

## Polyhapto-Aromatic Interactions in Lead(II) Coordination

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In its crystalline form, the Pb(II) complex of 1,3-diphenylpropane-1,3-dionate (dibenzoylmethanide, DBM<sup>-</sup>) can be regarded as containing polymeric chains of centrosymmetric, dimeric Pb<sub>2</sub>(DBM)<sub>4</sub> units linked through hexahapto interactions of the Pb atoms with phenyl groups from adjacent units. Each Pb atom also appears to be involved in intraunit dihapto-aromatic interactions, thus attaining a total hapticity of thirteen. Comparison with the analogous Sn(II) compound indicates that the unusually high coordination number may reflect the capacity of Pb(II) to act as both a Lewis acid and a Lewis base.

Details of the coordination chemistry of very heavy metal ions such as Pb(II) are frequently challenging to define.<sup>1</sup> In many Pb(II) complexes, lead–donor atom distances are widely spread, generating some arbitrariness in identification of a donor atom, hence the exact nature of the Pb coordination sphere and thus its geometry. In turn, this results in difficulty in resolving issues such as whether or not any lone pair formally present in the valence shell of Pb(II) is “stereochemically active”<sup>2,3</sup> and to what extent intermolecular attractions or repulsions may influence the form of what is defined as the molecular unit. From numerous structural studies of Pb(II) complexes of azaaromatic ligands,<sup>1d,2,4</sup> it has been argued that  $\pi$ -stacking plays an important role in determining the solid state lattices of such compounds, so that it was anticipated that this might be true for the Pb(II)

complex of the dibenzoylmethane (DBMH, = 1,3-diphenylpropane-1,3-dione)<sup>5</sup> anion. In fact, a crystal structure determination<sup>6</sup> indicates the situation to be somewhat more complicated.

Pb(DBM)<sub>2</sub> (=C<sub>30</sub>H<sub>22</sub>O<sub>4</sub>Pb. Anal. Calcd (found): C, 55.07 (54.5); H, 3.37 (3.35) %) deposits from methanol as unsolvated, pale yellow, monoclinic crystals, space group *P*2<sub>1</sub>/*c*, unit cell dimensions *a* 10.368(2), *b* 20.577(4), *c* 12.239(2) Å,  $\beta$  107.97(3)°. Considering DBM<sup>-</sup> as a bidentate *O*-donor ligand, the formulation Pb(DBM)<sub>2</sub> implies the presence of a four-coordinate Pb atom, a very low degree of coordination for Pb(II) in an *O*-donor environment, so that it is unsurprising that the structure solution shows the Pb atoms to occur in proximal pairs 4.139(2) Å apart due to *O*-bridging in a centrosymmetric dimer unit involving PbO<sub>5</sub> entities. The form of this “dimer” unit is, however, quite remarkable, the projection given in Figure 1 showing an apparently very strongly “hemidirected”<sup>3</sup> coordination sphere, thus suggesting that this system might be a particularly clear example of a stereochemically active lone pair.

Further analysis indicates that this interpretation of the crystal structure is an oversimplification, since the zigzag chains of Pb atom pairs lying parallel to the crystal *b* axis result from close “intermolecular” contacts of such dimer units in a manner illustrated for a single adjacent pair in Figure 2. Though the parallel orientation of some of the phenyl groups apparent here (as in the entire lattice) might be taken as indicative of  $\pi$ -stacking interactions, in fact it is at least partly a result of hexahapto interactions between the Pb atoms and phenyl groups from “separate” dimers. (Such

