Formation and Structure of the Novel Heptanuclear Lead(II) Oxo Cluster $[Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu_3\text{-}OMe)_4(\mu_2\text{-}I)_4]I_2$ with an Unprecedented Cage Structure

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A novel lead(II) cluster $[Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu_3\text{-}OMe)_4(\mu_2\text{-}I)_4]I_2$ (**1**) has been isolated from the reaction mixture of PbI_2 and pyrazine in DMF/MeOH solvent with a reasonable yield (46%). The X-ray crystallography shows that **1** exhibits a novel unprecedented cage structure with centered μ_3-O and μ_4-O atoms and four different coordination environments of lead atoms. It is the first structurally characterized example of a lead compound containing bridging oxo, methoxide and iodide ligands. Compound **1** crystallizes in the tetragonal space group $P42_1m$, $a = b = 11.7768(13)$, $c = 9.8606(16)$ Å, $Z = 2$, $V = 1367.6(3)$ Å^3.

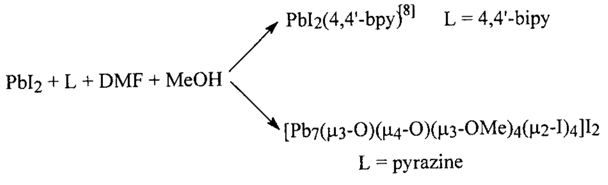
Introduction

Lead(II) alkoxides and oxo alkoxides have been extensively studied for their uses as molecular precursors to lead-containing metal oxide materials via chemical routes such as MOCVD and sol-gel processes.[1] There has been much research interest focused on the synthesis and spectroscopic characterization of lead alkoxide and oxoalkoxide complexes. However, only a limited number of crystal structures have been reported for lead alkoxides and oxoalkoxides. These include oxygen-free, monomeric, trimeric, and one-dimensional $Pb(OR)_2$ (R = 2,6-di-*tert*-butyl-4-methylphenyl,[2] *t*Bu,[3] *i*Pr,[3] and CH_2CH_2OMe[3]), and two oxygen-centered, regular polyhedral clusters $[Pb_4(\mu_4\text{-}O)(OSiPh_3)_6]$[4] and $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OiPr)_4]$.[5] Sita and coworkers[6] recently reported a novel lead(II) oxoalkoxide cluster $[Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu_2\text{-}OSiMe_3)_{10}]$ containing $Pb_4(\mu_4\text{-}O)$ and $Pb_3(\mu_3\text{-}O)$ units. Obviously the structures of lead alkoxides are highly dependent on the R groups and the method of preparation.

We have recently become interested in the construction of supramolecular structures using PbX_2 as the building blocks and have reported a novel 2-D coordination polymer $[PbI_2(4,4'\text{-bpy})]$ from the reaction of 4,4-bipyridine and PbI_2 in DMF/MeOH.[7] We intended to extend this chemistry from 4,4-bipyridine to pyrazine with the expectation of preparing a similar PbI_2 complex containing pyrazine ligands. We were surprised that the mixture of PbI_2 and pyrazine in MeOH/DMF gave a cluster complex $[Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu_3\text{-}OMe)_4(\mu_2\text{-}I)_4]I_2$ (**1**) reproducibly in 46% isolated yield, which contains bridging oxo, methoxide and iodide ligands. Lead(II) dimethoxide has been reported previously, although it was only poorly characterized due to its low solubility and air- and moisture-sensitivity.[8] To the best of our knowledge, there have been no lead oxomethoxide complexes reported in the literature. Herein we report the preparation of the unusual heptanuclear lead oxo cluster **1** and its unprecedented cage structure.

Results and Discussion

The syntheses of **1** and our previously reported cluster are summarized in Scheme 1, indicating how different products can be isolated by varying the ligand from 4,4-bipyridine to pyrazine. The formation of **1** can be rationalized as follows. As the basicity of pyrazine is greater than that of 4,4′-bipyridine, pyrazine could act as a stronger proton acceptor than 4,4-bipyridine in abstracting the proton of MeOH and H_2O and enhance coordination between lead(II) and the oxo and methoxide ligands. The low solubility of **1** might also favor its isolation from solution. A nitrogen-containing heterocyclic ligand plays a similar role in the preparation of transition metal clusters, for example $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$,[9] which was isolated from $FeF_3{\cdot}3H_2O$ and pyridine in MeOH.



