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Article

Structural Effects of the Lone Pair on Lead(II), and Parallels with the Coordination Geometry of Mercury(II). Does the Lone Pair on Lead(II) Form H-Bonds? Structures of the Lead(II) and Mercury(II) Complexes of the Pendant-Donor Macrocycle DOTAM (1,4,7,10-Tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane)

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The synthesis and structures of [Pb(DOTAM)]$(ClO_4)_2$·$4.5H_2O$ (**1**) and [Hg(DOTAM)]$(ClO_4)_2$·$0.5CH_3OH$·$1.5H_2O$ (**2**) are reported, where DOTAM is 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane. Compound **1** is triclinic, space group $P\bar{1}$, $a = 12.767(3)$ Å, $b = 13.528(2)$ Å, $c = 18.385(3)$ Å, $\alpha = 101.45(2)°$, $\beta = 93.32(2)°$, $\gamma = 90.53(2)°$, $Z = 4$, $R = 0.0500$. Compound **2** is monoclinic, space group *Cc*, $a = 12.767(3)$ Å, $b = 13.528(2)$ Å, $c = 18.385(3)$ Å, $\beta = 101.91(2)°$, $Z = 4$, $R = 0.0381$. The Pb(II) ion in **1** has an average Pb–N = 2.63 Å to four N-donors from the macrocyclic ring, and four O-donors (average Pb–O = 2.77 Å) from the amide pendant donors of the macrocycle, with a water molecule placed with Pb–O = 3.52 Å above the proposed site of the lone pair (Lp) on Pb. The Hg(II) in **2** appears to be only six-coordinate, with four Hg–N bond lengths averaging 2.44 Å, and two Hg–O from pendant amide donors at 2.41 Å. The other two amide donors appear to be noncoordinating, with Hg–O distances of 2.74 and 2.82 Å. A water situated 3.52 Å above the proposed site of the lone pair on Pb(II) in **1** is oriented in such a way that it might be thought to be forming a Pb–Lp···H–O–H hydrogen bond. It is concluded that that this is not an H-bond, but that the presence of the lone pair allows a closer approach of the hydrogens to Pb than would be true otherwise. The structural analogy in the VSEPR sense between Pb(II), which has the $5d^{10}6s^2$ outer electron structure, and the Hg(II) ion, which has the $5d^{10}$ structure, is examined. The tendency of Hg(II) toward linear coordination, with two short Hg–L bonds (L = ligand) at 180° to each other, and other donor groups at roughly 90° to this and at much longer bond distances, is paralleled by Pb(II). One of the short Hg–L bonds is replaced in the Pb(II) structures by the lone pair (Lp), which is opposite the short Pb–L bond, or in some cases 2–4 shorter Pb–L bonds.

Introduction

The structural effects of the lone pair of electrons in heavy post-transition elements such as Sn(II), Pb(II), and Bi(III), the “inert pair”, have been a subject of interest over the past few years. Some of the present authors have examined the lone pair in Pb(II),[1−3] and attempted to rationalize the structural effects. Several factors have become apparent through this work, and the work of many other authors, of whom a few are mentioned[4−13] of relevance to the discussion

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here. Mercury(II) is of interest[3] in that it is electronically equivalent in a VSEPR[14] (valence shell electron pair repulsion) sense to Pb(II) without the lone pair of electrons on it. Hg(II) has the $5d^{10}$ level as its outermost filled electronic level, while Pb(II) has the $5d^{10}6s^2$ structure. The pair of electrons in the $6s^2$ orbital of Pb(II) thus produces the steric effects in the VSEPR sense in relation to the structure of Hg(II) complexes. The structural chemistry of Hg(II) is dominated by its tendency to form linear complexes. This is usually true even when, superficially, the coordination number appears, for example, to be eight. Thus, in a typical complex such as the Hg(II) oxalato complex,[15] each Hg(II) is surrounded by eight oxygens from bridging oxalate groups. However, two of the Hg−O bonds, at an angle of 172° to each other (ideally 180°), involve short distances of 1.99 and 2.17 Å, while the six bonds at approximately right angles to these two short bonds are much longer, ranging from 2.62 to 2.85 Å. Only with very ionic bonding, such as in the $[Hg(NO_3)_4]^{2-}$ cation,[16] is there anything like regular eight coordination, although even here the four-membered chelate rings formed by the nitrates are somewhat asymmetric, with pairs of Hg−O bonds in each chelate ring that differ by about 0.1 Å. In contrast to Hg(II), the Pb(II) ion can be regarded[3] as having a tendency to form a linear complex where one of the coordination sites, in line with VSEPR theory, is occupied by the lone pair of electrons. At right angles to this linear structure are then much longer bonds, as found for Hg(II), with the difference that these Pb−L (L = ligand) bonds become even longer as the donor atoms are placed nearer to the lone pair. Pb(II) structures can range from those where the lone pair appears to have no steric effects, i.e., be sterically inactive or holodirected, to use the terminology of Glusker et al.,[11] or can show steric effects, and be hemidirected. In the holodirected case, all the Pb−L bonds are of intermediate length, and there are no marked differences in the Pb−L bond lengths, once corrected for differences in ionic radii of the donor atoms. In the hemidirected case, the characteristics of the sterically active lone pair are that (1) the Pb−L bonds on the side of the Pb away from the proposed site of the lone pair are shorter than in the rest of the complex, and may be unusually short for a Pb−L bond of that type; (2) there may be a gap in the coordination geometry at the site of the lone pair, or very long Pb−L bonds at this site, and (3) the Pb−L bonds become progressively longer as one moves from the site opposite the lone pair, to the position of the lone pair.

