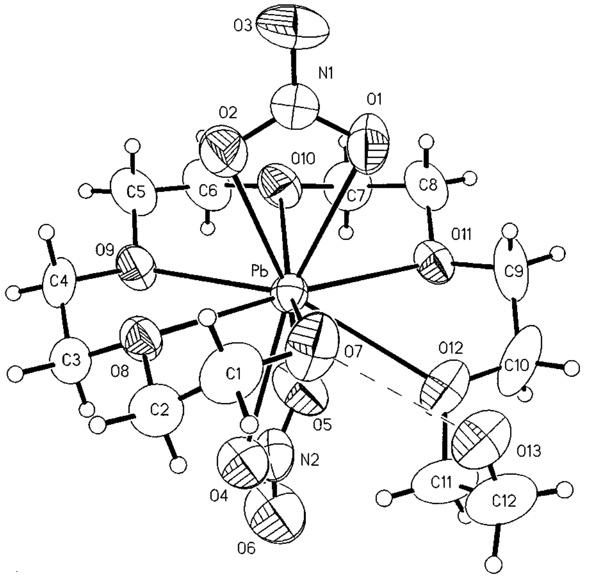

Figure 3. Thermal ellipsoid plot of the pseudocyclized EO6 in $[Pb(NO_3)_2(EO6)]$.

Å average) with the longest separations toward one end (O(11), O(12)) rather than in the middle as observed in $[Pb(NO_3)_2(EO4)]_n$ and $[Pb(NO_3)_2(EO5)]$. The *cis* O−Pb−O angles are almost identical (62.0(4)° average) up to the dangling end of the molecule where the smallest (O(11)−Pb−O(12) = 58.4(2)°) and largest (O(12)−Pb−O(7) = 66.4(2)°) are found.

The intermolecular hydrogen bond between O(13) and O(4) of a neighboring molecule creates hydrogen-bonded polymeric chains which propagate along *c*. The O(7)···O(13) and O(13)···O(4)A contacts are 2.72(1) and 2.84(1) Å, respectively.

$[PbBr(EO5)(\mu\text{-}Br)PbBr_2]\cdot H_2O$. The polymeric nature of this complex is depicted in Figure 4. A $[PbBr_3]_n$ polymer consisting of face-sharing octahedra propagates along the unit cell axis *a*. Two *trans* bromides in each Pb octahedron of the polymer (the Br(2) and Br(4) positions) are triply bridging, and each coordinates to one $[PbBr(EO5)]^+$ fragment (Pb(1) and Pb(2), respectively).

The polymeric chains are also held together by a complex hydrogen-bonding network involving the alcoholic EO5 termini and the water molecules. One alcoholic position in each glycol (O(6), O(7)) donates a hydrogen bond to the $[PbBr_3]_n$ polymer (Br(5)A and Br(6), respectively). The other alcoholic terminus

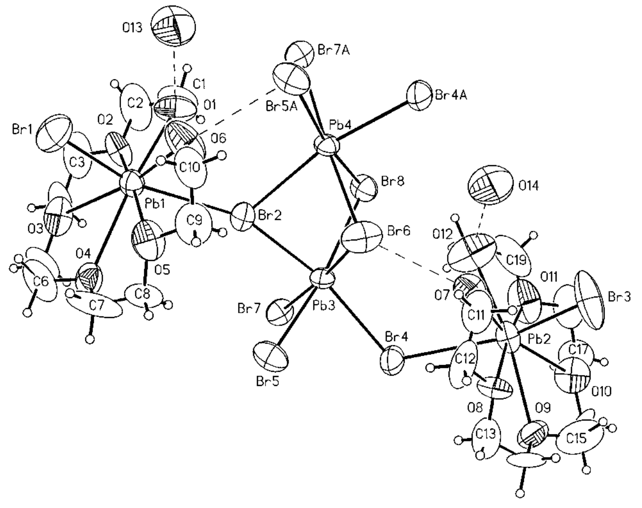

Figure 4. A portion of the polymeric [PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O. The symmetry code is $A = x - 1, y, z$.