Scheme 1

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Compound **1** is insoluble in common organic solvents, which prevents its characterization in solution. The crystal structure of **1** was determined by X-ray crystallography. A labeled ORTEP diagram of the cluster cation of **1** is shown in Figure 1 and bond lengths and bond angles are listed in Table 1. The structure of the cluster **1** exhibits C_{2v} symmetry with a C_2 axis through Pb(3), O(3) and O(1). There are four symmetrically different sets of lead atoms which vary in the type and number of coordinated ligands. The pyramidal Pb(2) and Pb(2A) are three-coordinate with one μ_4-O and two μ_3-OMe ligands, while Pb(1) and Pb(1A) are in an inverted square-pyramidal configuration surrounded by one μ_4-O, one μ_3-O, and two μ_3-OMe ligands. More interesting is the mixed coordination environment around Pb(4) and Pb(4A), and Pb(3). Pb(4) and Pb(4A) are coordinated by two μ_3-OMe and two iodide ligands, and the unique Pb(3) is in an inverted square pyramidal I_4O environment. The coordination spheres of all four Pb atoms in **1** are strongly distorted as a result of the presence of the stereochemically active $6s^2$ lone-pair electrons on the Pb^{II} cations. The Pb−O bond lengths fall into three different categories depending on the environments of the O atoms. The mean bond lengths of Pb-(μ_3-O), Pb-(μ_4-O), and Pb−OMe are 2.20(3), 2.28(2), 2.439(17) Å, respectively. The Pb−I bond lengths of 3.198(2)−3.302(3) Å are normal.[10−12] *The cage structure of **1** can also be viewed as being built-up from a $Pb_4(\mu_4\text{-}O)$ unit bonded to Pb(4), Pb(4A) and Pb(3) through four μ_3-OMe groups, a μ_3-O and four iodide atoms. The μ_4-O(1) atom tetrahedrally bridges Pb(2), Pb(2A), Pb(1), and Pb(1A). The planar μ_3-O is surrounded by Pb(1), Pb(1A) and Pb(3). A similar three-coordinate planar configuration has been observed in the lead(II) thiolate cluster $[Pb_5O(SR_F)_8]\cdot 2C_7H_8$ [R_F = 2,4,6-trsi(trifluromethylphenyl)].[13]

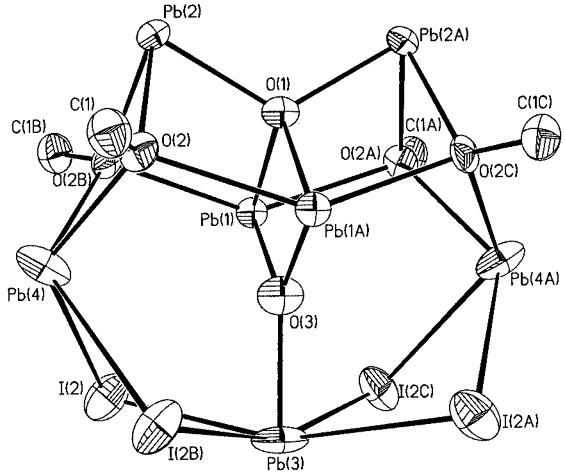

Figure 1. The ORTEP diagram of cluster cation of **1**

The Pb^{II} atoms of the cluster cation are involved in weak interactions with the anion I^- as shown in Figure 2, where each I^- anion links three cationic clusters to form an extensive three-dimensional supramolecular assembly through the six weak interactions [I(1)···Pb(1a)(1 − *y*, *x* − 1, 1 − *z*), 3.63(2); I(1)···Pb(2), 3.68(2); I(1)···Pb(2a) (*y*, 1 − *x*, 1 − *z*), 3.49(2); I(1)···Pb(2b) (1 − y, −1 + *x*, 1 − *z*), 3.49(2); I(1)···Pb(3a) (*y*, 1 − *x*, 1 − *z*), 4.01(2) and I(1)···Pb(4), 3.48(2) Å].