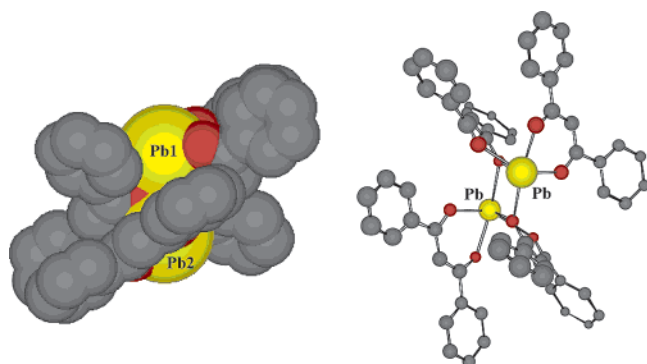
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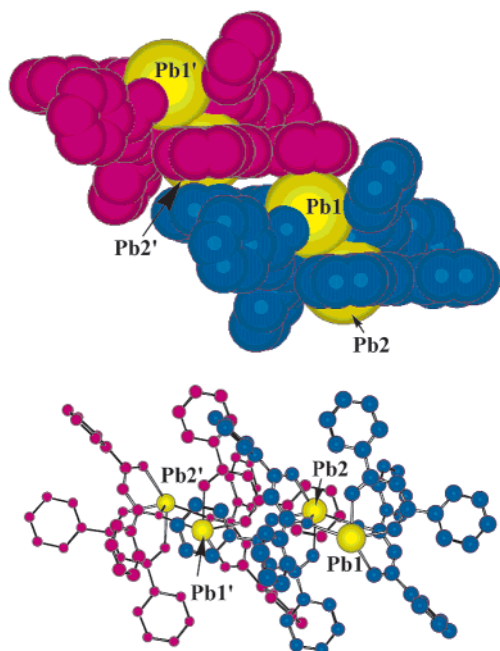
<sup>‡</sup> University of Zanjan.

- (1) For recent discussions of the issues, see: (a) Esteban, D.; Avecilla, F.; Platas-Iglesias, C.; Mahia, J.; de Blas, A.; Rodriguez-Blas, T. *Inorg. Chem.* **2002**, *41*, 4337. (b) Sanchiz, J.; Esparza, P.; Villagra, D.; Domínguez, S.; Mederos, A.; Brito, F.; Araujo, L.; Sánchez, A.; Arrieta, J. M. *Inorg. Chem.* **2002**, *41*, 6048. (c) Thompson, L. K.; Zhao, L.; Xu, Z.; Miller, D. O.; Reiff, W. M. *Inorg. Chem.* **2003**, *42*, 128. (d) Harrowfield, J. M.; Shahverdizadeh, G. H.; Soudi, A. A. *Supramol. Chem.* **2003**, *15*, 367.
- (2) Harrowfield, J. M.; Miyamae, H.; Skelton, B. W.; Soudi, A. A.; White, A. H.; et al. *Aust. J. Chem.* **1996**, *49*, 1029, 1043, 1051, 1067, 1081, 1089, 1099, 1111, 1121, 1127, 1135, 1147, 1157, 1165.
- (3) Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W. *Inorg. Chem.* **1998**, *37*, 1853.
- (4) Hall, A. K.; Harrowfield, J. M.; Morsali, A.; Soudi, A. A.; Yanovsky, A. *CrystEngComm* **2000**, *2*, 82 (No. 13).

- (5) Complexes of the 1,3-diphenylpropane-1,3-dionate anion, DBM<sup>-</sup>, are of continuing interest for the variety of their properties. See, for example: (a) Soldatov, D. V.; Henegouwen, A. T.; Enright, G. D.; Ratcliffe, C. J.; Ripmeester, J. A. *Inorg. Chem.* **2001**, *40*, 1626. (b) Xiong, R.-G.; You, X.-Z. *Inorg. Chem. Commun.* **2002**, *5*, 677 and references therein.
- (6) The crystal structure determination was performed under the supervision of Dr. Z. Starikova at the X-ray Structural Centre, General and Technical Chemistry Division, Academy of Science of Russia, INEOS, Vavilov Str., 28, Moscow B-334, 117813, Russia. E-mail: star@xray.ineos.ac.ru. Data pertinent to the present discussion are given in the figures and text, but to ensure recognition of the fact that none of the authors of the present manuscript is a formally trained crystallographer, the figures have not been presented in a conventional crystallographic style.

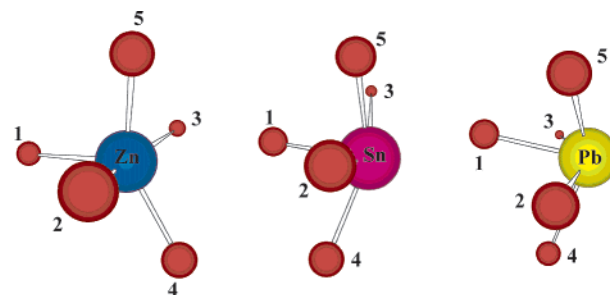


**Figure 1.** (Left) Space-filling representation of the dimeric unit  $\text{Pb}_2(\text{DBM})_4$  perpendicular to the  $\text{Pb}\cdots\text{Pb}$  vector and indicating the “vacancies” above/below the Pb atoms. (See also Figure 3.) (Right) Ball-and-stick representation of the dimer showing the simply chelating and bridging-chelating  $\text{DBM}^-$  ligands (Pb = yellow, O = red, C = gray).



