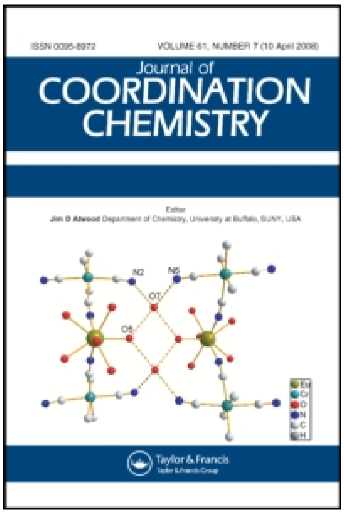

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A LEAD(II) COMPLEX WITH ETHYLENEDIAMINE CONTAINING A BRIDGING ACETATE GROUP: DIRECT SYNTHESIS AND CRYSTAL STRUCTURE

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To cite this Article Polyakov, Valery and Kokozay, Vladimir(1994) 'A LEAD(II) COMPLEX WITH ETHYLENEDIAMINE CONTAINING A BRIDGING ACETATE GROUP: DIRECT SYNTHESIS AND CRYSTAL STRUCTURE', Journal of Coordination Chemistry, 32: 4, 343 — 347

To link to this Article: DOI: 10.1080/00958979408024253

URL: http://dx.doi.org/10.1080/00958979408024253

J. Coord. Chem., 1994, Vol 32, pp. 343–347
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A LEAD(II) COMPLEX WITH ETHYLENEDIAMINE CONTAINING A BRIDGING ACETATE GROUP: DIRECT SYNTHESIS AND CRYSTAL STRUCTURE

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(Received November 16, 1993)

A direct method of obtaining $PbEnAc_2$ (Ac = CH_3COO En = ethylenediamine) is reported. The crystal structure of the compound was determined by X-ray techniques. $PbEnAc_2$ is monoclinic, space group $P2_1/c$, with cell parameters $a = 5.532(1)$, $b = 24.185(5)$, $c = 7.630(1)$ Å, $V = 1010.22(47)$Å^3, $Z = 4$; calculated density is 2.534 g/cm^3. Two different types of acetate group were found. The first is cyclic and the second is bridging. The bridging acetate group links neighboring lead atoms into polymeric chains.

KEYWORDS: lead (II), X-ray structure, ethylenediamine, acetate

INTRODUCTION

Diffusion through the product forming at the reaction surface largely influences lead oxide reactions with ammonium salts solutions.[1] Shortage of ligand diffusing to the reaction surface can be one of the reasons for ethylenediamine bridging in the compound $PbEn_2Br_2$, obtained by direct synthesis.[2] While continuing development of direct synthesis methods with metal oxides, we have prepared and investigated a lead(II) complex with ethylenediamine.

EXPERIMENTAL

The preparation of initial compounds, methods of synthesis and investigation of products are similar to those reported[3]. For the preparation of $PbEnAc_2$, the following method was used. Some 2.23 g (0.01 mol) of PbO, 1.54g (0.02 mol) of NH_4Ac, 20 cm^3 of dimethylsulfoxide (DMSO) and 1.34 cm^3 (0.02 mol) of ethylenediamine (En) were placed in a flask and the mixture was stirred for one hour at 50 – 60°C. The resulting colourless solution was allowed to stand at room temperature. This resulted in crystals separating from the solution. These were filtered, washed with dry isopropanol, and dried *in vacuo* at room temperature

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(yield: 2.85 g (74%)). Calcd. for $PbEnAc_2$: Pb, 53.77; N, 7.27; C, 18.70; H, 3.66%. Found: Pb, 53,0; N, 7.1; C, 18.7; H, 3.6%.

It should be noted that variation of initial PbO:En mol ratios in the range 1:1 – 3 does not influence complex composition. The best yield was found for PbO:En near 1:2. This complex is colourless and insoluble in water. $PbEnAc_2$ dissolves in DMF and DMSO on heating.

Infrared spectra were recorded on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. Absorptions characteristic of acetate ion were found at $\nu_{as}(CO)$ = 1560 cm^{-1} and at $\nu_s(CO)$ = 1400 cm^{-1}. The difference between the absorptions (160 cm^{-1}), according to ref. 4, indicate bridging acetate groups.

Crystallographic measurements were made at 20°C using an Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$-scan mode (the ratio of scanning rates, ω/θ, was 1.2). The intensities of 2236 unique reflections were collected within the range $2 \leq \theta \leq 56°$ using graphite-monochromated MoKα radiation (λ = 0.71073Å). The structure was solved with direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement 1638 reflections with $I \leq 36$ (I) were used. About 60% of hydrogen atoms were located in difference Fourier maps; positions of the remaining hydrogen atoms were calculated. All hydrogen atoms were included in the final refinement with fixed positional and thermal ($Biso = 6$ Å^2) parameters. Convergence was obained at $R = 0.027$ and $R_{\omega} = 0.039$; *GOF* was 1.46 (118 refined parameters; largest peak in the final difference map was 0.90 e/Å^3); the weighting scheme ω = $\{\Delta^2(F) + 0.0016\ F^2\}^{-1}$ was used. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using the DIFABS program[5] were applied. All structural calculations were carried out with a PDP-11/23+ computer using SDP-PLUS software.[6] Positional and thermal parameters (B_{eq}) derived from the last cycle of least square refinement, along with their associated standard deviations are presented in Table 1.

