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Insight into coordination of dilead unit by molecules of 4-thiazolidinone-2-thione: Structural and computational studies

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ABSTRACT

The reaction of Pb^{2+} ions with 4-thiazolidinone-2-thione (Hrd) yields to coordination of the uncommon dilead unit ($Pb_2{}^{2+}$) by the N-deprotonated molecule of the ligand. The powder structure determination of the complex reveals an almost planar dimeric structure with the {N,S} coordination mode. The intermolecular distance of the Pb–Pb moiety (3.51(4) Å) is lower than the van der Waals parameter suggesting the formation of a bond. The structure in the solid state and DFT calculations of molecular orbitals and the presence of a bond critical point between the lead atoms clearly demonstrate the existence of a single bond within the Pb–Pb unit formed by the 6p orbital electrons. The lone pairs of the 6s orbitals do not participate in bonding with the ligand atoms and are likely bisdirected. FT-IR and FT-Raman spectra confirm the molecular structure since all the modes of the NH group disappear in the spectra of the complex, while the stretching mode of the C=S bond shifts to lower values, as would be expected for this coordination fashion.

1. Introduction

Coordination of lead cations is of considerable interest because of their neurotoxic action in living organisms by binding to the thiol and/or phosphate groups in DNA, proteins, and cell membranes [1,2]. Lead ions are also accumulated in the oxygen-rich sites of bones, where they replace calcium ions [3]. Therefore, there is a need to design a chelating agent that can react with lead ions selectively and efficiently. Although, some molecular structures with the divalent lead ions coordinated to N, S, and O atoms are widely known [4], examples of this cation interacting with a molecule containing all of these atoms have not been reported so far. Presently, we describe a new example of such coordination with 2-sulfanylidene-1,3-thiazolidin-4-one (rhodanine, Hrd) – a simple molecule that belongs to the sulfur-containing N,O-heterocycles. The presence of the thioamide and keto groups yields to a strong ability of the molecule to bind metal ions. And this feature is used in the application of rhodanine as an antimicrobial and antibacterial agent in pharmacology [5,6], and in industry as a binding reagent of Au^{3+}, Pd^{2+}, Pt^{4+}, and Hg^{2+} [7–9]. In our previous work [10] we reported the molecular structure of the rhodanine complex with Ag^{+} ions. Here, the coordination occurs due to the N-deprotonation of the ligand (Rd) and the binding of metal ions *via* the nitrogen and the exocyclic sulfur atoms, whereas the exocyclic oxygen atom remains non-bonded.

Generally, the heterocyclic ligands with the C(=S)–NH– moiety tend to coordinate through the thiolate group, forming a strong M–S bond and a secondary M–N bond. On the other hand, the organic compounds with the C(=O)–NH– group occasionally create, apart from the M–N bonding, the M–O bond [11–13]. Among many complexes of rhodanine derivatives, some of them show the M–S bonding only (complexes with Pd^{2+}, Cd^{2+} and Zn^{2+} ions) [14–16] with bond lengths varying in the wide range of 1.641–2.605 Å. However, there have also been known coordination modes through N, S, and O atoms simultaneously as has been found for complexes with Pd^{2+}, Au^{3+} and Tl^{3+} ions [17,18]. Therefore, it has been claimed that the coordination fashion of this class of organic compounds adopts geometries of various nuclearities with great structural complexity that can be modulated by the nature of the metal ion as well as a substituent attached to the heterocyclic ring [19].

The coordination compounds of the Pb^{2+} ion exhibit rich diverse geometries for which the presence and the activity of the 6s lone pair of electrons is highly responsible [4,20]. In the majority of complexes, this lone pair is stereochemically active (the hemidirected lone pair) and the ligand-to-metal bonds are distributed

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unevenly, throughout only part of the globe around the metal center. For the complexes with the holodirected (stereochemically inactive but binding active) lone pair, the ligand-to-metal bonds are located around the metal ion whereas the bisdirected lone pair is splinted on both sides of the equatorial plane of a complex. Usually, the bonding limit and the angular distribution of ligands are used in classification of the lead coordination. Recently, crystallographic studies have shown that complexes with the Pb–N, Pb–S, and Pb–O bonds arranged in the hemidirected geometry possess a coordination number from 2 to 5 [4]. Furthermore, these studies have revealed that none of these atoms in the ligand structure is preferable as the most probable site of coordination. It is suggested only that for complexes with the coordination number of 4 and 5, the primary lead–ligand bonding exists with the S and O atoms, respectively. The nature of the Pb–S and Pb–O bonding, explained on the basis of DFT for PbO and PbS [21], is chemically dependent on the stereochemically active lone pair of the lead cation. The Pb–O bonding is formed due to coupling of the unfilled 6p orbitals of Pb with the antibonding combination of the Pb 6s and the O 2p orbitals. That results in the net asymmetry of electron density around Pb^{2+}. However, this kind of orbital coupling cannot appear between lead and sulfur atoms because of the higher energy of the S 3p orbitals than those of the oxygen atom, and therefore the more stable and symmetrical distribution of electron density around Pb^{2+} is observed for the PbS bond. Apart from the lead–ligand interactions, the Pb containing compounds also exhibit the dilead contacts. This specific attraction, which overcomes the Coulombic Pb^{2+}–Pb^{2+} repulsion, is possible due to the presence of the relativistically contracted 6s and 6p orbitals of the lead atom. And they result in an enhanced electronegativity of the metal cation and formation of the stable, relatively inert outer lone pair of electrons (the inert-pair effect) [22–24]. On the other hand, the unusual oxidation state of +1 of Pb has been very rarely observed [25], and its chemistry has not been widely discussed [26]. The formation of the covalent Pb^{1+}–Pb^{1+} entity with a bond length of 3.04 Å has been found in the butterfly-like complex with phosphazenide. The bent geometry around the Pb–Pb dimer suggests the involvement of the 6p electrons in bonding, while the 6s electron lone pairs are stereochemically active.

