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LEWIS-BASE ADDUCTS OF LEAD(II) COMPOUNDS VI.* SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MONONUCLEAR (DIACETATO-O,O')(1,10-PHENANTHROLINE) LEAD(II)

A. A. Soudi

Department of Chemistry, Faculty of Sciences, University of Zanjan, Zanjan, Islamic Republic of Iran

Abstract

The synthesis and single-crystal X-ray structure determination of the title compound (phen)$Pb(O_2CMe)_2$ is described. The complex crystallizes in the monoclinic space group $P2_1/c$, $a = 7.823(3)$, $b = 12.421(4)$, $c = 9.262(2)$ Å, $\beta = 79.92(3)°$, $Z = 4$, yielding R 0.048 for 3210 independent reflections. The coordination number around the lead atom is six. [Pb-N 2.54(2), 2.56(4)],[Pb-0, 2.19-2.22].

Introduction

In 1962, Pirtea *et al.* reported the complex formation of Pb(II) with 1,10-phenanthroline [1], in which metal/ligand stoichiometries had the range of 1:1 to 1:4 and the coordination number of 6,8,9 or 10 for Pb(II) center was predicted. In spite of this variety, only a few crystal structures of these complexes have been reported to date [2, 3]. The structural determination of only one 1:1 adduct of this type is known and this contains lead(II) with a coordination number of nine [4]. In this paper, the synthesis and characterization of a 1:1 adduct in which lead(II) has a coordination number of six is reported.

Experimental Section

Materials

All chemicals were used as obtained without further purification.

Keywords: Molecular structure; (phen)$Pb(O_2CMe)_2$; Synthesis

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Physical Measurements

Elemental analysis was carried out on a Heraeus elemental analyzer, CHN-O-RAPID. Infrared spectrum was recorded on a Perkin-Elmer 297 spectrophotometer and melting point by a Gallenkamp melting point apparatus, using a capillary and without further correction.

Synthesis

1,10-phenanthroline monohydrate (0.14 g, 0.7 mmol) was dissolved in methanol (30 mL), a solution of lead(II) acetate trihydrate (0.26 g, 0.7 mmol) in methanol (10 mL) was added and the solution allowed to stand. Overnight, a crop of yellow-white crystals of increasing size deposited. The crystals were filtered off, washed with methanol and dried *in vacuo*. The melting point was 267°C. (Found: C, 37.98; H, 2.80 N, 5.55, $C_{16}H_{14}N_2O_2Pb$ requires C, 38.01; H, 2.77; N, 5.53%).

Structure Determination

A suitable crystal of the adduct was attached to the end of a glass fiber and mounted on a Syntex diffractometer using XTAL program system on a SUN computer. Unit cell of the compound at 20°C was obtained by least-square fits of the setting angles of 28 reflections. The data are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects in the usual manner [5]. The structure was solved via Patterson and Fourier synthesis. The function minimized during least-squares refinements was $\Sigma_w(|F_o|-|F_c|)^2$ with final convergence to $R=\Sigma||F_o|-|F_c||\Sigma|o|=0.048(w=1\sigma^2(1))$. Scattering factors for all atoms were taken from reference 6.

Table I. Crystal data for (phen)Pb(O_2CMe)$_2$

formula	$(C_{12}H_8N_2)Pb(CH_3CO_2)_2$
fw	505.48
space group	$P2_1/c$
a, Å	7.823(3)
b, Å	12.421(4)
c, Å	9.262(2)
β, deg	79.92(3)
V, Å	899.99(4)
Z	4
d_{calc}, g/cm^3	1.92(2)
cryst.size	0.34 × 0.26 × 0.41
μ, cm^{-1}	94.8
radiation (monochromated in incident beam)	MoKα(λ = 0.78022 Å)
temp, °C	20±2
transm factors: max, min	0.920, 0.821
R	0.048
R_w	0.059

Results and Discussion

The reaction of 1,10-phenanthroline with Pb(MeCO$_2$)$_2$.3H$_2$O in methanolic solution (1:1) at room temperature was found to produce crystals of (phen)Pb(O_2CMe)$_2$. The infrared spectrum of the compound clearly shows that in the solid state both acetate anions are also coordinated. Thus ν (CO_2) at 1555 and 1421 cm^{-1} are observed, indicating the presence of a bidentate MeCO$_2$ ion [7]. Crystals of the adduct consist of (phen)Pb(II) units (Figure 1) with

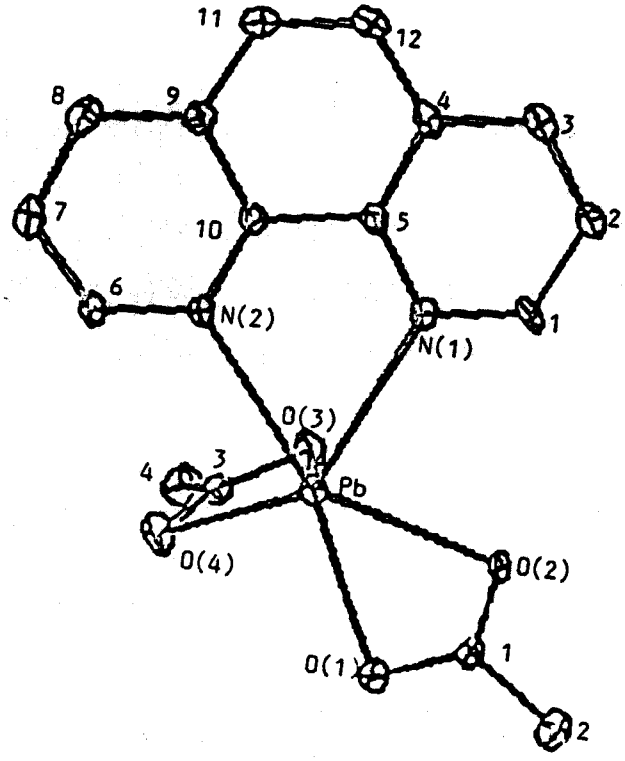

Figure 1. Prospective view and atom numbering of (MeCO$_2$)$_2$Pb(phen).

acetate anions bound to the lead(II) center. The average Pb-O bond is 2.204 Å, characteristic of bidentate acetato-metal bonding [7]. Two acetate planes are diverted from perpendicular planes to the plane of (phen)Pb(II) by 41.2°. Both acetate planes are coplanar with Pb(II), but those two planes are unsymmetrical. The Pb-N bond lengths in the complex are 2.54(2) and 2.56(4) which are consistent with previous reports [3,4]. The lead(II) center attains a coordination number of six (two Pb-N and four Pb-O interactions) and the lead atom does not deviate from the 1,10-phenanthroline plane as it does in bis(phen)Pb(II)^{II} adduct [3]. The reason may be due to the lack of the second 1,10-phenanthroline. In the complex, there is a large vacancy in the coordination sphere between the two acetate ions possibly indicative of a stereochemically active lone pair [8].

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