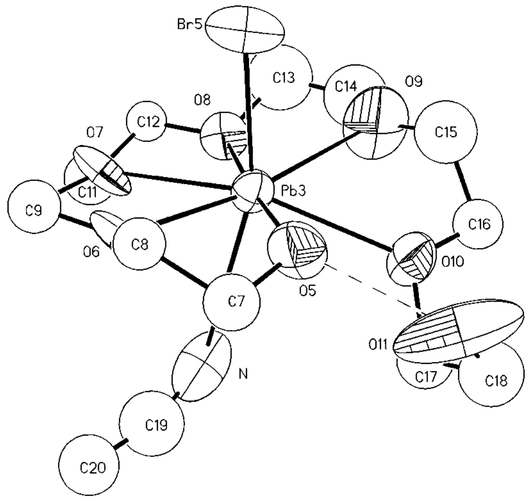

Figure 5. Top view of the eight-coordinate cation in [PbBr(NCMe)(EO6)]$_2$[PbBr$_2$(EO6)][PbBr$_3$]$_2$ showing the bent Br(5)−Pb(3)−N angle.

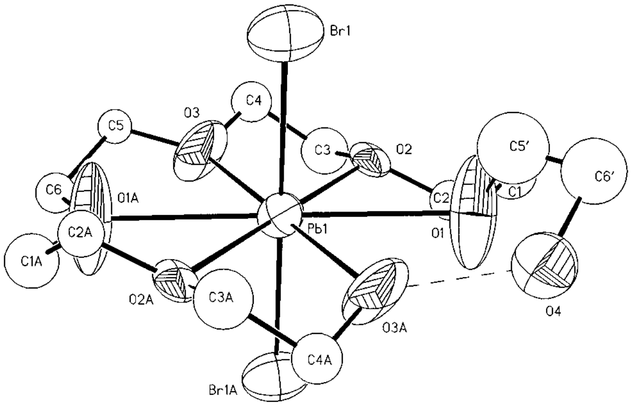

Figure 6. ORTEP plot of the neutral moiety in [PbBr(NCMe)(EO6)]$_2$[PbBr$_2$(EO6)][PbBr$_3$]$_2$. The symmetry code is $A = -x, 2 - y, -z$.

in each ligand (O(1), O(12)) donates a hydrogen bond to an uncoordinated water molecule (O(13), O(14)). The water molecules in turn donate one hydrogen bond to the [PbBr$_3$]$_n$ polymer (O(13) to Br(2)A; O(14) to Br(4)A) and one to the middle etheric oxygen (O(13) to O(4)A; O(14) to O(9)A) of the glycol related by a unit translation along *a*.

The eight-coordinate Pb(1) and Pb(2) geometries are severely distorted with the two *trans* bromides deviating from linearity by as much as 23.2°. (The Br(1)−Pb(1)−Br(2) and Br(3)−Pb(2)−Br(4) angles average 159(2)°.) The EO5 ligand wraps in nearly a template fashion around each metal center giving Pb(1) and Pb(2) approximate hexagonal-bipyramidal geometries. Each set of six oxygen donor atoms deviates as much as 0.47 Å out of their mean plane. The largest deviations from planarity are for O(3) and O(10), −0.43 and 0.47 Å, respectively. These positions are similarly bent away from the μ_3-Br positions with Br(2)−Pb(1)−O(3) = 116.0(5)° and Br(4)−Pb(2)−O(10) = 122.3(5)° angles. Both positions are surrounded by the expected torsion angles and are interestingly adjacent to the etheric sites accepting hydrogen bonds from the water molecules.

There is a wide range in Pb−O distances with the Pb−O$_{\text{alc}}$ separations ranging from 2.47(3) to 2.70(3) Å and averaging 2.59(8) Å. The Pb−O$_{\text{eth}}$ distances are longer, ranging from 2.72(3) to 2.92(2) Å, with a 2.80(7) Å average. In each case, the middle oxygens that accept a hydrogen bond (O(4), O(9)) exhibit the longest Pb−O distances. As observed in [Pb(NO$_3$)$_2$(EO5)], the six *cis* O−Pb−O angles involving the two longest (central) oxygen atoms (O(3), O(4); O(9), O(10)) are all less than 60° (58.4(8)°, average), the remainder average greater than 60° (63(2)°).

Both EO5 ligands have an identical conformation that is closely related to the symmetrical D_{3d} form of 18-crown-6. The O−C−C−O torsion angles alternate ±g and the C−O−C−C torsion angles are all anti.

