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LEWIS BASE ADDUCTS OF LEAD(II) COMPOUNDS IV*, SYNTHESIS AND CRYSTAL STRUCTURES OF (DINITRATO) (1,4,8,11- TETRA-AZAANDECANE) LEAD(II)

A. A. Soudi

Department of Chemistry, Faculty of Sciences, University of Zanjan, P. O. Box 45195/313, Zanjan, Islamic Republic of Iran

Abstract

The synthesis and single-crystal X-ray structure determination of the title compound (dinitrato) (1,4,8,11-tetra-azaandecane) lead(II) is described. Crystals are monoclinic, $P2_1/c$ $a = 10.271$ (2) Å, $b = 13.524$ (4)Å, $c = 11.298$ (6) Å, $\beta = 94.68$ (3), $Z = 4$, R, Rw, 0.036 and 0.041, respectively. The lead atom is eight-coordinate [Pb-N, 2.44 (2) - 2.55 (1)], [Pb-0, 2.87 (1) - 3.06 (2)].

Introduction

Although the aliphatic polyamines have a major role in coordination chemistry, and their complexes with some transition metal ions have been investigated in recent years [1], only a few synthesis and structural studies of their complexes with lead(II) have been reported to date [2-6]. To develop knowledge of the interaction of Pb (II) with the variety of these ligands, the synthesis and structural characterization of 1:1 adduct of lead(II) nitrate with $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$(1,4,8,11-tetra-azaandecane)(L) is reported.

Experimental Section

Physical Measurements

Elemental analysis was carried out on a Heraeus elemental analyser, CHN-O-RAPID. Infrared spectrum was recorded on a Perkin-Elmer 297 spectrophotometer. X-ray crystallographic data were collected with an Enraf-Nonius CAD4 diffractometer.

Keywords: Synthesis and structure of tetramine lead(II) nitrate

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Preparation of LPb $(NO_3)_2$

0.331 g (1.0 mmol) of $Pb(No_3)_2$ in fine powder form was placed at the bottom of a branched glass tube and a solution of 0.16 g (1.0 mmol) of the ligand (L) in 25 ml of ethanol was poured into the tube. The end of the tube containing $Pb(NO_3)_2$ was kept in an oil bath at 333 K and the other end at ambient temperature (*ca* 292 - 294 K). After a few days, crystals formed in the lower temperature region were filtered off, washed with ethanol and ether then air dried, yield 0.38 g, 78%. Anal. calcd. for $C_7H_{20}N_6O_6Pb$: C, 17.10; H, 4.10; N, 17.10. Found: C, 17.14; H, 4.09; N, 17.08%.

X- ray Structural Determinations

The approximate unit-cell dimensions were determined from rotation and Weissenberg photographs. A crystal of dimensions 0.30 x 0. 33 x 0.40 mm was attached to the end of a glass fiber and mounted on the diffractometer, employing graphite-monochromated Mo Kα radiation. More accurate unit-cell dimensions and the orientation matrix used for data collection, were obtained from a least-squares fit of the setting angles of 20 reflections. The intensities of 1822 independent reflections were measured at room temperature by θ-2θ scan technique. The structure

was solved by Patterson heavy atom method using SHELXS 86 [7]. The positions of all hydrogen atoms were determined from successive Fourier difference maps after isotropic refinement. Refinement was by full-matrix least-square techniques based on F to minimize the quantity of $\Sigma w (|F_o| - |F_c|)^2$ with $w = 1\sigma^2(F)$ using XTAL program [8]. Scattering factors for all atoms were taken from reference 9. Crystallographic data, selected bond lengths and angles are given in Tables I and II, respectively.

Results and Discussion

The infrared spectrum shows that in the solid state nitrate anions are also coordinated. The N-O stretching frequency was observed as a very strong, broad band centered at 1380 cm^{-1} and in addition there are three weak bands at 1765, 1745 and 1735 cm^{-1} which are assigned to nitrate combination frequencies. The latter bands are particularly indicative of coordinated nitrate (monodentate and/or bidentate) [10].

The crystal structure of the adduct (Figure 1) has been determined in order to establish the exact coordination sphere lead(II) centers and the mode of coordination of NO_3^- anions. The lead atoms are eight coordinate, PbN_4O_4; four of the coordination sites are occupied by the nitrogen atoms of the quadridentate ligand.

The ligand coordination is an asymmetrical open chain in which Pb-N distances vary from 2.44Å to 2.55Å. Hydrogens of N2 and N3 are disposed either side and the lead atom is 1.38Å out of the main N4 plane of the ligand (L). This is similar to a macrocyclic tetramine lead(II) complex which was synthesized earlier [11]. There is one symmetrically bidentate nitrate anion with Pb-01 = 2.87 (1)Å and Pb-02 = 2.91 (2)Å and two NO_3^- which are bidentate to two different Pb^{2+} ions, bridging between two LPb^{2+} moieties. The most reasonable explanation is that the lone pair of the Pb^{II} occupies part of the space between 01, 02, 04, 07, although not as much as an individual ligand atom.