**Figure 2.** Approximately orthogonal views of an adjacent dimer pair in the lattice of  $\text{Pb}(\text{DBM})_2$ . All atoms other than Pb of a given dimer are shown in a common color (violet or blue). In the space-filling view, close approaches of Pb to the face of a phenyl ring can be seen, while the ball-and-stick view shows that the yellow Pb atoms are centered over these rings.

aromatic $\cdots$ aromatic interactions as can be identified appear to be of the “edge-to-face” type<sup>7</sup> and involve  $\text{C}\cdots\text{C}$  separations  $\sim 3.6$  Å.) Each Pb atom is situated 3.408(3) Å from the centroid of the phenyl group associated with the adjacent dimer, and  $\text{Pb}\cdots\text{C}$  separations are 3.598(3), 3.626(3), 3.658(3), 3.695(3), 3.729(3), and 3.747(3) Å, showing that the interaction is not perfectly symmetrical but justifying its description as hexahapto ( $\eta^6$ ). Recognizing these  $\text{Pb}\cdots\text{C}$  interactions and considering the known occurrence of  $\text{M}\cdots\text{C}$  interactions in metal 1,3-diketonate complexes,<sup>8</sup> a search was made generally for  $\text{Pb}\cdots\text{C}$  approaches and it appears that Pb in  $\text{Pb}(\text{DBM})_2$  may also be involved in an  $\eta^2$



	M-O1	M-O2	M-O3	M-O4	M-O5
Zn	2.071	1.986	2.088	1.985	1.980
Sn	2.167	2.151	2.982	2.344	2.264
Pb	2.308	2.295	2.713	2.354	2.457

**Figure 3.** Representations of the  $\text{MO}_5$  units present in crystalline  $[\text{M}_2(\text{DBM})_4]$  entities (M = Zn,<sup>5a</sup> Sn,<sup>12</sup> Pb) and atom separations/Å within them. In all cases, oxygen atoms 1 and 3 are those involved in bridging.

interaction ( $\text{Pb}\cdots\text{C}$  3.583(3), 3.741(3) Å) with the phenyl group closest to the bridging-*O* donor. Thus, rather than a  $\text{PbO}_5$  coordination sphere of a highly unusual form, the complex can be considered to contain a tridecahapto  $\text{PbO}_5\text{C}_8$  center with an irregular but “holodirected” coordination sphere. While  $\pi$ -arene complexes of Pb(II) are uncommon, they are characterized by exceptionally high coordination numbers.<sup>9</sup> In the formally hexadecahapto species  $[\text{Pb}(\text{o-xylene})_2(\text{Cl}_2\text{AlCl}_2)_2]$ ,<sup>9</sup> the  $\text{Pb}\cdots\text{C}$  distances (range 3.083(6)–3.309(5) Å) are significantly shorter than in the present case, as is true also for polymeric  $[\text{Pb}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl}_2\text{AlCl}_2)_2]\cdot\text{C}_6\text{H}_6$ <sup>10</sup> (3.09(4)–3.13(4) Å), but in binuclear  $[\text{Pb}_2\{\text{SeC}_6\text{H}_2(\text{CF}_3)_3\}_4(\text{toluene})_2]$ <sup>11</sup> the  $\text{Pb}\cdots\text{C}(\text{Ar})$  distances of 4.05, 3.96, 3.86, 3.72, 3.59, and 3.52 Å (not given in the original work) are, on average, slightly longer than in  $\text{Pb}(\text{DBM})_2$ . Thus, polyhapto aromatic coordination of Pb(II) appears to be yet another factor which can make varying contributions to the stability of complexes of this metal ion.