The μ_3-Br distances to the glycol wrapped Pb(1) and Pb(2) are the longest of any of the Pb−Br separations in this compound, averaging 3.40(3) Å. The terminal Pb(1)−Br(1) and Pb(2)−Br(3) distances are the shortest, averaging 2.709(6) Å, and the Pb−Br bridging distances are asymmetric, ranging from 2.904(4) to 3.213(4) Å, with the two longest such interactions involving the Pb-μ_3-Br separations (Pb(3)−Br(4) = 3.213(4) Å; Pb(4)−Br(2) = 3.212(4) Å). The very long Pb-μ_3-Br separations and the deviation of the *trans* Br−Pb−Br angles from linearity could be indicative of a stereochemically active lone pair resulting from the strong covalent terminal Pb−Br bonds. However, it is difficult to further assess any potential stereochemical activity due to the lack of a vacant coordination site and the absence of consistent trends in the bonding parameters. Furthermore, perturbations of the Pb(1) and Pb(2) coordination geometries due to hydrogen-bonding interactions and the steric demands of the polymer backbone would obscure all but the most obvious effects.

[PbBr(NCMe)(EO6)]$_2$[PbBr$_2$(EO6)][PbBr$_3$]$_2$. The formula unit for this complex consists of two [PbBr(NCMe)(EO6)]$^+$ cations (Figure 5), one neutral [PbBr$_2$(EO6)] moiety (Figure 6), and an anionic [PbBr$_3$]$_{2n}$$^{2n-}$ polymer. Unlike [PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O, there are no interactions (not even hydrogen bonds) between the anionic polymer and the EO6 complexed Pb^{2+} moieties.

The anionic polymer consists of face-sharing octahedra that propagate along *c* and is similar to that in [PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O. The Pb−Br interactions in the polymer are all μ_2-bridging and range from 2.969(4) to 3.130(5) Å, averaging 3.05(6) Å.

The neutral [PbBr$_2$(EO6)] molecule resides on a crystallographic center of inversion, and the EO6 is consequently disordered. Pb(1) has a hexagonal-bipyramidal geometry with a terminal, axial Pb(1)−Br(1) distance of 2.982(6) Å, much longer than the terminal Pb−Br separations in the cation or in [PbBr(EO5)(μ-Br)PbBr$_2$]·H$_2$O. As observed in [Pb(NO$_3$)$_2$(EO5)], the EO6 ligand uses only six of its seven donors to coordinate Pb(1). The open end of the EO6 chain is between O(1) and O(3)A (related by a crystallographic inversion center) or between O(3) and O(1)A. Thus, the ethyl linkage (C(5)−

C(6)) and the corresponding terminal fragment (C(5)′, C(6)′, O(4)) are present at 50% occupancy.

The ligand pseudocyclizes via a hydrogen bond donated from O(3)A to O(4). O(4) in turn donates a hydrogen bond to Br(1) in a symmetry-related Pb(1) unit. The coordinated portion of the EO6 ligand mimics 18-crown-6 in its D_{3d} conformation, but the O(1)−C(5)′−C(6)′−O(4) angle of 131.0° is severely distorted from gauche, most likely due to the dangling nature of this portion of the glycol ligand. The oxygen atoms are planar to ±0.073 Å with such a small deviation from planarity possibly due to averaging of disordered positions. (Note the large thermal parameter distortion above and below the hexagonal plane for O(1).)

The $[PbBr(NCMe)(EO6)]^+$ cation exhibits interesting similarities and differences from the neutral moiety. The EO6 ligand again uses only six of seven donors to coordinate Pb(3), and it again pseudocyclizes by donating a hydrogen bond from the coordinated alcoholic terminus O(5) to the uncoordinated O(11). However, the conformation and coordination parameters of the ligands are different. O(5)−O(9) are planar to 0.18 Å, but O(10) and O(11) deviate 1.4 Å above this plane, which places O(11) into position to accept the hydrogen bond from O(5). The EO6 conformation deviates from that observed in the neutral moiety starting with the torsion angles from C(14)−O(9)−C(15)−C(16) onward. Both O(8)−C(13)−C(14)−O(9) and O(9)−C(15)−C(16)−O(10) are −g and C(14)−O(9)−C(15)−C(16) is distorted from anti at −107.8°. In addition, the C(16)−O(10)−C(17)−C(18) torsion angle is severely distorted from anti at 84.5°. Similar distortions in the EO6 molecule coordinated in the neutral $[PbBr_2(EO6)]$ are obscured by the disorder.