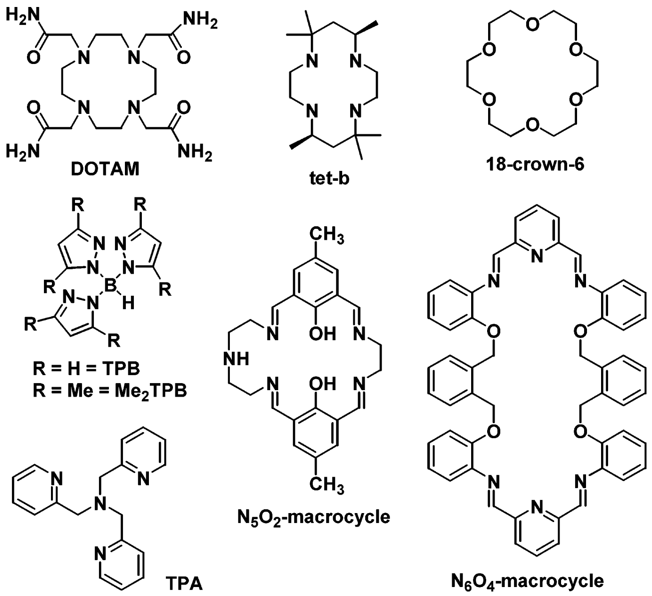

Figure 1. Ligands discussed in this paper.

Glusker et al.[11] have carried out wave-mechanical calculations on Pb(II) complexes that agree with the empirical observation that Pb(II) complexes with oxygen donor ligands and high coordination number are more likely to be holodirected, while hemidirected complexes are more likely to be of low coordination number and involve nitrogen or carbon donor ligands. The parallel between Hg(II) and Pb(II) is seen in that Hg(II) complexes that have higher coordination numbers with no sign of linearity tend to be oxygen donor complexes such as $[Hg(NO_3)_4]^{2-}$, which display the maximum coordination number for Hg(II) of eight. The tendency of metal ions in the vicinity of Au in the periodic table to linear coordination, or retention of a pair of electrons in the 6s orbital, is related[17] to relativistic effects, which are at a maximum at Au(I), and fall off rapidly as one moves away from Au. Thus, the low energy of the 6s orbital leads to a large energy difference between it and the 6p orbitals, making the formation of an sp^3 hybrid difficult. In addition, large spin−orbit coupling effects[17] split the 6p subshell into two levels, further inhibiting the formation of an sp^3 hybrid. Therefore, the tendency to form an sp hybrid and produce linear coordination is at a maximum at Au(I). There may also be a contribution from hybridization with the $5d_{z^2}$ orbital that results in linear coordination geometry. Relativistic effects are stronger in Hg(II) than Pb(II), reflected in the greater tendency of Hg(II) toward linear coordination geometry than that for Pb(II) in analogous environments to display a stereochemically active lone pair.

Reported here are the structures of the Hg(II) and Pb(II) complexes of DOTAM (see Figure 1 for structures of ligands). The Pb(II) DOTAM complex displays a sterically active lone pair, i.e., is hemidirected. Of interest is a water molecule situated directly above the proposed site of the lone

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pair that appears from the orientation of the H-atoms possibly to be H-bonded via one of its hydrogens to the lone pair. It is considered whether this really might represent a Pb···H−O−H H-bond. The structure of the Hg(II) complex of DOTAM is considered in relation to the coordination geometry around the Hg(II), and how this relates to the Pb(II) structure.