Crystal data for compound of composition $C_6H_{14}N_2O_4Pb$ are as follows: monoclinic, space group $P2_1/c$, cell parameters a = 5.532(1), b = 24.185(5), c = 7.630(1) Å, V = 1010.22(47) Å^3, Z = 4; calculated density is 2.534 g/cm^3; μ = 168.1 cm^{-1}, $F(000)$ = 712.

Table 1 Final coordinates (Å) and standard deviations (in parentheses).

	x/a	y/b	z/c	B_{eq}*
Pb	0.63847(5)	0.35963(1)	1.01950(4)	2.587(5)
O(1)	0.2988(9)	0.3070(2)	0.8619(7)	2.9(1)
O(2)	0.563(1)	0.2435(2)	0.9723(9)	4.3(1)
O(3)	1.043(1)	0.4135(3)	1.0131(8)	4.3(1)
O(4)	1.374(1)	0.4523(3)	1.1615(8)	4.4(1)
N(1)	0.791(1)	0.3355(2)	0.7503(8)	2.4(1)
N(2)	0.475(1)	0.4244(2)	0.8021(9)	2.9(1)
C(1)	0.359(1)	0.2571(3)	0.893(1)	2.7(1)
C(2)	0.172(2)	0.2139(3)	0.828(1)	3.8(2)
C(3)	1.153(1)	0.4417(3)	1.1395(9)	2.3(1)
C(4)	1.003(2)	0.4656(3)	1.271(1)	3.6(2)
C(5)	0.755(1)	0.3809(3)	0.623(1)	2.9(2)
C(6)	0.508(2)	0.4061(3)	0.623(1)	3.6(2)

* The temperature factors have the form B_{eq} = 4/3 $\{B_{11}a^2a^{*2} + ...2B_{23}bcb^*c^*\cos\alpha\}$.

DISCUSSION

The close lead atom coordination environment shown in Figure 1 is formed by two ethylenediamine nitrogen atoms, N(1) and N(2), and two oxygen atoms of each acetate group, 0(1) and 0(2); approximate bonds distances are 2.4 - 2.6 Å (Table 2). The remote environment is formed by two other acetate oxygen atoms, 0(2) and 0(4b), which are located at a distance from the lead atom of 2.9 - 3.0 Å. We have observed such a distinction in bonds lengths for lead complexes earlier[7,8] and one can explain this effect by means of different electron participation in bond formation.

The lead atom is deviates only a little (0.18 Å) from the plane formed by O(2), O(3) and O(4b) towards the coordinated ethylenediamine molecule. The lone electron pair is evidently located on the other side of this plane[9]. Therefore, the donor atoms of nearest coordination environment form a bisphenoid, which, taking into account the further environment and the lone electron pair, is transformed into a capped octahedron.[9]

There are two different chelated acetate groups in the complex, cyclic and bridging. Both lead - oxygen interatomic distances for the bridging group are 0.1 - 0.2 Å longer then for the cyclic group. We have previously observed such bridging bond enlargement for ethylenediamine[2].