The terminal Pb(3)−Br(5) separation is short at 2.741(5) Å. The eight-coordinate geometry around Pb(3) is completed by a very long 3.09(4) Å contact to the nitrogen of an acetonitrile solvent molecule, with the N−Pb(3)−Br(5) angle compressed to 158.8(8)°. The overall geometry is a very distorted hexagonal bipyramid or a very distorted dodecahedron. The structure is similar to that observed for $[PbBr(EO5)(\mu\text{-Br})PbBr_2]\cdot H_2O$ where a bent Br−Pb−Br angle and one short and one long Pb−Br distance were observed.

The one $Pb(3)-O(5)_{alc}$ separation is 2.57(3) Å and the $Pb(3)-O_{eth}$ separations have a 0.17 Å range and average 2.70(7) Å. Three of these latter interactions are longer than the other two and all three long separations are on the same side (O(8)−O(10)).

It appears that the single covalent Pb−Br interaction results in a stereochemically active lone pair with its electron density contributing to the long, bent interaction with the solvent. In $[PbCl(18\text{-crown-}6)][SbCl_6]$,[34] the metal center is Ψ-hexagonal bipyramidal and Dehnicke and co-workers have concluded that the site presumably occupied by the lone pair electron density is vacant. Closer examination of the cell packing and distances to symmetry-related positions showed that each Pb center has three nearly equidistant Cl positions from an adjacent $SbCl_6^-$ anion (two at ∼3.8 Å and one at ∼3.9 Å) surrounding the proposed lone pair site. While these distances are at the limits of Pb−Cl bonds, they do occupy stereochemically significant positions surrounding the proposed lone pair site, a situation analogous to the Bi^{3+} structures we have previously characterized.[28,29] The location and significance of these Cl positions actually provides further evidence supporting the presence of the lone pair. The Pb−Cl separation is 2.510(7) Å and the Pb−O distances average 2.75(5) Å. In $[Pb(NCMe)_3(18\text{-crown-}6)][SbCl_6]_2$,[34] where there is no covalent Pb−X bond to activate the lone pair, three acetonitrile molecules coordinate Pb (two on one side of the crown ether and one opposite) at roughly equivalent distances (Pb−N = 2.70(3) Å, average). The Pb−O distances in this compound average 2.70(8) Å.

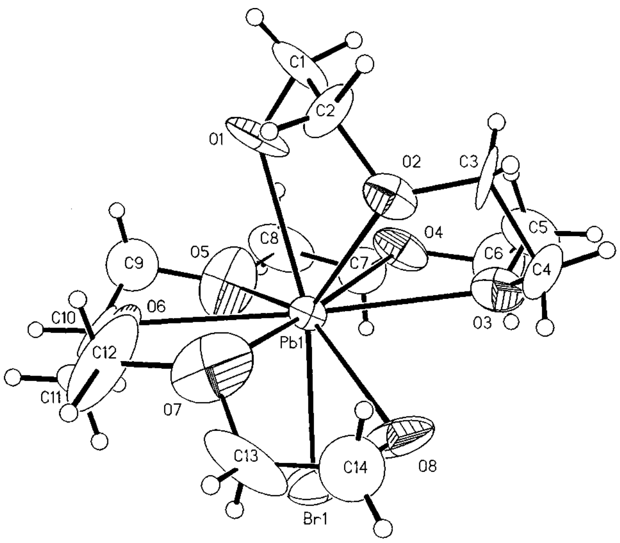

Figure 7. Coordination environment of the cation in $[PbBr(EO7)][PbBr_3]$.

[PbBr(EO7)][PbBr₃]. This polyether complex consists of an anionic $[PbBr_3]^-$ polymer and a PEG-wrapped $[PbBr(EO7)]^+$ cation (Figure 7). The anionic polymer propagates along the unit cell direction *c* and consists of face-sharing octahedra. Each bromine is bridging and the Pb(2)−Br(2−4) distances have a 0.314 Å range and average 3.1(1) Å. The only interaction between the cation and anionic polymer is a hydrogen bond donated from O(8) to Br(2). (The Pb(2)−Br(2) distance of 3.232(4) Å is the longest such interaction in this complex.) The other alcoholic terminus donates a hydrogen bond to Br(1) of a neighboring cation producing hydrogen-bonded polymeric chains of cations.

