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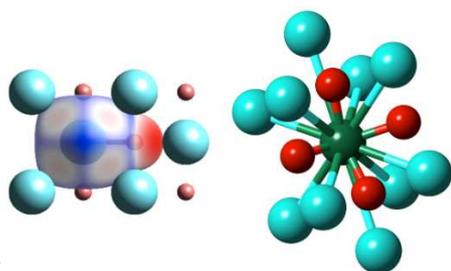
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# Lead(II): Lewis acid and occasional base, as illustrated by its complex with 1,5-naphthalenedisulfonate and 5-methyl-1,10-phenanthroline†

Jack Harrowfield\*<sup>a</sup> and Pierre Thuéry\*<sup>b</sup>

**A crystal structure determination of the Pb(II) coordination polymer [Pb(Mephen)(1,5-nds)(H<sub>2</sub>O)]<sub>n</sub> provides not only evidence of the common action of Pb(II) as a Lewis acid but also clear proof of its ability, in the solid state at least, to act as a Lewis base. This action as a base is attributed to the presence of a valence shell lone pair and its identification here is further evidence for the occasional but not universally detectable influence of the lone pair on the metal ion stereochemistry.**

The suggestion by Moore and Pauling in 1941, in a powder-diffraction structural study of litharge (tetragonal PbO),<sup>1</sup> that a valence shell lone pair might determine the stereochemistry of the Pb(II) coordination environment proved to have a remarkable and enduring influence on subsequent diverse studies of the coordination chemistry of Pb(II).<sup>2,3</sup> The gas phase electron configuration of Pb<sup>2+</sup> has the highest energy electron pair placed in the 6s orbital and thus it is often said that Pb(II) may have a stereochemically active 6s<sup>2</sup> lone pair, although clearly the electron pair cannot remain in an s orbital if it is to produce coordination sphere asymmetry and the supposedly inert nature of the 6s<sup>2</sup> electrons has been described as a "myth" of Pb(II) coordination chemistry.<sup>2</sup> Indeed, DFT calculations on litharge<sup>4</sup> have shown that the lead 6s orbital interacts strongly with oxygen 2p orbitals to give a non-spherically-symmetrical electron density. Theoretical calculations have also indicated that Pb...Pb bonding may be significant<sup>4,5</sup> and consideration of the Hirshfeld surface<sup>6</sup> for tetragonal PbO (Fig. 1), derived for its crystal structure<sup>7</sup> using CrystalExplorer,<sup>8</sup> provides clear evidence for this, so that the actual influence of any lone pair in PbO is unclear.



**Fig. 1** A view of litharge, showing adjacent Pb (blue) and O (red) atoms (left). A view of a single Pb atom (green) of PbO and its four nearest neighbour O (red) atoms and the ten Pb atoms (blue) within 4 Å (right).

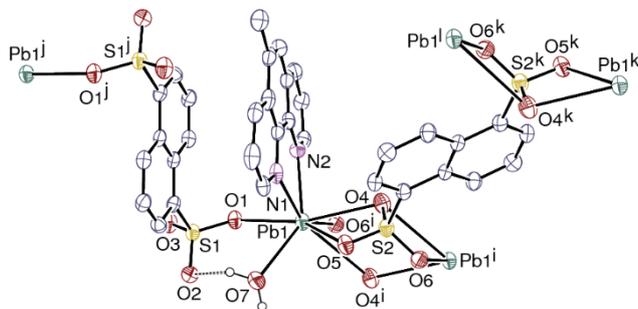
Given the delocalised electronic structure of solid PbO, it is possible that the characteristics of this material are not shared by the numerous coordination complexes of Pb(II) where multidentate ligands limit the proximity of the Pb(II) centres.<sup>2,3,9-11</sup> Only in complexes involving small clusters with monatomic O or N bridges, *e.g.*<sup>12-14</sup> or in some diorganolead "diplumbenes"<sup>15</sup> is there clear evidence for the retention of Pb...Pb interactions or "plumbophilicity", in some cases associated with Pb...Pb separations shorter than those in metallic Pb. Thus, in general there is some reason to expect that lone pair effects may be more easily detected in the structures of Pb(II) coordination compounds, recognising in general also that this may depend upon the specific nature of the donor atoms involved.<sup>2-5</sup> Sulfur donor atoms, for example, are expected to have minimal orbital interaction with lead 6s and thus not to favour detectable lone pair effects on stereochemistry.<sup>4,5</sup> It is worth noting here that transition metal complexes provide numerous examples where non-bonding d electrons appear to have no stereochemical influence (*e.g.* the three pairs of t<sub>2g</sub> electrons in [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>).