As part of our investigation into the coordination ability of rhodanine, we have studied its complex with lead ions spectroscopically and structurally. The experimental support for the existence of the lead complex of the ligand was gained from the Fourier transform normal Raman (FT-Raman), infrared (FT-IR) spectra as well as from the secondary ion mass spectrometry (TOF-SIMS). These results are consistent with structure determined from X-ray powder diffraction. Insight into the molecular structure of the complex and its vibrational features is additionally provided by DFT calculations.

2. Experimental

2.1. Synthesis of Pb–Rd complex

Hrd, the ligand was bought in POCh SA (powder form, orange, p.a. purity) and used without further purification. Solutions of $(CH_3COO)_2Pb \times 3H_2O$ in methanol were mixed with a solution of Hrd in the methanol in 1:2 or 1:1 mol ratios. After mixing, pH of solutions decreased from 8 (for the Hrd solution) to 5. The mixtures were stirred for 30 min at room temperature. The yellow deposit was filtered out, transferred to the 4× distillated water and stirred another 30 min to eliminate impurities. The color of the solids changed from yellow to dark pink. The UV–Vis spectra of the filtrate indicated the presence of rhodanine (252 and 296 nm) and lead(II) acetate (208 nm) only. No other bands were observed. These spectra were recorded on an Evolution 60 spectrophotometer with a resolution of 1 nm in a region of 190–1100 nm in a quartz cell of 1 cm. The powder was filtered out and rinsed with water. Then, the solids were dried out at room temperature, which yielded a pink powder suitable for the powder diffraction structural analysis. The same method of synthesis was employed by using water as a solvent. FT-MIR spectra of all complexes were identical, which indicates the same molecular structure of the lead complexes. The synthesized complex is insoluble in water, methanol, ethanol, acetone, DMSO, and DMF. Elemental analysis showed that M:L is 1:1, regardless of the M:L molar ratio used initially. *Anal.* Calc. for $C_3H_2NOS_2Pb$ (339.39): C, 10.62; H, 0.59; N, 4.13%. Found: C, 11.06, H, 0.83, N, 3.88%. This molar ratio was confirmed also by AAS.

2.2. Vibrational spectra

For FT-Raman measurements, a few milligrams of solids of Hrd and its lead complex were measured on metal discs directly. Five hundred and twelve scans were collected (with a resolution of 4 cm^{-1}) for Hrd and its complex, respectively. Spectra were recorded on a FT-Raman Spectrometer Nicolet NXR 9650 equipped with a Nd:YAG laser, emitting at 1064 nm, and a germanium detector cooled with liquid nitrogen. The output power of the laser was 300 mW for both samples. Fourier transform mid-infrared (FT-MIR, 256 scans) and Fourier transform far-infrared (FT-FIR, 512 scans) spectra were run in KBr pellets and low molecular weight polyethylene discs, respectively. Resolution was 4 cm^{-1} (MIR) and 2 cm^{-1} (FIR). FT-IR spectra were measured on Bruker (IFS 48) and Bio-Rad (FTS 60 V) spectrometers in the mid and far IR regions, respectively. Frequency accuracy is estimated as ±1 cm^{-1}.

2.3. Powder diffraction

The X-ray pattern was collected on a Philips X'Pert Pro diffractometer with a Bragg–Brentano geometry using Cu Kα radiation ($\lambda = 1.54178$ Å), from 3.5° to 90° 2θ angle, at 298 K. The obtained powder pattern was indexed using the PROSZKI package [27]. The diffraction pattern also contained a few undefined peaks, which may indicate impurities in the sample. However, the low concentration of these impurities did not affect our analysis. A complete model was found by the global optimization method using the program FOX [28]. The Rietveld refinement of the structure was carried out by using the JANA2000 software [29], and was converged to satisfactory agreement factors ($R_p = 9.58\%$, $R_{wp} = 5.56\%$). However, in order to obtain a chemically reasonable crystal structure rigid body refinement was necessary. The March – Dollase function was used for preferred orientation correction [30].

2.4. TOF-SIMS measurements

The TOF-SIMS IV (ION-TOF GmbH, Germany) instrument was used in the recording of mass spectra of the solid sample of Pb–Rd. The conditions of measurement were as follows: beam of Bi_3^+ primary ions with acceleration of 20 eV and beam current of 0.5 pA. The mass spectrum was collected from a surface of 100 μm × 100 μm.

2.5. Computational details

Density functional calculations were carried out for geometry optimization, simulation of electronic structure and vibrational spectra. These calculations were performed with the GAUSSIAN 03 program package [31]. Calculations of molecular structures of the complex were carried out by using the LanL2DZ basis set [32] at