The geometry of the cation is distorted by the unusual (for Pb^{2+} structures) wrapping pattern of the EO7 ligand. The five oxygen atoms, O(3)−O(7), are planar to within 0.11 Å, while O(8) deviates 1.40 Å out of this plane. Both O(2) and O(1) are bent sharply upward to occupy coordination sites opposite the long Pb(1)−Br(1) separation of 2.926(4) Å. At the O(1), O(2) end of the ligand there are three consecutive gauche O−C−C−O torsion angles of like sign (C(1)−C(2), C(3)−C(4), C(5)−C(6)) and two nearly gauche C−O−C−C torsion angles. In addition, O(2) and O(3) exhibit the longest Pb(1)−O separations (2.85(2) and 2.80(3) Å, respectively).

There does not appear to be any activation of lone pair electron density. The terminal Pb(1)−Br(1) separation is longer than in $[PbBr(EO5)(\mu\text{-Br})PbBr_2]\cdot H_2O$ or the cation in $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$ (lone pair activity was noted in the latter), and the two Pb(1)−O distances opposite Br(1) are not unusually long. The Pb(1)−O(2) separation of 2.85(2) Å is the longest within the compound; however, this could easily be due to the strain associated with its dislocation toward an axial position. The $Pb(1)-O(1)_{alc}$ distance of 2.69(3) Å is statistically identical to the $Pb(1)-O(8)_{alc}$ separation of 2.70(3) Å. In the two instances where long Pb−Br distances and no stereochemically active lone pair were observed, the terminal bromine has accepted at least one hydrogen bond ($[PbBr(EO7)][PbBr_3]$ and the $[PbBr_2(EO6)]$ moiety in $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$).

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(34) von Arnim, H.; Dehnicke, K.; Maczek, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1704.

Discussion

An important part of the selective extraction of Pb^{2+} by crown ethers is the favorable complexation of the metal ion by the macrocycle resulting in the formation of a neutral, extractable species. In nitrate media, the latter is accomplished with two *trans* nitrate anions and the formation of complexes like $[Pb(NO_3)_2(18\text{-crown-}6)]$.[16,33] The suitability of this arrangement of ligands around Pb^{2+} is further demonstrated by $[Pb(NO_3)_2(EO5)]$ and $[Pb(NO_3)_2(EO6)]$. Despite utilizing flexible acyclic PEGs, essentially the same ligand conformation and Pb^{2+} coordination sphere are observed as in the 18-crown-6 complex. Even the pentadentate EO4 in $[Pb(NO_3)_2(EO4)]_n$ coordinates Pb^{2+} in an equatorial plane, although it cannot completely encircle the metal ion.

The ability of metal ions to arrange PEGs into crown ether-like conformations has also been observed in the structures of several $Sr(NO_3)_2$,[35] $Ba(NO_3)_2$,[36] $Ln(NO_3)_3$,[37] $Cd(NO_3)_2$,[36] and $Bi(NO_3)_3$,[28] complexes. In these complexes, the size of the metal ion generally asserts more influence on the structure than its Lewis acidity. By contrast, the hard/soft-acid/base characteristics of a metal ion come into play when the anion is a halide. We found the covalent pyramidal BiX_3 (X = Cl, Br) unit to control PEG coordination in a number of cases, forming pseudocyclic out-of-cavity crown ether-like complexes with stereochemically active lone pair electron density.[29] On the other hand, lanthanide halide complexes with PEGs show helical wrapping and are completely controlled by sterics.[37]

The three lead bromide/PEG structures reported here show striking similarities and unique differences. In two examples, $[PbBr(EO5)(\mu\text{-}Br)PbBr_2]\cdot H_2O$ and the cation in $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$, one terminal covalent Pb−Br bond appears to activate lone pair electron density. A stereochemically active lone pair was also observed opposite the axial Cl in $[PbCl(18\text{-crown-}6)][SbCl_6]$.[34] In two other examples, $[PbBr(EO7)][PbBr_3]$ and the $[PbBr_2(EO6)]$ moiety in $[PbBr(NCMe)(EO6)]_2[PbBr_2(EO6)][PbBr_3]_2$, the terminal Pb−Br distances were long and no stereochemically active lone pair was observed. The common feature is that, regardless of the type of Pb−Br interaction, the PEGs generally coordinate in an equatorial crown ether-like fashion.