A difficulty in establishing that lone pair effects exist in Pb(II) complexes is that the lone pair itself is not directly observable. Various criteria of lone pair activity have therefore been explored and the VSEPR (Valence Shell Electron Pair Repulsion Theory) approach, for example, has been used to rationalise the coordination sphere geometry of numerous aminocarboxylate complexes in terms of active lone pairs,<sup>16</sup> reflecting probably the specific nature of the donor atoms.<sup>17</sup> There are, however, instances where the unsymmetrical coordination sphere geometry of a Pb(II) complex is mimicked in an analogous complex of a metal ion lacking a potential valence shell lone pair,<sup>18</sup> so that in general more sophisticated analyses based on whether the coordination sphere may be described as holo- or hemi-directed<sup>10</sup> (not always obviously<sup>19</sup>) and/or whether there is an obvious coordination sphere vacancy, particularly one associated with unusually long bonds and large bond angles involving nearby donor atoms,<sup>3</sup> and on high-level computation,<sup>2,3,20</sup> have been applied.

One criterion of the presence of a lone pair that has been relatively little explored, however, is that of whether weak interactions of the lone pair as a donor can be discerned. In a survey of the structures of Pb(II) complexes of ligands containing aromatic units,<sup>21</sup> it has been deduced that approximately 3% of these structures provide evidence of interactions between the metal and these units, described by the authors as involving donation of the Pb(II) lone pair into antibonding orbitals of the aromatic systems. There is some ambiguity, however, as to whether these contacts do arise thus or are simply due to polyhaptic  $\pi$ -donation from the aromatic ligand to the Pb(II)

centre,<sup>22</sup> and in a more recent investigation concerning Pb(II) and several other metal ions and the effects of the interactions on luminescence properties,<sup>23</sup> it has been concluded (supported by DFT calculations) that the interaction is one of ligand donation to the metal ion. Where there should be no ambiguity is when the atom approaching Pb is incapable of donation, as expected for hydrogen bonding. While a careful investigation<sup>24</sup> of this possibility for [Pb(DOTAM)](ClO<sub>4</sub>)<sub>2</sub>·4.5H<sub>2</sub>O (DOTAM = 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetra-azacyclododecane) led to the conclusion that any Pb-lone pair...H interaction was too minor to justify description as an hydrogen bond, this was qualified by the uncertainty in the exact orientation of the water molecule hydrogen atom involved. Two other possibilities drawn from the extant literature considered in reference 24, one involving an apparent Pb...H separation as short as 2.7 Å, also involved this difficulty. Nonetheless, our calculation of the Hirshfeld surface for the [Pb(DOTAM)](ClO<sub>4</sub>)<sub>2</sub>·4.5H<sub>2</sub>O structure as described provides evidence that there is a Pb-lone pair...H interaction beyond dispersion. There is less uncertainty in the orientation of an hydrogen atom substituent on an aromatic ring and in the structure of [Pb(Mephen)(1,5-nds)(H<sub>2</sub>O)] (**1**), where Mephen is 5-methyl-1,10-phenanthroline and 1,5-nds is 1,5-naphthalenedisulfonate, a complex obtained during recent attempts to produce mixed-metal complexes with naphthalenedisulfonate ligands,<sup>25</sup> there is more conclusive evidence for hydrogen bonding by a Pb(II) lone pair. Complex **1** is the third to be obtained with Pb(II) and the 1,5-nds<sup>2-</sup> ligand, after [Pb<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(1,5-nds)]<sup>26</sup> and [Pb(phen)(1,5-nds)(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O],<sup>27</sup> which crystallize as three- and one-dimensional polymers, respectively.