Experimental Section

Materials. The ligand DOTAM was synthesized as described previously.[18]

Synthesis of [Pb(DOTAM)]$(ClO_4)_2$·4.5H_2O (1). (Compound **1** can be described as 1,4,7,10-tetrakis (carbamoyl-methyl)-1,4,7,10-tetraazacyclododecane lead(II) perchlorate hydrate.) DOTAM (0.2413 g; 0.594 mmol) was dissolved in methanol (25 mL) and refluxed. A solution of $Pb(ClO_4)_2$ (0.2413 g; 0.594 mmol) in methanol (6 mL) was added dropwise, and the refluxing continued for 2 h. The solution was allowed to cool, and ethanol (30 mL) was added. The mixture was stirred overnight at room temperature. A white precipitate slowly appeared, and was filtered off and washed twice with ethanol (15 mL). The crystalline material was then dried under reduced pressure. Anal. Calcd for $C_{16}H_{32}N_8O_8PbCl_2$·4.5H_2O: C, 23.31%; H, 4.16%; N, 13.59%. Found: C, 23.31%; H, 4.19%; N, 13.41%. **CAUTION:** Organic perchlorates may present an explosion hazard.

Synthesis of [Hg(DOTAM)]$(ClO_4)_2$·0.5CH_3OH·1.5H_2O (2). (Compound **2** can be described as 1,4,7,10-tetrakis (carbamoyl-methyl)-1,4,7,10-tetraazacyclododecane mercury(II) perchlorate.) DOTAM (0.2797 g; 0.698 mmol) was dissolved in 80% methanol (20 mL) and refluxed. A solution of $Hg(ClO_4)_2$·3H_2O (0.350 g; 0.772 mmol) in methanol (6 mL) was added dropwise, and the refluxing continued for 2 h. The solution was allowed to cool, and a white precipitate appeared and was filtered off and washed twice with ethanol (20 mL). The complex was then dried under reduced pressure.

Anal. Calcd for $C_{16}H_{32}N_8O_8HgCl_2$·0.5CH_3OH·1.5H_2O: C, 23.51%; H, 4.42%; N, 13.29%. Found: C, 23.57%; H, 4.09%; N, 13.15%. **CAUTION:** Organic perchlorates may present an explosion hazard.

Molecular Structure Determination. Mounted crystals of **1** and **2** were placed in a cold nitrogen stream (Siemens LT-2) maintained at −80 °C. A Siemens P4 four-circle diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the XSCANS software suite.[19] The structure was solved by Patterson synthesis, and refined to convergence.[20] Crystal coordinates and details of the structure determinations of **1** and **2** have been deposited with the CSD.[21]

Results and Discussion

The structures of the cationic complexes of **1** and **2** are seen in Figures 2 and 3. Details of the structure determinations are given in Table 1, and selected bond lengths and angles for **1** and **2** are given in Tables 2 and 3. Structure **1** contains two distinct Pb(II) DOTAM individuals, which are similar, except that in one there is a water molecule placed 3.52 Å above the putative site of the lone pair, while in the other there is an amide nitrogen in the same position at a distance of 4.1 Å. Both of these structures appear to have sterically active lone pairs. Indications of this are the following: (1) The Pb−L bonds located over the proposed position of the lone pair are very long. Thus, Pb(1)−O(29) = 3.52 Å in one individual, while the closest approach to Pb(2) in the vicinity of the lone pair is by N(8) (Pb(2) to N(8) = 4.06 Å) in the other, which is probably not really a bond at all, since it is well away from the site where the lone pair is situated. (2) The Pb−N bonds, which are further from the lone pair, are shorter at an average value of 2.63 Å than the Pb−O bonds (average Pb−O 2.77 Å), whereas M−O bonds are usually shorter than M−N bonds because of the smaller ionic radius of O than of N[21]. (3) There appears to be a gap in the coordination geometry of one of the individuals at least (Pb(2)), where the closest contact is with an amide nitrogen of the Pb(1) DOTAM cation at 4.06 Å, as mentioned above.

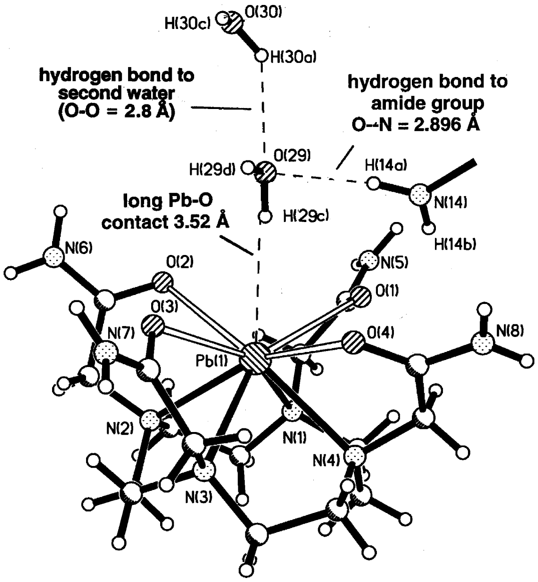

Figure 2. The structure of one of the two complex cations in **1**, showing the numbering scheme. Also shown are the waters in the vicinity of the Pb(1) atom, one of which (O(29)) is bonded to the Pb(II) ion at the proposed site of the stereochemically active lone pair. The hydrogens on O(29) are somewhat uncertain in their position, so that H(29d) is shown only to indicate that it appears to be directed toward Pb(1). The H-bonding of the water represented by O(29) to an adjacent water (O(30)) and an amide group (N(14)) from a neighboring Pb(II) DOTAM cation is shown.