Table 3 compares the average bonding parameters in these PEG complexes with several related Pb^{2+},[16,34,38−48] Hg^{2+},[24,49−52] Cd^{2+},[26] Ba^{2+},[36] and Sr^{2+} [35] complexes with PEGs and crown ethers. The $Pb-O_{eth}$ separations in Table 3 have a range of 0.62 Å, but despite coordination numbers ranging from 7 to 11 most cluster around 2.70−2.80 Å. The longest such distances involve carboxylate anions[38,43] or are anionic species, such as $[Pb(NO_3)_3(benzo\text{-}15\text{-crown-}5)]^-$.[16] The Ba−O and Sr−O separations bracket the average Pb−O distances with Ba^{2+} on the high end and clustered around 2.85 Å, and Sr^{2+} at the low end near 2.70 Å.

An interesting aspect of this work is the comparison of the lead halide/PEG complexes with the mercury halide/PEG structures. The effective ionic radius of Hg^{2+} is slightly smaller than Pb^{2+}, although the covalent nature of the linear X−Hg−X (X = Cl, Br, I) moiety increases the metal radius, which can affect PEG coordination. In 18-crown-6 complexes of Hg^{2+},[24] the O−C−C−O torsion angles expand to near 75° versus an average of 64° in Pb^{2+} complexes such as $[Pb(NO_3)_2(18\text{-crown-}6)]$.[16,33] When PEGs are complexed to Hg^{2+}, the torsion angle strain is relieved by the acyclic nature of PEGs, which results in successively longer (from the middle out) Hg−O separations. Even when there are available coordination sites, one end of the PEG ligand remains uncoordinated due to this effect. The $Hg-O_{eth}$ distances tend to have large ranges with averages clustering around 2.8−2.9 Å. The two EO5 complexes of Pb^{2+} exhibit opposite trends: all donors are coordinated and the M−O distances are longest in the middle of the chain, becoming shorter toward the two ends.

Table 3 shows the broad range in formulations, coordination numbers, and geometries in Pb^{2+}/polyether complexes. The majority of nitrate complexes have shown a preference for 10-coordination with the polyether wrapping the equatorial plane of the metal center. Achievement of a 10-coordinate geometry has been forced by inducing bridging interactions as in $[Pb(NO_3)_2(EO4)]_n$ or stoichiometric variations as in $[Pb(NO_3)(12\text{-crown-}4)_2][Pb(NO_3)_3(12\text{-crown-}4)]$ and $[Pb(L)_2][Pb(NO_3)_3(L)]_2$ (L = 15-crown-5, benzo-15-crown-5). The anions in the 15-membered macrocyclic complexes are 11-coordinate and this appears to be more favorable than steric unsaturation. The halide complexes primarily afford eight-coordinate complexes, even at the expense of foregoing potential donor interactions with the ether. The unifying theme in the halide and nitrate complexes is the pseudohexagonal bipyramidal geometries. The "pseudo" prefix is used because the bidentate nitrate complexes are formally 10-coordinate, however, a useful description of the geometries is hexagonal bipyramidal. This geometric arrangement has been observed in many of the complexes listed in Table 3 and appears to be a favored geometry in higher coordinate Pb^{2+} complexes.

Conclusions

Small-chain PEGs can wrap $Pb(NO_3)_2$ equatorially mimicking crown ethers and producing extractable species. Nazarenko demonstrated that PEGs can be fairly effective extractants for lead and indicated that their selectivity may be greater than those of crown ethers.[53,54] The structural results presented here would indicate that any selectivity would be the result of the appropriate size of Pb^{2+} for the five-membered Pb−O−C−C−O− chelate rings. The cyclic nature of crown ethers produces some strain when coordinated to Pb^{2+} which is relieved when the acyclic PEGs are utilized.