Table 1. Crystal data and structure refinement for **1**

Empirical formula	$C_4H_{12}I_6O_6Pb_7$
Formula mass	2367.94
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Tetragonal, $P42_1m$
Unit cell dimensions	a = 11.7768(13) Å, α =90° b = 11.7768(13) Å, β = 90° c = 9.8606(16) Å, γ = 90°
Volume (Å^3)	1367.6(3)
Z	2
Calculated density (Mg/m^3)	5.750
Absorption coefficient (mm^{-1})	49.712
F(000)	1952
Crystal size (mm)	0.011 × 0.009 × 0.009
θ range for data collection (°)	2.07 to 26.02
Limiting indices	$-14 \le h \le 7$, $-14 \le k < 14$, $-12 \le l \le 12$
Reflections collected	9808
Independent reflections	837 (R_{int} = 0.0684)
Absorption correction	Empirical
Max. and min. transmission	0.639 and 0.590
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	837/24/65
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0420, wR_2 =0.1008
Largest diff. peak and hole (e·Å^{-3})	2.824 and −2.724

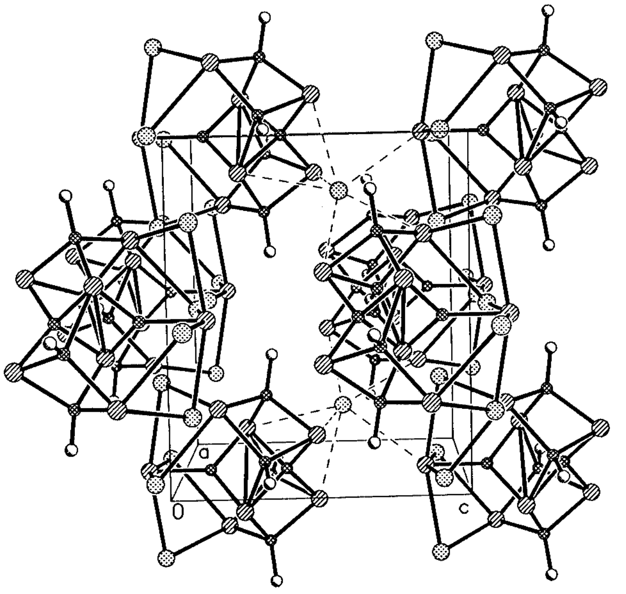

Figure 2. The cell packing of the crystal structure of **1** showing the weak interactions

Conclusions

In summary, a novel heptanuclear lead(II) cluster **1** has been isolated and characterized by X-ray crystallography.

Table 2. Bond lengths [Å] and angles [°] for **1** (symmetry transformations used to generate equivalent atoms: A: $-x + 2$, $-y + 1$, z; B: $y + 1/2$, $x - 1/2$, z; C: $-y + 3/2$, $-x + 3/2$, z)