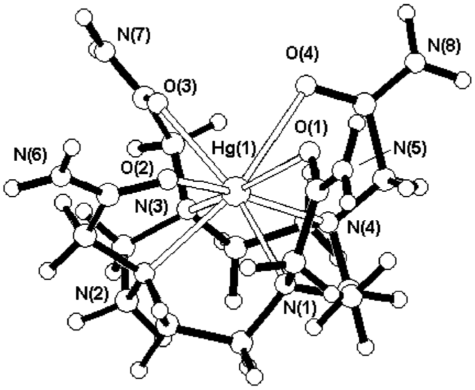

Figure 3. The structure of the complex cation in **2**, showing the numbering scheme.

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Table 1. Crystallographic Data for $[Pb(DOTAM)](ClO_4)_2{\cdot}4.5H_2O$ (**1**) and $[Hg(DOTAM)](ClO_4)_2{\cdot}0.5CH_3OH{\cdot}1.5H_2O$ (**2**)

	1	**2**
empirical formula	$C_{16}H_{41}N_8O_{16.5}PbCl_2$	$C_{16.5}H_{35.5}N_8O_{14}HgCl_2$
M	887.64	841.50
T/K	293(2)	167(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	Cc
a/Å	12.767(3)	11.849(5)
b/Å	13.528(2)	21.292(7)
c/Å	18.385(3)	11.349(2)
α/deg	101.45(2)	90
β/deg	93.32(2)	101.91(3)
γ/deg	90.53(2)	90
U/Å^3	3106.2(14)	2802(2)
Z	4	4
μ/mm^{-1}	5.687	5.764
reflns collected	11304	2612
indep reflns	10932	2612
final R indices $[I \geq 2\sigma(I)]$	R1= 0.0500, wR2 = 0.0961	R1 = 0.0381, wR2 = 0.0878
R indices (all data)	R1 = 0.0905, wR2 = 0.1240	R1 = 0.0557, wR2 = 0.1033

Table 2. Selected Bond Lengths and Angles for $[Pb(DOTAM)](ClO_4)_2{\cdot}4.5H_2O$ (**1**)

Bond Lengths (Å)

Pb(1)−N(1)	2.654(8)	Pb(1)−N(2)	2.641(8)	Pb(1)−N(3)	2.629(9)
Pb(1)−N(4)	2.610(0)	Pb(1)−O(1)	2.777(8)	Pb(1)−O(2)	2.902(8)
Pb(1)−O(3)	2.667(7)	Pb(1)−O(4)	2.770(8)	Pb(2)−N(9)	2.627(8)
Pb(2)−N(10)	2.572(9)	Pb(2)−N(11)	2.614(8)	Pb(2)−N(12)	2.666(8)
Pb(2)−O(5)	2.783(7)	Pb(2)−O(6)	2.711(7)	Pb(2)−O(7)	2.675(7)
Pb(2)−O(8)	2.883(8)	Pb(1)−O(29)	3.52(2)	Pb(2)−N(8)	4.06(2)

Bond Angles (deg)

N(1)−Pb(1)−N(2)	69.0(3)	N(1)−Pb(1)−N(3)	105.9(3)
N(1)−Pb(1)−N(4)	69.7(3)	N(1)−Pb(1)−O(1)	61.3(2)
N(1)−Pb(1)−O(2)	82.7(2)	N(1)−Pb(1)−O(3)	152.3(2)
N(1)−Pb(1)−O(4)	123.0(2)	O(1)−Pb(1)−O(29)	68.6(3)

Table 3. Selected Bond Lengths and Angles in $[Hg(DOTAM)](ClO_4)_2{\cdot}0.5CH_3OH{\cdot}1.5H_2O$

Bond Lengths (Å)

Hg(1)−N(1)	2.432(11)	Hg(1)−N(2)	2.468(12)	Hg(1)−N(3)	2.415(11)
Hg(1)−N(4)	2.453(13)	Hg(1)−O(1)	2.391(9)	Hg(1)−O(2)	2.735(11)
Hg(1)−O(3)	2.434(10)	Hg(1)−O(4)	2.815(12)		

Bond Angles (deg)

