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Beyond holo/hemidirectionality in Pb(II) complexes: Can the valence lone pair be *bisdirected*?

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ABSTRACT

In this contribution, we investigate, by means of Density Functional Theory computations coupled to the analysis of the Electron Localisation Function (ELF), a new possible topology of the Pb^{2+} valence lone pair. The possibility of bisdirectionality is uncovered for the first time and reveals another character of lead complexes beyond holo/hemidirectionality.

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As for most all heavy metals, Lead has no biological role. Whatever its blood concentration, its presence induces a poisoning better known as *saturnism* [1–9]. Few theoretical studies have been devoted to better understand and master the biochemical impact of Pb^{2+} at the molecular scale. Previous quantum chemistry studies performed in our laboratory have shown the importance of the lone pair of the Pb^{2+} cation [10–16]. Indeed, going from penta- to hexacoordination at Pb^{2+} usually implies a relocalisation of the electron density of this lone pair, which is able to redistribute between hemidirected structures (stereochemically active lone pair) and holodirected structures (stereochemically inactive lone pair). Such a transition is pictured on Fig. 1 for tetra- and octaqua complexes using the topological analysis of the Electron Localization Function [17–19], which allows to localize $V(\text{Pb})$, the basin corresponding to the valence lone pair.

Such a topological transition exists whatever the nature of neutral ligand(s) [13,15], but a question remains. Does any other shape for the valence lone pair exist? In this contribution, we explore such a possibility by means of Density Functional Theory (DFT) and the topological analysis of the ELF function.

For flexible ligands, hemidirectionality results from the fact that Pb^{2+} spreads the ligands within a single hemisphere to have its valence lone pair expanding within the other hemisphere. When this is not possible any more due to strong steric and electrostatic interactions between the ligands, holodirectionality is observed and the lone pair loses its stereochemical activity. But what for rigid ligands such as cycles?

Let us first consider a conjugated 5-oxygen cycle (thereafter 'cycle A', described on the top of Fig. 2). As it is too small to keep $\text{Pb}(\text{II})$ in its centre, the cation goes on one side of the cycle, planarity is lost, and a hemidirected structure is engendered. Let us notice that the integrated ELF volume of the oxygen lone pairs amount to about 60 au^3 (vs. 65 au^3 for the non-metallated cycle).

A second possibility occurs when the cycle is large enough to keep the cation inside.

Let us start with a non-planar cycle, e.g. a conjugated 6-sulphur ring (thereafter 'cycle B' depicted on the bottom of Fig. 2). The sulphur atoms are responsible for the non-planarity of the system because of their lone pair spatial organization. Indeed, such lone pairs form two groups. The first one encompasses those pointing towards the cation: they have an ELF integrated volume of 138 au^3 (vs. 160 au^3 for the non-metallated cycle). The second group is made of the lone pairs pointing outside the ring. As they are not constrained by Pb^{2+} , they exhibit a volume of 161 au^3 , comparable to those computed for the non-metallated cycle. Sulphur lone pairs are thus more voluminous than those of oxygen, which explains their alternate distribution and splitting into two groups. This 'steric effect' implies a strong distortion of the ligand: it results to the complexation of the cation on one side. A hemidirected structure is obtained, as shown in Fig. 2 (bottom).

The last possibility is the case of a large enough planar cycle: we here consider a conjugated 6-oxygen ring (thereafter 'cycle C' depicted on Fig. 3). In that case, the oxygen lone pairs exert forces in a planar and equatorial way on the cation. This electronic constraint splits the lone pair into two hemispheres on both sides of the equatorial plane. This illustrates a new behaviour of the valence lone pair of $\text{Pb}(\text{II})$, namely the possibility of being *bisdirected*.