Pb(1)−O(3)	2.22(2)	Pb(3)−I(2)	3.198(2)
Pb(1)−O(1)	2.34(2)	Pb(3)−I(2B)	3.198(2)
Pb(1)−O(2A)	2.565(17)	Pb(4)−O(2B)	2.417(18)
Pb(1)−O(2B)	2.565(17)	Pb(4)−O(2)	2.417(18)
Pb(1)−Pb(1A)	3.632(3)	Pb(4)−I(2B)	3.302(3)
Pb(2)−O(1)	2.240(16)	Pb(4)−I(2)	3.302(3)
Pb(2)−O(2)	2.336(17)	O(1)−Pb(2A)	2.240(16)
Pb(2)−O(2B)	2.336(16)	O(1)−Pb(1A)	2.34(2)
Pb(3)−O(3)	2.16(4)	O(2)−C(1)	1.48(3)
Pb(3)−I(2C)	3.198(2)	O(2)−Pb(1A)	2.565(17)
Pb(3)−I(2A)	3.198(2)	O(3)−Pb(1A)	2.22(2)
O(3)−Pb(1)−O(1)	74.2(10)	O(2)−Pb(4)−I(2B)	81.7(4)
O(3)−Pb(1)−O(2A)	93.2(5)	O(2B)−Pb(4)−I(2)	81.7(4)
O(1)−Pb(1)−O(2A)	71.7(4)	O(2)−Pb(4)−I(2)	129.3(4)
O(3)−Pb(1)−O(2B)	93.2(5)	I(2B)−Pb(4)−I(2)	82.44(9)
O(1)−Pb(1)−O(2B)	71.7(4)	Pb(3)−I(2)−Pb(4)	85.90(7)
O(2A)−Pb(1)−O(2B)	139.4(7)	Pb(2)−O(1)−Pb(2A)	120.3(14)
O(1)−Pb(2)−O(2)	77.9(7)	Pb(2)−O(1)−Pb(1A)	108.28(16)
O(1)−Pb(2)−O(2B)	77.9(7)	Pb(2A)−O(1)−Pb(1A)	108.28(16)
O(2)−Pb(2)−O(2B)	75.4(9)	Pb(2A)−O(1)−Pb(1)	108.28(16)
O(3)−Pb(3)−I(2C)	80.78(5)	Pb(2)−O(1)−Pb(1)	108.28(16)
O(3)−Pb(3)−I(2A)	80.78(5)	Pb(1A)−O(1)−Pb(1)	101.8(12)
I(2C)−Pb(3)−I(2A)	85.75(8)	C(1)−O(2)−Pb(2)	122.9(15)
O(3)−Pb(3)−I(2)	80.78(5)	Pb(2)−O(2)−Pb(4)	103.5(7)
I(2C)−Pb(3)−I(2)	91.31(9)	C(1)−O(2)−Pb(1A)	107.1(15)
I(2A)−Pb(3)−I(2)	161.57(10)	Pb(2)−O(2)−Pb(1A)	98.4(6)
O(3)−Pb(3)−I(2B)	80.78(5)	Pb(4)−O(2)−Pb(1A)	109.1(6)
I(2C)−Pb(3)−I(2B)	161.57(10)	C(1)−O(2)−Pb(4)	114.2(15)
I(2A)−Pb(3)−I(2B)	91.31(9)	Pb(3)−O(3)−Pb(1)	125.1(7)
I(2)−Pb(3)−I(2B)	85.75(8)	Pb(3)−O(3)−Pb(1A)	125.1(7)
O(2B)−Pb(4)−O(2)	72.4(8)	Pb(1)−O(3)−Pb(1A)	109.8(15)
O(2B)−Pb(4)−I(2B)	129.3(4)		

The isolation of **1** implies that a suitable choice of base and alkoxide ligand could lead to the formation of novel mixed-coordinate lead clusters.

Experimental Section

Materials and Methods: All chemicals are commercially available and were used without further purification, except PbI_2, which was prepared by the reaction of PbO with HI 35%. C, H and N analyses were carried on a Perkin−Elmer 240C elemental analyzer. IR spectra were recorded on a Bruker Optik Gmbh spectrophotometer (range: 400−4000 cm^{-1}) as KBr pellets.

Preparation of 1: Single crystals of **1** were grown at room temperature by using a layered solution approach. The bottom solution layer, contained within a long straight tube, consisted of PbI_2 (0.239 g, 0.5 mmol) dissolved in DMF. A mixed-solvent layer of methanol/DMF (1:1) was carefully placed on top of the PbI_2 solution using a syringe. Finally, pyrazine (a stoichiometric quantity relative to the PbI_2) dissolved in methanol was added to the top of the buffer. As the layers slowly mixed, well-formed crystals of **1** appeared that were suitable for X-ray single-crystal analysis. Yield 77.8 mg, 46% (based on PbI_2). $C_4H_{12}I_6O_6Pb_7$ (2368.0): calcd. C, 2.03, H 0.51; found C 2.22, H 0.63. IR (KBr): $\tilde{\nu}$ = 603.86 cm^{-1} (vs), 682.04 (m), 750.83 (w), 838.09 (w), 1401.10 (s), 1608.43 (m).

X-ray Crystallographic Analysis: X-ray data were collected at 293 K on a Bruker Apex CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.7103Å) by using the $\theta/2\theta$ scan mode. An empirical absorption correction was applied to the data, and structure solution and refinement on F^2 were done. The structures were solved by direct methods by using SHELXS 97[14] and refined by full-matrix least-squares calculation on F^2 with SHELXL 97.[15] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Crystal data, data collection parameters, and refinement statistics for **1** are listed in Table 1. Relevant bond lengths and bond angles for **1** are collected in Table 2.

CCDC-184695 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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