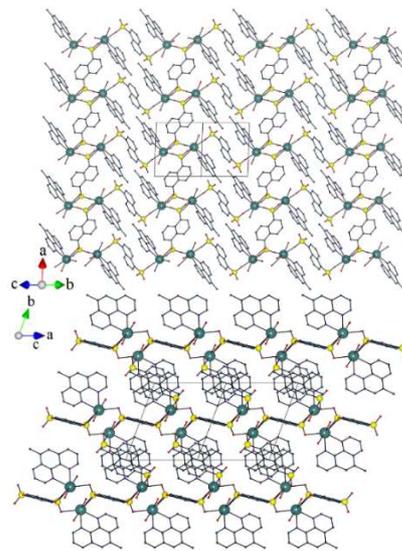
Complex **1** was synthesized under solvo-hydrothermal conditions<sup>‡</sup> and its crystal structure was determined.§ The unique lead atom is chelated by Mephen [Pb1–N1 2.482(5), Pb1–N2 2.515(5) Å, both on the short side of the distribution of Pb–phen bond lengths reported in the Cambridge Structural Database (CSD, v. 5.38),<sup>28</sup> which average 2.62(10) Å], and by one sulfonate group [Pb1–O4 2.740(4), Pb1–O5 2.801(4) Å], and it is bound in unidentate fashion to two more sulfonate oxygen atoms [Pb1–O1 2.491(4), Pb1–O6<sup>i</sup> 2.811(4) Å] and a water ligand [Pb1–O7 2.729(4) Å] (Fig. 2). A more distant contact with O4<sup>i</sup>, at



**Fig. 2** View of complex **1** with carbon-bound hydrogen atoms omitted. The hydrogen bond is shown as a dashed line. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes:  $i = 1 - x, 1 - y, 2 - z$ ;  $j = 1 - x, 2 - y, 1 - z$ ;  $k = -x, 1 - y, 2 - z$ ;  $l = x - 1, y, z$ .

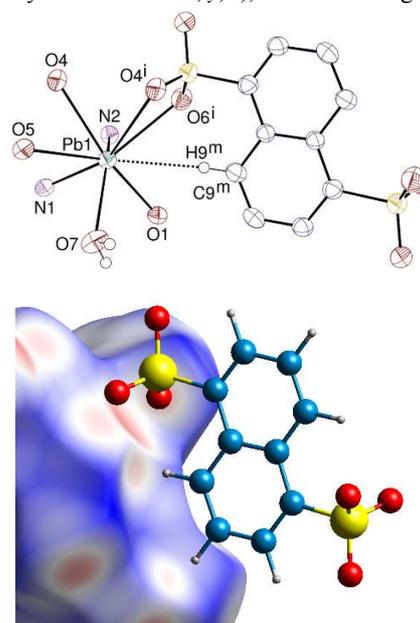
3.276(5) Å, may also be considered as a bonding interaction (see below). The Pb(II) cation is thus in an eight- or seven-coordinate environment, depending on whether the last interaction is considered or not, which has a hemidirected character. The two centrosymmetric 1,5-nds<sup>2-</sup> ligands are bound to either two or four lead atoms, with the sulfonate coordination modes  $\kappa^1O$  and  $\mu_2\text{-}\kappa^2O, O':\kappa^2O, O''$  ( $\mu_2\text{-}\kappa^2O, O':\kappa^1O''$  if the longest bond is disregarded) different from those in the previously reported Pb(II)

complexes.<sup>26,27</sup> With 93 metal complexes reported in the CSD, 1,5-nds is a rather frequent ligand, but no example of the bis-chelating coordination mode observed here has been reported, the sulfonate groups being often mono- or bidentate. A binodal, two-dimensional polymeric network parallel to (0 1 1) is formed in **1**, with the point (Schläfli) symbol<sup>29</sup>  $\{4.6^2\}_2\{4^2.6^2.8^2\}$  (Fig. 3).



**Fig. 3** Views of the two-dimensional assembly (top) and the packing (bottom). Hydrogen atoms are omitted.

The Hirshfeld surface for the asymmetric unit shows that in addition to bonding interactions with Mephen, sulfonates and water (among which bonding to O4<sup>i</sup> appears to be significantly greater than dispersion), the Pb(II) centre has one further interaction involving an aromatic hydrogen atom pertaining to a 1,5-nds<sup>2-</sup> ligand, which is located in the otherwise empty space in the cation coordination sphere (H9<sup>m</sup>...Pb1 3.01 Å, C9<sup>m</sup>–H9<sup>m</sup>...Pb1 174°; symmetry code:  $m = x + 1, y, z$ ), as shown in Fig. 4. This