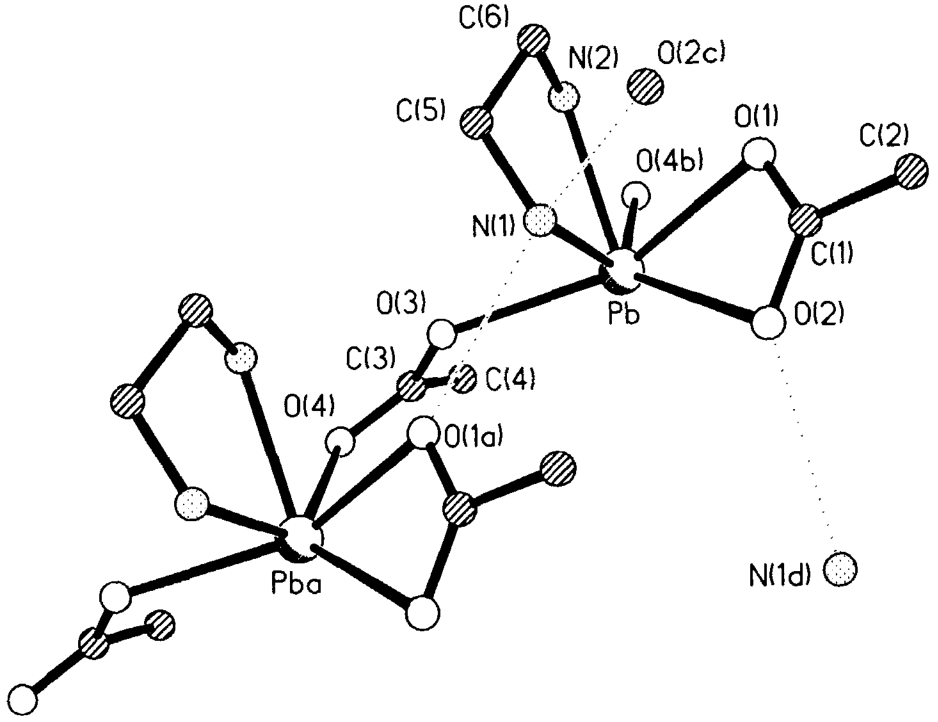

Figure 1 Fragment of the PbEnAc$_2$ polymeric chain. The presupposed H-bonds are shown as dotted lines. Symmetry codes: a) 1 + x,y,z; b) -1 + x, y, z; c) x, 0.5 + y, -0.5 + z; d) x, 0.5 + y, 0.5 + z.

Table 2 Internuclear distances (Å) and angles (deg).

(1)	Coordination polyhedron of Pb(II).		
Pb-O(1)	2.439(5)	O(1)-Pb-O(2)	48.4(2)
Pb-O(2)	2.855(5)	O(1)-Pb-O(3)	149.1(2)
Pb-O(3)	2.595(6)	O(1)-Pb-O(4)	100.9(2)
Pb-O(4b)	2.967(6)	O(1)-Pb-N(1)	78.0(2)
Pb-N(1)	2.403(6)	O(1)-Pb-N(2)	79.0(2)
Pb-N(2)	2.366(6)	O(2)-Pb-O(3)	127.1(2)
		O(2)-Pb-O(4)	136.0(2)
		O(2)-Pb-N(1)	73.5(2)
		O(2)-Pb-N(2)	121.9(2)
		O(3)-Pb-O(4)	95.7(2)
		O(3)-Pb-N(1)	72.3(2)
		O(3)-Pb-N(2)	84.2(2)
		O(4)-Pb-N(1)	138.5(2)
		O(4)-Pb-N(2)	66.2(2)
		N(1)-Pb-N(2)	73.0(3)
		Pb-O(1)-C(1)	103.8(4)
		Pb-O(2)-C(1)	84.6(5)
		Pb-O(3)-C(3)	125.4(5)
		Ph-O(4)-C(3)	109.0(5)
		Pb-N(1)-C(5)	110.7(4)
		Pb-N(1)-C(5)	110.7(4)
		Pb-N(2)-C(6)	111.4(4)
(2)	Cyclic acetate group		
O(1)-C(1)	1.266(8)	O(1)-C(1)-O(2)	122.8(7)
O(2)-C(1)	1.245(9)	O(1)-C(1)-C(2)	116.6(6)
C(1)-C(2)	1.51(2)	O(2)-C(1)-C(2)	120.6(6)
(3)	Bridging acetate group		
O(3)-C(3)	1.265(9)	O(3)-C(3)-O(4)	125.1(7)
O(4)-C(3)	1.23(1)	O(3)-C(3)-C(4)	117.6(7)
C(3)-C(4)	1.51(1)	O(4)-C(3)-C(4)	117.2(6)
(4)	En molecule		
N(1)-C(5)	1.459(9)	N(1)-C(5)-C(6)	110.3(7)
N(2)-C(6)	1.48(2)	N(2)-C(6)-C(5)	110.8(6)
C(5)-C(6)	1.49(1)		

The cyclic acetate group is coordinated to the lead atom through 0(1) and 0(2) atoms and forms a four-membered ring where the angle O(1)-C(1)-O(2) is *ca* 122° and the angle O(1)-Pb-O(2) is *ca* 48°. A difference in Pb-O(1) and Pb-O(2) bond (≈ 0.4 Å) distances testifies to the acetate group having a pseudochelate function.[10] All atoms of this group are located in a plane. The lead atom deviates from this plane by 0.25 Å. The dihedral angle between planes formed by O(2), O(3), O(4b) and Pb, O(1), O(2) atoms is 46.3°.

The second acetate group is a bridging one and links neighboring lead atoms into polymeric chains. The bridging group is distorted slightly more than the cyclic one (the angle O(3)-C(3)-O(4) is *ca* 125° and C(3) atom is deflected 0.01 Å from the plane formed by other atoms of this group).

The cyclic En molecule forms a five-membered ring where the angle N(1)-Pb-N(2) is 73.0°. The Pb-N-C angles are close to tetrahedral, as is characteristic for this ethylenediamine coordination manner. The N-C distances are 1.47 Å, and C-C 1.49 Å. The En molecule possesses the *gauche* conformation with a dihedral angle of 56°.

In the structure, there are two presupposed H-bonds: N(1)...O(1a) ($1+x, y, z$) and

N(1)...O(2c) (x, $0.5+y$, $-0.5+z$). The first has a length of 2.897 Å and links the noted atoms of one polymeric chain. The second is weaker (2.996 Å) and links different polymeric chains.

Supplementary Data

Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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