N(1)−Hg(1)−N(2)	74.4(4)	N(1)−Hg(1)−N(3)	120.0(4)
N(1)−Hg(1)−N(4)	76.7(4)	N(1)−Hg(1)−O(1)	69.5(3)
N(1)−Hg(1)−O(2)	82.1(4)	N(1)−Hg(1)−O(3)	159.4(4)
N(1)−Hg−O(4)	123.9(4)		

The complex cations of **1** thus fulfill the requirements outlined in the Introduction for a stereochemically active lone pair, or hemidirected coordination geometry. It is clear that Pb(II) can show a whole range of differing extents of distortion of its coordination sphere, depending on the level of steric activity of the lone pair. At one extreme it is hemidirected, and at the other extreme it is holodirected. The extent of distortion can be discerned using a type of plot that was demonstrated previously.[3] If one plots the Pb−L bond length against the angle made between the Pb−L bond and the proposed position of the lone pair on the Pb(II) ion (the L−Pb−Lp angle, Lp = lone pair), one obtains a diagram as seen in Figure 4.

The position of the lone pair in a structure is located as follows. Where there is a rotational axis of symmetry in the complex, the lone pair, if present, should lie on this axis of symmetry, which will be the only symmetry axis. In the latter case the position of a lone pair should be confirmed by the presence of factors such as those outlined in the Introduction, namely, a gap in the coordination geometry at the position of the lone pair, or very long Pb−L bonds at this point. An additional confirming factor would be one or more unusually short Pb−L bonds opposite the proposed lone pair. For $[Pb(DOTAM)]^{2+}$ the lone pair is located on the 4-fold axis of symmetry of the complex. If there is no axis of symmetry in the complex, then the lone pair will be located where there is a gap in the coordination geometry, or unusually long Pb−L bonds. The position of the lone pair can be more accurately pinned down by an unusually short bond opposite the proposed site of the lone pair. Where there are two, or sometimes three or four, shorter Pb−L bonds opposite the site of the lone pair, the axis passing through the lone pair should intersect the angle made by the two short bonds, or pass through the center of the triangle created by the three shorter Pb−L bonds. In the case of $[Pb(DOTAM)]^{2+}$ here, the 4-fold axis passing through the lone pair passes through the center of the square created by the four short Pb−N bonds. When the position of the lone pair has been correctly decided, a curve such as seen in Figure 4 will have the minimum amount of deviation from a smooth curve passing through the points.

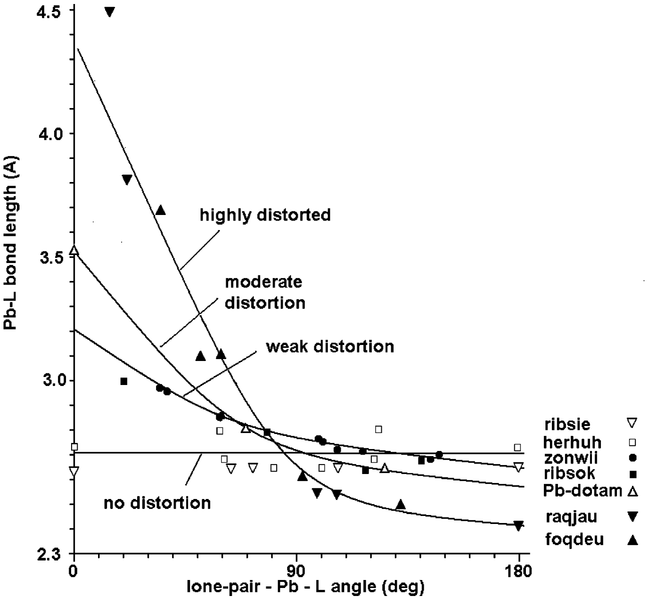

Figure 4. Plot of Pb−L bond length versus Lp−Pb−L angle for a variety of Pb(II) complexes. The plots show that as the Lp−Pb−L angle approaches zero, i.e., the ligand donor atom moves closer to the lone pair on Pb(II), the Pb−L bond lengths tend to get longer. In the case where the inert pair is stereochemically inactive (CSD reference codes RIBSIE[10] (▽) and HERHUH[22] (□)) there is no systematic variation in Pb−L bond lengths as one moves around the coordination polyhedron. These two complexes have been included in the figure by arbitrarily assigning a position to a lone pair on the Pb(II), even though one is not present. The complexes $[Pb(TPB)_2]$ (RIBSOK[10] (■)) and $[Pb(N_6O_4\text{-macrocycle})]^{2+}$ (ZONWII[23] (●)) are included as examples of weak distortion by the lone pair on Pb(II). $[Pb(DOTAM)]^{2+}$ (△) from this work is included as an example of moderate distortion. The complexes $[Pb(\text{tet-b})(O_2C{-}CH_3)]^+$ (RAQJAU[4] (▼)) and $[Pb(N_5O_2\text{-macrocycle})(CH_3CN)(ClO_4)]^+$ (FOQDEU[24] (▲)) are included as examples of very strong distortion of the coordination sphere of Pb(II).