Useful comparison may be made of the present structure with those known for other  $\text{M}(\text{II})(\text{DBM})_2$  species where M = Zn<sup>5a</sup> and Sn.<sup>12</sup> The Zn(II) compound is known in both mononuclear and dinuclear forms, and in the latter an  $\text{M}_2\text{O}_2$  rhomb is the bridging unit formed by two  $\text{MO}_5$  entities (Figure 3), just as in the Pb(II) analogue. The geometry of the  $\text{ZnO}_5$  units, however, can be described as close to trigonal bipyramidal,<sup>5a</sup> and certainly there is no unique and large gap in the coordination sphere, nor is there a close approach of a ligand phenyl group to the metal. The Sn(II) complex, in contrast, strongly resembles the Pb in that the  $\text{SnO}_5$  unit is “hemidirected” (Figure 3) and both  $\eta^2$  and  $\eta^6$  interactions with ligand phenyl groups can be considered to occur through the face remote from the *O*-donors. Side lengths of the  $\text{Sn}_2\text{O}_2$  rhomb in the binuclear unit (2.167, 2.982 Å) are somewhat more disparate than in the Pb compound (2.308, 2.713 Å), and separations  $\text{Sn}\cdots\text{C}(\text{Ar})$  ( $\eta^2$  3.721, 3.948;  $\eta^6$  3.695, 3.756,

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3.758, 3.886, 3.889, 3.938 Å) are significantly longer. Given the familiarity of chemistry in which Sn(II) acts as a Lewis base,<sup>13,14</sup> one interpretation of this structural information could be that Sn is acting as an electron pair donor toward an ( $\eta^6$ ) aromatic ring which is depleted in electron density as a result of the attachment of carbonyl/enolate substituents. If this is so, the fact that M $\cdots$ C separations are shorter for Pb than Sn (while M $\cdots$ O separations are longer) indicates that the polyhaptic interactions of Pb are stronger than those of Sn in these particular compounds. Assuming, nonetheless, that both interactions are weak on an absolute scale, their manifestation could be significantly affected by other weak interactions in the system and possibly the slight expansion of the Pb<sub>2</sub>(DBM)<sub>4</sub> unit reflected in the longer M–O bonds reduces repulsive interactions with an intruding phenyl group from an adjacent dimer. (This, of course, would be true also if the metal–arene interaction were taken to be of the type where the metal is the acceptor {Lewis acid}.) That the interactions giving rise to a polymeric form in the solid are stronger for the Pb than for the Sn compound may explain

(13) See, for example: Breedlove, B. K.; Fanwick, P. E.; Kubiak, C. P. *Inorg. Chem.* **2002**, *41*, 4306.

(14) References specifically referring to the action of Sn(II) 1,3-diketonate complexes as Lewis bases include: (a) Cornwell, A. G.; Harrison P. G. H. *J. Chem. Soc., Dalton Trans.* **1975**, 821. (b) Ewings, P. F. R.; Harrison, P. G.; Fenton, D. E. *J. Chem. Soc., Dalton Trans.* **1975**, 1722. (c) Ewings, P. F. R.; Harrison, P. G. *Inorg. Chim. Acta* **1978**, *28*, L167.

why the latter is of low solubility in all common solvents, whereas the Sn compound dissolves readily in solvents ranging in polarity from methanol to hexane.

The <sup>13</sup>C MAS (with Total Suppression of Spinning Sidebands (TOSS)) spectrum of Pb<sub>2</sub>(DBM)<sub>4</sub> is very similar to that of the Zn analogue,<sup>5a</sup> so that if any specific chemical shift differences arise as a result of the  $\pi$  interactions with Pb, they are within the resolution of this measurement. The two resonances for the 1,3-diketonate methine carbon atoms are significantly further apart in the Pb compound ( $\delta$  90.5, 101.0) than in the Zn compound ( $\delta$  93.3, 96.5<sup>5a</sup>), consistent with there being a greater difference between the bridging-chelate and simple chelate DBM<sup>-</sup> units, with this possibly a reflection of the polyhaptic interactions, but there is at present no direct measure of changes in aromatic carbon electron density which would enable a distinction between donor and acceptor functions of the aromatic ring to be made.

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**Supporting Information Available:** Synthesis and crystallization of the complex. Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. A full description of the structure solution has been deposited as a CIF with the CCDC, deposition number CCDC 215200.

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