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(35) Rogers, R. D.; Jezl, M. L.; Bauer, C. B. *Inorg. Chem.* **1994**, *33*, 5682.
(36) Rogers, R. D.; Bond, A. H.; Bauer, C. B., unpublished results, 1996.
(37) Rogers, R. D.; Bauer, C. B. In *Molecular Recognition: Receptors for Cationic Guests*; Gokel, G. W., Ed.; *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Elsevier: Amsterdam, Vol. I, pp 315−355.
(38) Malinovskii, S. T.; Simonov, Y. A.; Nazarenko, A. Y. *Kristallografiya* **1992**, *37*, 90.
(39) Shin, Y.-G.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Polyhedron* **1993**, *12*, 1453.
(40) Krasnova, N. F.; Simonov, Y. A.; Dvorkin, A. A.; Korshunov, M. B.; Yakshin, V. V.; Malinovskii, T. I. *Izv. Akad. Nauk Mold. SSR, Ser. Fiz.-Tekh. Mat. Nauk* **1984**, 63.
(41) Krasnova, N. I.; Simonov, Y. A.; Korshunov, M. B.; Yakshin, V. V. *Kristallografiya* **1987**, *32*, 499.
(42) Brügge, H. J.; Fölsing, R.; Knöchel, A.; Dreissig, W. *Polyhedron* **1985**, *4*, 1493.
(43) Malinovskii, S. T.; Simonov, Y. A.; Nazarenko, A. Y. *Kristallografiya* **1990**, *35*, 1410.
(44) Nazarenko, A. Y.; Rusanov, E. B. *Pol. J. Chem.* **1994**, *68*, 1233.
(45) Nazarenko, A. Y.; Kronikovski, O. I.; Fonari, M. S.; Kravtsov, V. C.; Simonov, Y. A.; Malinovski, T. J. *Supramol. Chem.* **1995**, *4*, 259.
(46) Nicholson, D. G.; Sylte, I.; Vasudevan, A. K.; Sæthre, L. J. *Acta Chem. Scand.* **1992**, *46*, 358.
(47) Nazarenko, A. Y.; Rusanov, E. B. *Polyhedron* **1994**, *13*, 17.
(48) von Arnim, H.; Dehnicke, K.; Maczek, K.; Fenske, D. *Z. Naturforsch.* **1993**, *48b*, 1331.
(49) Iwamoto, R. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1114.
(50) Iwamoto, R. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1118.
(51) Weber, G. *Acta Crystallogr., Sect. B* **1980**, *36*, 2779.
(52) Iwamoto, R. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1123.
(53) Nazarenko, A. Y.; Pyatnitskii, I. V. *Zh. Neorg. Khim.* **1987**, *32*, 1006.
(54) Nazarenko, A. Y.; Kronikovskii, O. I.; Sukhan, V. V. *Zh. Neorg. Khim.* **1987**, *32*, 2233.

One aspect of Pb^{2+} chemistry, which will affect the separations of this ion, is its stereochemical lone pair activity. In the structures reported here, lone pair activity is absent in the nitrate complexes as expected from the lack of covalent interactions with the metal ion. Formation of covalent Pb−X bonds, on the other hand, does activate the lone pair. In the design of a separation process for Pb^{2+}, choice of extractant and choice of anion should keep this in mind.

The structural results indicate that EO5 is the most appropriate choice of PEG for Pb^{2+} complexation. The six oxygen donors can arrange themselves in a nearly hexagonal equatorial plane leaving two axial sites for anion coordination. Longer chains either leave one end dangling or force unusual coordination geometries which leave no room for anion coordination. Smaller chains result in coordinative unsaturation which must be filled with solvent or bridging ligands.

Lead(II) halides are capable of forming interesting coordination polymers in the solid state. It appears from the results presented here that PEGs may be useful in mediating the formation of these polymers. (We have found a similar effect in Cd(II) halide/PEG complexes.[27]) Given the current high level of interest in inorganic coordinating polymers, the use of crown ethers and PEGs to control polymer formation and produce novel polymers should be studied further.

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Supporting Information Available: Listings of full crystallographic details, bond distances and angles, torsion angles, fractional coordinates, hydrogen atom locations, and anisotropic thermal parameters (60 pages). Ordering information is given on any current masthead page.

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