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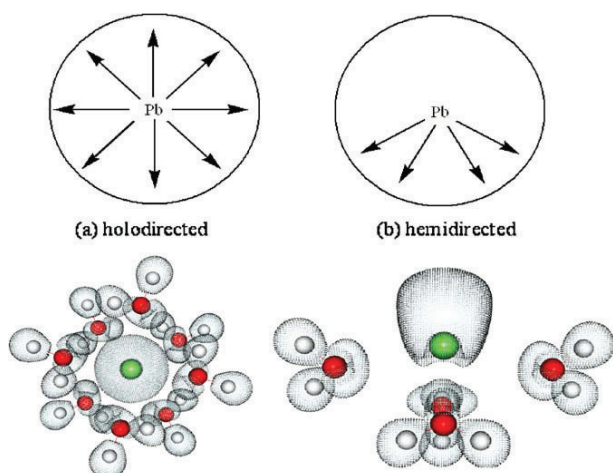


Fig. 1. Holodirectionality vs. hemidirectionality: Pb(II) interacting with 8 (left) and 4 (right) water molecules. Arrows display the ligand distribution [16].

To deeper understand the characteristics of such bisdirectionality, we performed some energy decomposition analysis of the Pb(II)-ligand complexation energies using the Reduced Variational Space (RVS) analysis approach [20] for cycles A and C (Table 1).

We first observe (ΔE values: interaction energies) that cycle C provides a more stable complex with Pb(II) than cycle A. The ligand polarization energies are almost identical whereas the specific cation polarization has a value close to zero when bisdirectionality is encountered. The charge transfer energy contribution is quite lower in the case of bisdirectionality. Indeed, the higher complexation energy for cycle C when compared to cycle A is clearly related to a

larger electrostatic and exchange–repulsion energy, the sum of which constitutes the E_i component of the interaction energy decomposition. This component is able to compensate the loss of charge transfer energy. This energy analysis provides some interesting hints for the development of future new generation molecular mechanics [21–24] dedicated to Pb^{2+} complexes, the results of which will be reported in due time.

To conclude, it is hoped that the present work will stimulate further studies to investigate whether bisdirectionality can have an impact on lead chemistry and spectroscopy.

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Appendix A. Technical Appendix

All ELF computations have been performed with a modified TopMOD package [25,26] using electronic densities computed by GAUSSIAN 03 [27] at the B3LYP/SDD/6-31++G** level on fully optimized structures [28–31].

Details about ELF and its use in bioinorganic chemistry can be found in a recent review paper [12]. RVS computations have been performed at the Hartree–Fock level by means of the GAMESS package [32].