**Fig. 4** View of the lead(II) environment showing the hydrogen bond as a dashed line (top). Part of the Hirshfeld surface mapped with  $d_{\text{norm}}$  showing the three red dots corresponding to the interactions between Pb(II) and the three atoms O4<sup>i</sup>, O6<sup>i</sup> and H9<sup>m</sup> (bottom).

interaction must be interpreted as a genuine case of hydrogen bonding by Pb(II), having none of the uncertainty associated to the location of water hydrogen atoms.<sup>24</sup> It is notable that a similar situation is found in the closely related complex [Pb(phen)(1,5-nds)(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O],<sup>27</sup> for which the Hirshfeld surface shows a Pb···H-aromatic contact at 3.03 Å, but this was not commented upon. In [Pb<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(1,5-nds)]<sup>26</sup> and [Pb(adpa)(NO<sub>3</sub>)<sub>2</sub>] (adpa = *N*-(9-anthracenylmethyl)-*N*-(2-pyridinylmethyl)-2-pyridinethanamine),<sup>23</sup> however, while there are Pb···H-aromatic approaches at 3.26 and 3.03 Å, respectively, the Hirshfeld surfaces do not indicate interactions beyond dispersion, showing that the detection of any greater degree of interaction may be very subtly influenced by the overall crystal lattice.

Among other intra- or intersheet interactions found in the lattice of **1**, the water ligand is involved in hydrogen bonding to uncoordinated sulfonate oxygen atoms [O···O distances 2.813(6) and 2.884(6) Å], one hydrogen atom of Mephen is possibly involved in CH···π interactions with 1,5-nds<sup>2-</sup> (H···centroid 2.63 Å), and several CH···O(sulfonate) weak hydrogen bonds are present (H···O 2.40–2.93 Å). Several parallel-displaced π-stacking interactions may be present as well [centroid···centroid distances 3.555(4)–4.007(4) Å], but they do not appear to exceed dispersion in the Hirshfeld surface.

The evidence presented herein of Pb(II) lone pair hydrogen bonding reinforces the very extensive computational and indirect experimental evidence of the role of a lone pair of electrons in determining the metal ion's stereochemistry. While there must be a pair of electrons present within the valence shell and thus some consequences of this, the present results, placed in their literature context, also show that the bonding capacity of the lone pair is very limited.

#### Conflicts of interest

There are no conflicts of interest to declare.

#### Notes and references

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† Electronic Supplementary Information (ESI) available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format.

‡ Synthesis of **1**: 1,5-ndsNa<sub>2</sub> (17 mg, 0.05 mmol), Pb(NO<sub>3</sub>)<sub>2</sub> (17 mg, 0.05 mmol), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (25 mg, 0.05 mmol), 5-methyl-1,10-phenanthroline (10 mg, 0.05 mmol), *N*-methyl-2-pyrrolidone (0.2 mL), and demineralized water (0.9 mL) were placed in a 15 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving colourless crystals of complex **1** within one week (14 mg, 40% yield). Anal. calcd. for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>7</sub>PbS<sub>2</sub>: C, 39.15; H, 2.57; N, 3.97. Found: C, 39.19; H, 2.54; N, 4.04%.

§ The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>30</sup> (Mo Kα radiation, λ = 0.71073 Å); they were processed with HKL2000,<sup>31</sup> and absorption effects were corrected with SCALEPACK.<sup>31</sup> The structure was solved by intrinsic phasing with SHELXT,<sup>32</sup> and refined by full-matrix least-squares on F<sup>2</sup> with SHELXL-2014.<sup>33</sup> Drawings were made with ORTEP-3<sup>34</sup> and VESTA.<sup>35</sup> Crystal data for **1**: C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>7</sub>PbS<sub>2</sub>, *M* = 705.70, triclinic, space group P $\bar{1}$ , *a* = 10.7014(3), *b* = 11.1489(4), *c* = 11.3358(6) Å, α = 84.683(2), β = 65.943(2), γ = 63.957(2)°, *V* = 1103.44(8) Å<sup>3</sup>, *Z* = 2. Refinement of 317 parameters on 4194 independent reflections out of 41554 measured

reflections (*R*<sub>int</sub> = 0.067) led to *R*1 = 0.036, *wR*2 = 0.082, *S* = 1.064, Δρ<sub>min</sub> = -2.64, Δρ<sub>max</sub> = 0.80 e Å<sup>-3</sup>.

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