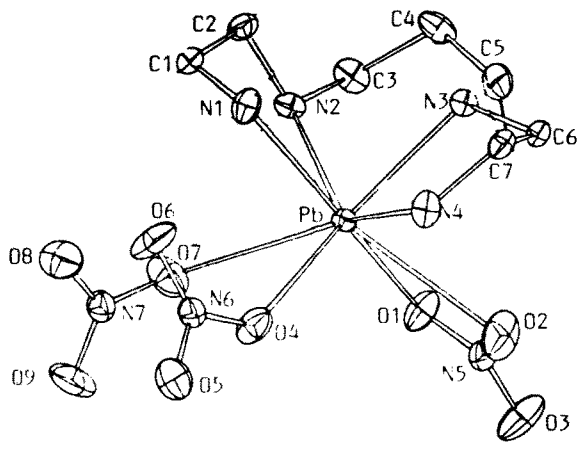

Figure 1. Prospective view and atom numbering of LPb $(NO_3)_2$

Table I. Crystallographic data

formula	Pb $(C_7H_{20}N_4)$ $(NO_3)_2$
fw	491.48
crystal system	monoclinic
space group	$P2_1/c$
a, Å	10.271 (2)
b, Å	13.524 (4)
c, Å	11.298 (6)
β, deg	94.68 (3)
V, Å^3	1569 (2)
Z	4
d_{calc}, g/ cm^3	1.89
cryst size, mm^3	0.30 x 0. 33 x 0.40
temp, °C	22 ± 2
μ (MoKα), cm^{-1}	131.3
radiation (graphite monochromated)	MoKα (λ = 0.72031 Å)
range of transmission factors	0.24 - 0.52
scan method	θ - 2θ
data collcn range (2θ), deg	2-48
range of h, k, l	+ 16, +21, +29
no. of reflcns measd	1822
no. of unique data (I > 2.5 σ (I))	1685
R, R_w	0.036, 0.041

Table II. Selected bond distances (Å) and angles (deg) of LPb $(NO_3)_2$

Pb-N1	2.44(2)	Pb-O1	2.87(1)
Pb-N2	2.46(4)	Pb-O2	2.91(2)
Pb-N3	2.55(1)	Pb-O4	3.06(2)
Pb-N4	2.47(2)	Pb-O7	3.03(1)
N1-C1	1.46(6)	N4-C7	1.48(4)
C1-C2	1.55(5)	C7-C6	1.52(2)
N1-Pb-N2	73.4(5)	C1-N1-Pb	108.1(2)
N1-Pb-N3	83.6(2)	C2-N2-C3	115(4)
N1-Pb-N4	74.8(3)	N1-Pb-04	83.6(2)
O1-Pb-O4	108.2(6)	N1-Pb-O2	155.1(5)
O2-Pb-O7	110.4(4)	N2-Pb-O4	102.3(4)
O1-N5-O2	119(3)	N1-Pb-O7	101.8(5)

References

1. Wilkinson, G. *Comprehensive coordination chemistry*, Pergamon Books Ltd., **2**, 23-72, (1987).
2. Miyamae, H., Toriyama, H., Abe, T., Hihara, G. and Nagata, M. *Acta Cryst.*, **C40**, 1559, (1984).
3. Hihara, G., Miyamae, H. and Nagata, M. *Chem Lett.*, 1653, (1985).
4. Hihara, G. , Mitani , K., Miyamae, H. and Natata, M. *Bull. Chem. Soc. Jpn.*, **60**, 1361, (1987).

5. Miyamae, H., Yoshinara, K., Hihara, G. and Nagata, M. *Acta Cryst.*, **C44**, 1528, (1988).
6. Miyamae, H., Nishikawa, H., Hagitome, K., Hihara, C. and Nagata, M., *Chem. Lett.*, 1907, (1988).
7. Sheldrick, G. M. *SHELX 86, Program for the crystal structures*, University of Gottingen, F.R.G., (1987).
8. Hall, R. H. and Stewart, J. M., *XTAL, Users manual version*, 2.4 U. W. A. Press, (1988).
9. *International tables for X-ray crystallography*, Kynoch. Birmingham, England. Vol. 4, (1974).
10. Addison, C.C., Logan, N., Wallwork, S. C. and Garner, C. D. *Q. Rev. Chem. Soc.*, **25**, 289, (1971).
11. Alcock, N. W., Herron, N. and Moore, P. *J. Chem. Soc., Dalton Trans.*, 1486, (1979).