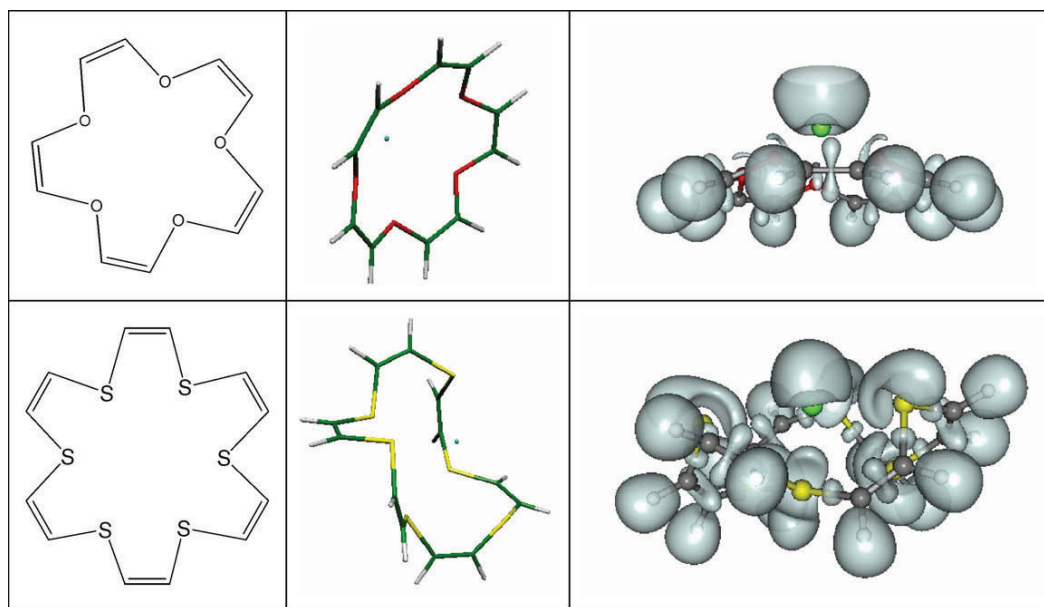


Fig. 2. Top: conjugated 5-oxygen cycle (cycle A: 1,4,7,10,13 penta-oxa-cyclopentadeca-2,5,8,11,14,17 pentaene) interacting with Pb(II): the optimized structure is hemidirected. Bottom: conjugated 6-sulphur cycle (cycle B: 1,4,7,10,13,16 hexathia-cyclooctadeca 2,5,8,11,14,17 hexaene) interacting with Pb(II): the optimized structure is hemidirected.

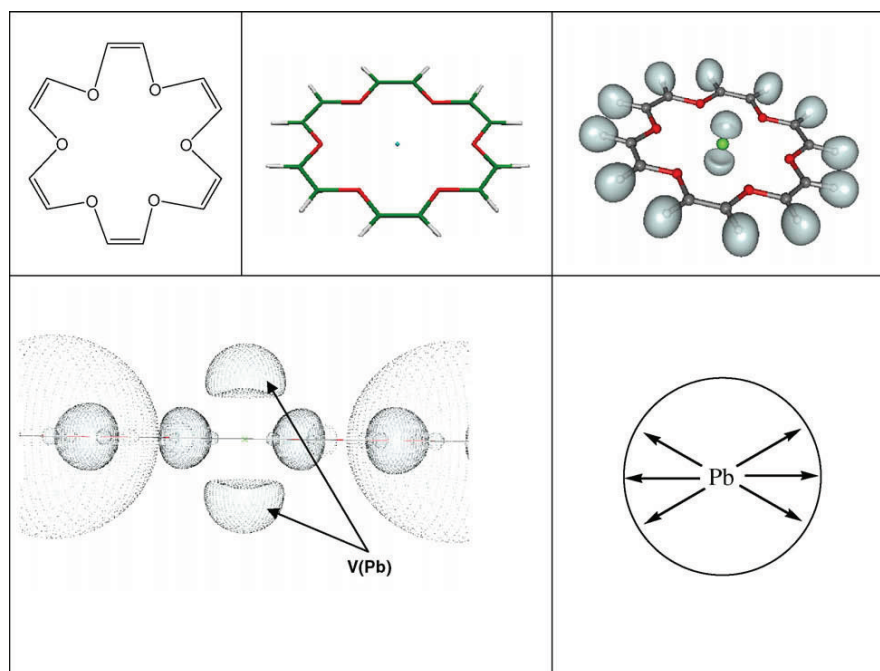


Fig. 3. Conjugated 6-oxygen cycle (cycle C: 1,4,7,10,13,16 hexaoxa-cyclooctadeca-2,5,8,11,14,17 hexaene) interacting with Pb(II): the complex is planar and the valence lone pair appears *bisdirected* as shown by V(Pb), its corresponding ELF basin. Arrows display the ligand repartition.

Table 1

RVS contributions to the Hartree–Fock interaction energies (ΔE , kcal/mol). RVS interaction energies are corrected from the basis set superposition error (BSSE).

	ΔE	E_1	$E_{\text{pol}}(\text{ligands})$	$E_{\text{pol}}(\text{Pb})$	E_{CT}
Cycle A (5–O)	–172	–66	–81	–3.5	–25
Cycle C (6–O)	–184	–89	–84	–0.6	–10

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