One sees that, for each complex analyzed, the relationship between the L−Pb−Lp angle and the Pb−L bond length is such that as the L−Pb−Lp angle gets larger, the Pb−L bond length gets shorter. However, the complexes in Figure 4 show differing degrees of distortion. Thus, at one extreme, the complex[22] [Pb(18-crown-6)(SCN)$_2$] appears to be holodirected with no discernible distortion of the coordination geometry. All the Pb−L bond lengths, once corrected for differences in ionic radii of the donor atom, appear to be about 2.7 Å. (Correction for different ionic radius[23] involves no change for Pb−O bonds, subtraction of 0.06 Å for Pb−N bonds, and of 0.3 Å for Pb−Cl and Pb−S bonds.) Thus, in this complex, no lone pair can be discerned, and one of the Pb−O bonds was arbitrarily chosen as the site of the lone pair so that the complex could be included in Figure 4. At the other extreme are highly distorted structures, where the short Pb−L bonds are about 2.4 Å, and long Pb−L bonds, if present at all, are over 4.0 Å on the side of the Pb opposite the shortest bond. The two examples in Figure 4 are a macrocyclic complex of Pb(II) with long bonds to a perchlorate,[24] and a Pb(II) complex of a tetraaza macrocycle[4] with a long bond to an acetate oxygen. Weak distortion is observed within a large macrocycle[25] that envelopes the Pb(II) somewhat like a tennis-ball seam. The longest bonds are 2.95 Å, and the shortest bonds are 2.65 Å. It seems likely that the macrocyclic structure of the ligand is involving the amount of distortion that can take place, in line with the observation that steric effects are sufficient to cause either distortion, or no distortion at all, in Pb(II) complexes of otherwise similar ligands.[10] These two complexes are included in Figure 4. It is seen that, although the nonsterically hindered tris-pyrazolyl borate (TPB) complex of Pb(II) does in fact have a stereochemically active lone pair in terms of the analysis in Figure 4, the amount of distortion is weak. We can in fact characterize the level of stereochemical activity of the lone pair in a Pb(II) complex by the difference in length between the projected shortest (at L−Pb−Lp = 180°) and longest bonds (at L−Pb−Lp = 0°) in a diagram such as Figure 4. Thus, we have the following table.

difference in projected bond length (Å)	example	CSD reference	level of distortion
0	[Pb(18-crown-6)(SCN)$_2$]	HERHUH	none
0−0.7	[Pb(TPB)$_2$]	ZONWII	small
0.7−1.1	[Pb(DOTAM)]$^{2+}$	this work	medium
1.1−2.0	[Pb(tet-b)CH$_3$COO]$^+$	RAQJAU	large
>2	[Pb(C(SiPh$_2$CH$_3$)Cl]$_2$	ZUMCAL	complete

The structural analysis of [Pb(DOTAM)]$^{2+}$ carried out here suggests that H(29c) of the water O(29) is placed so as to suggest a Pb···H−OH H-bond, as shown in Figure 2. Positioning in a structural analysis of an H so close to the heavy Pb atom cannot be given too much credibility without further careful analysis. The point of interest, then, is whether the proposed lone pair is merely coordinated to the water through its oxygen with a rather long Pb−O bond, or whether this might actually represent a Pb···H−OH H-bond. A search of the Cambridge Structural Database (CSD)[21] reveals that there are many structures of Pb(II) that resemble the present Pb(II) DOTAM complex in having at least one nitrogen donor coordinated to the Pb(II), as well as some oxygen donors forming long Pb−O bonds. Typical Pb−O lengths to these oxygens situated near the proposed site of the lone pair are (CSD reference code in parentheses) 3.691 Å (FOQSEU),[24] 3.635 Å (GIWQIM),[26] 3.759 Å (FICQIR),[6] 3.386 Å (FICSIT),[6] 3.619 Å (LORLOT),[27] 3.263 Å (RAQJAU),[4] and 3.334 Å (FICLEI).[6] One sees that the Pb−O bond length of 3.52 Å found here for the water situated over the site of the proposed lone pair in [Pb(DOTAM)]$^{2+}$ is thus not very different from other similar complexes. This is significant when one realizes that the oxygens in several of these complexes do not come from water,[4,24] but anions such as perchlorate or nitrate, and therefore cannot involve H-bonding to Pb(II). The problem with placing the H-atoms on O(29) accurately can be addressed to some extent by considering the two conventional H-bonds that hold this water in place. There is a second water molecule at O(30), and an amide group at N(14), both of which form H-bonds with O(29). One H-bond has O(29) as the acceptor of an H atom from N(14), and in the other O(29) directs an H toward O(30). This has the potential of allowing us to place the remaining hydrogen of O(29) in a theoretical position, assuming as near as possible to tetrahedral geometry around O(29) involving the H-atom of the O(29) water molecule, and the H-atoms from O(30) and N(14), while preserving an H−O(29)−H angle of 104.5° for the O(29) water molecule. The resulting structure is shown in Figure 5. Figure 5 suggests that one of the two lone pairs expected on O(29) from VSEPR is most likely utilized in H-bonding to N(14). One H is oriented toward O(30), leaving open the placement of the remaining lone pair and H atom. In neither possible

