

Research Note

LEWIS BASE ADDUCTS OF LEAD(II)
COMPOUNDS VII*
SYNTHESIS AND STRUCTURAL
CHARACTERIZATION OF MONONUCLEAR
(DICHLORO) (1,4,10,13-TETRA-OXA-7, 16-
DIAZA-CYCLOOCTADECANE) LEAD(II)

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Abstract

The reaction of PbCl_2 with 1,4,10,13-tetra-oxa-7, 16-diaza-cyclooctadecane ($\text{L} = \text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$) yielded colourless crystals of LPbCl_2 . The complex crystallizes in monoclinic space group, $C2/c$, $a = 7.90(2)$, $b = 14.75(3)$ and $c = 17.36(3)$ Å, $\beta = 101.75(3)^\circ$, $Z = 4$ and $R = 0.083$. The coordination number around the lead atom is eight. [Pb-N, 2.36(1), 2.70(4)], [Pb-O, 2.41(3)-2.57(3)], [Pb-Cl, 2.51(4), 2.57(4)].

Introduction

The synthesis of inorganic salts and complexes of lead(II) are of great interest [1-3], particularly since it is believed that the lead(II) ion, by virtue of its large atomic size, is capable of giving a high coordination environment

[4-6]. The feature of the valence shell lone-pair 6s electrons of Pb(II) in most of its complexes has given an exceptional role to this metal ion, and to some extent it is possible to predict its activity or activeness [7]. In this paper, we record a study of one of the lead(II) adducts, in which the lone pair is apparently active.

Keywords: Synthesis and Structure of $(\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4)_2\text{PbCl}_2$

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Experimental Section

Materials

All chemicals were used as obtained without further

purification.

Physical Measurements

Elemental analysis was carried out on a Perkin-Elmer analyzer. Infrared spectrum ($400\text{--}4000\text{ cm}^{-1}$) was recorded on an FT-IR, DR-8001 Shimadzu spectrophotometer with sample prepared as KBr pellet, and melting point by a Gallenkamp melting point apparatus using capillary and without further correction.

Synthesis

To a solution of $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$ (0.26 g, 1 mmol) in water (10 ml) was added an aqueous solution of PbCl_2 (0.28 g, 1 mmol). The reaction vessel was at ambient temperature for 24 hours. The white precipitate product was dissolved in ethanol and filtered off. The filtrate was dried over a water bath and the solid material was crystallized from acetonitrile. Suitable crystals for X-ray diffraction were obtained from 1:1 acetonitrile-ethanol solution. (Found: C, 26.5; H, 4.8; N, 5.2, $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4\text{Cl}_2\text{Pb}$ requires C, 26.6; H, 4.8; N, 5.2%).

Structural Determination

A crystal of the adduct was attached to the end of a glass fiber and mounted on a Siemens R3m/V diffractometer using XTAL program [8]. Intensity data were corrected for Lorentz and polarization effects in the usual manner [9]. The structure was solved via Patterson synthesis. Scattering factors for all atoms were taken from reference [10].

Results and Discussion

On the basis of chemical analysis and room temperature single crystal X-ray studies, 1:1 adduct of L with lead(II)

chloride (Fig. 1) has been authenticated and characterized as discrete mononuclear species, perhaps rather surprisingly in the light of the known bridging behaviour of halide species in their lead(II) complexes [11]. The infrared spectrum of the compound shows that in the solid state, all oxygens and nitrogens are bonded to Pb^{2+} ion. Thus, (N-H C-N and C-O) at 3225 , 1041 and 1097 cm^{-1} are observed respectively, all indicating rather lower frequencies compared with the free ligand. In this complex, the lead(II) atom may be regarded as eight-coordinate $\text{N}_2\text{O}_4\text{PbCl}_2$. An interesting feature of Cl disposition in this structure is that the halides are not perpendicular to the macrocycle pseudo plane (Fig. 2), as is the case in the

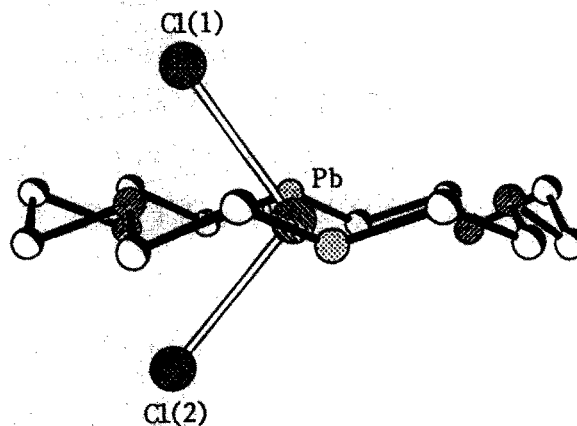


Figure 2. The three dimensional view of the molecule $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4\text{PbCl}_2$ from the angle which shows the activity of the valence shell electron pair of Pb^{2+} . The electrons may be considered as being opposite to the Cl atoms. (The bonds between Pb and the ligand L are omitted for clarity).

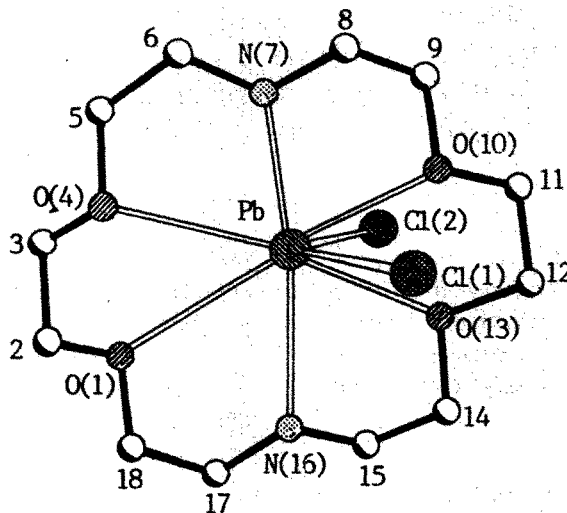


Figure 1. Prospective view and atom numbering of LPbCl_2

complex LPbSCN [12]. Thus, the lone pair valence shell electrons of lead(II) ion are stereochemically active [13], and while the chelate ligand around the central ion shows a pseudo centre of symmetry, two chloride atoms are located at one side of the lead atom with Cl(1)-Pb-Cl(2), 105.6°. Therefore, it can be deduced that Pb and two Cl atoms are at a pseudo C_2 plane of symmetry and the lone pair 6s electrons are opposite the chlorides. Consequently, by virtue of this active lone pair, the coordination number of lead(II) in the complex rises to nine.

Supporting Information Available

A structure determination (Table I), anisotropic thermal parameters, remaining bond length and bond angles and atomic coordinates for the hydrogen atoms (Table II), are available from the authors.

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