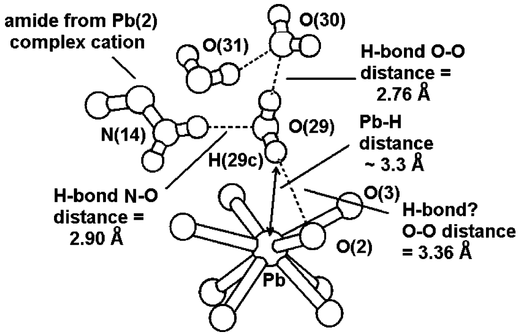

Figure 5. The H-bonding in the vicinity of the Pb(II) atom. The hydrogens on O(29) were placed at calculated positions as described in the text. There are two possible orientations for H(29c), the H atom not involved in H-bonding to O(30). One is shown, where the H(29c) on O(29) is oriented toward O(2), forming a long contact (3.36 Å) that may be a weak H-bond. In the alternate orientation, H(29c) forms a similar contact with O(3). In neither orientation does the lone pair on O(29) point directly at Pb(1). H(29c) is actually close to the surface of the Pb(II) ion, and may represent something like an agostic contact between the hydrogen and the Pb(II) ion, facilitated by the presence of the lone pair.

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orientation of the lone pair on O(29) does it appear to be oriented toward Pb(1). It may be that the water of O(29) is held in place solely by H-bonds to N(14) and O(30). In Figure 2 the arrangement has been selected where H(29c) of the water is oriented toward the amide O(2) of the complex cation. In this arrangement the O(29)$\cdots$O(2) distance is 3.36 Å, possibly too long to be a strong H-bond. In the alternate arrangement, exchanging the lone pair and H(29d), there is now a long "H-bond" involving H(29c) and O(3). The water at O(29) is thus primarily held in place by H-bonds to O(30) and N(14), and possibly long weak H-bonding type interactions between the H-atoms on O(29) and one of the two amide oxygens O(2) and O(3). The H(29c) atom on O(29) appears to be close to Pb(1) in either possible orientation, so that it may be held to the Pb by something like an agostic interaction, aided by the presence of the lone pair. A search of the CSD[21] reveals two structures[4,6] where the placement of a water molecule over Pb(II) is of interest in relation to possible H-bonding to Pb. In these two structures the hydrogens of these water molecules appear to be somewhat directed toward the lone pair on Pb(II), but with Pb−O distances at 3.263[4] and 3.334 Å that are shorter than the Pb−O(29) distance found here. It is interesting that, bearing in mind the difficulty of placing H-atoms near a heavy Pb atom, in these structures the placement of the H-atoms resembles that found here, with one hydrogen on the water close to the surface of the Pb atom, but not pointing directly at it. It may be that the lone pair on Pb(II) can at least minimize the repulsion toward hydrogens on water molecules, which normally makes water molecules coordinate in a much more upright position, so that they can approach the surface of the Pb(II) more closely.

The $[Hg(DOTAM)]^{2+}$ complex shows a coordination number that is probably six, with four nitrogens at an average distance of 2.441 Å, and two of the oxygens from pendant amide groups at 2.410 Å. Two more oxygen donors from pendant amide groups are situated at 2.735 and 2.815 Å. This structure resembles that of the Cd(II) and Zn(II) DOTAM complexes,[18] where six short bonds are present, plus two long contacts with amide oxygen donors. It seems that, despite the preference of Hg(II) for two-coordination, it is not able to achieve this in the more rigid cyclen type of ring present in DOTAM. In fact, of the 29 structures in the CSD that appear to contain eight-coordinate Hg(II), only two can be regarded as having anything approaching regular eight-coordinate geometry. These are the already mentioned $[Hg(NO_3)_4]^{2-}$ cation,[15] and the complex $[Hg(TPA)_2]^{2+}$ which has[28] eight nitrogen donors at approximately equal Hg−N bond lengths. A further aspect highlighted by this complex is that distortion of the geometry of Hg(II) and Pb(II) complexes appears to be promoted by differences in tendencies to covalent M−L bond formation among the donor atoms. Thus, the sterically constrained Hg(II) complex of cryptand-2,2,2 still has[29] the two more covalent Hg−N bonds short at 2.20 Å, with the six more ionic Hg−O bonds all close to 2.69 Å, whereas the TPA complex is not distorted. The majority (16) of the apparently eight-coordinate Hg(II) complexes are of the type $[Hg(18\text{-crown-}6)X_2]$, where X may be simple unidentate ligands such as Cl^-, Br^-, I^-, or CN^-, where the structure shows long Hg−O bonds of about 2.8 Å, with short bonds to the axial ligands. The very strong tendency of Hg(II) to achieve in effect linear 2-coordination, with other donor atoms at much longer distances, is preserved in most cases of apparent eight-coordination. For $[Hg(DOTAM)]^{2+}$ reported here the rigidity of the macrocyclic ring of DOTAM prevents adoption of anything approaching a linear structure. However, the reluctance of Hg(II) to adopt regular eight-coordination is shown by the fact that Hg(II) in its DOTAM complex is effectively only six-coordinate. In contrast, Pb(II) is able to display a stereochemically active lone pair, but the rigidity of the macrocyclic ring of DOTAM means that, instead of a single very short Pb−N (Pb−N ∼ 2.3 Å) opposite the lone pair, four fairly short Pb−N bonds to the macrocylic ring with longer Pb−N bonds of 2.63 Å are placed opposite the lone pair.

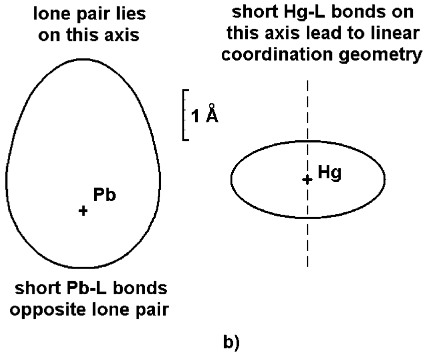

Figure 6. The shapes of the Pb(II) and Hg(II) ions where they show high distortion from regular coordination geometry in their complexes. The shape of Pb^{2+} ion was derived from Figure 4, from the curve for strongly distorted complexes (RAQJAU[4] and FOQDEU[24]). The shape of the Hg(II) ion was derived from the apparent ionic radius of the Hg(II) in the direction of the two short Hg−Cl bonds, and the six long Hg−O bonds at right angles to these, in $[Hg(18\text{-crown-}6)Cl_2]$ (CESZOP[28]).

One can extract apparent shapes for Pb(II) ions in their distorted situations from a diagram such as Figure 4. The apparent ionic radius as a function of Lp−Pb−L angle is obtained by subtracting the ionic radius of oxygen (1.23 Å) from the M−L distances indicated by the curves in Figure 4, and then plotted as seen in Figure 6. For both Pb(II) and Hg(II), examples of highly distorted ions have been selected, which would be,[4,30] for example, $[Pb(\text{tet-b})CH_3COO^-]^+$ or $[Hg(18\text{-crown-}6)Cl_2]$. Thus, in these highly distorted complexes the Pb(II) ion appears to be egg-shaped, while Hg(II) is flattened into a disk. The disk shape for the Hg(II) complex was derived by drawing an oval with the short diameter the sum of the ionic radii of Hg(II) in the direction of the short Hg−Cl bonds, and the long diameter the apparent ionic radius in the direction of the long Hg−O bonds in $[Hg(18\text{-crown-}6)Cl_2]$.[30]

The VSEPR based analogy between the structures of Pb(II) and Hg(II) complexes pointed out here appears to be

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quite useful. The analogy suggests why there is a short bond opposite the lone pair in Pb(II) complexes, and why this is at 180° to the position of the lone pair. The tendency to ionic bonding of donor atoms has parallel effects in Hg(II) and Pb(II), with more ionic bonding leading to more regular geometry in both cases, with no linear bonding in Hg(II), or stereochemically active lone pair in the Pb(II) complexes. An additional aspect not discussed here in any detail is the fact that, with smaller numbers of ligands that form more covalent bonds, Hg(II) may form regular tetrahedral complexes, such as $[HgCl_4]^{2-}$ or trigonal planar $[HgI_3]^-$. In line with VSEPR expectations, the Pb(II) ion forms[31] the trigonal pyramidal complex $[PbCl_3]^-$, with Cl−Pb−Cl bond angles of 92.5°, or numerous[21] two-coordinate complexes with sterically hindering groups such as trialkylsilyl groups, that all have a bent L−Pb−L structure.

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Supporting Information Available: Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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