LEWIS-BASE ADDUCTS OF LEAD(II) COMPOUNDS V.* SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MONONUCLEAR (ACETATO-0,0') BIS(2,2'-BIPYRIDINE) (PERCHLORATO-0,0') LEAD(II) AND BIS(2,2'-BIPYRIDINE) BIS(PERCHLORATO-0,0') LEAD(II)

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Abstract

The synthesis and single-crystal X-ray structure determination of the title compound [$(bipy)_2 Pb(O_2CMe)(O_2ClO_2)$] (**1**) and [$(bipy)_2 Pb(ClO_4)_2$] (**2**) is described. Compound (1) crystallizes in the triclinic space group $P1(2)$, a= 7.384(2), b= 12.824(3), c= 10.622(6) Å, α= 73.41(2), β= 80.98(2), γ= 73.68(2)°, Z= 2, and R= 0.033 for 3408 independent reflections. Compound (**2**) crystallizes in the monoclinic space group $P2_1/n(14)$, a= 6.883(5), b= 13.010(4), c= 10.710(5) Å, β= 91.26(2)°, Z= 2, and R= 0.048 for 3290 independent reflections.

Introduction

The coordination chemistry of lead(II) with 2,2-bipyridine(bipy) has been investigated since 1976 [1], although not extensively. However, until recent years there was no report of any single-crystal X-ray determination for this series of complexes [2]. The coordination number of Pb(II) centers in these types of complexes usually exceeds six and coordination numbers of 8, 9 and 10 with very irregular coordination polyhedra appear to be quite common [3].

As part of the continuing structural and synthetic studies of Pb(II)-nitrogen donor ligands, here the synthesis and structure of the mononuclear (acetato-O,O') bis(2,2'-bipyridine)-(perchlorato-O,O') lead (II) and bis(2,2'-bipyridine) bis(perchlorato-O,O') lead(II), which are novel compounds of their type, are reported.

Keywords: $(bipy)_2 Pb X_2$ type complexes

*Part IV. *J.Sci. I.R. Iran*, 6,4, 220-222, (1995).

Experimental Section

Materials

All chemicals were used as obtained without further purification.

Physical Measurements

Elemental analysis was carried out on a Heraeus elemental analyser, CHN-O-RAPID. Infrared spectra were recorded on a Perkin-Elmer 297 spectrometer.

Preparation of [$Pb(bipy)_2(O_2CMe)(ClO_4)$]. (1)

A mixture of 1:1 ratio of lead(II) perchlorate hexahydrate (0.25 g, 0.5 mmol) and lead(II) acetate trihydrate (0.19 g, 0.5) in methanol (10 ml) was added to hot solution of 2,2'-bipyridine(0.31 g, 2 mmol) in methanol (20 ml),

Table I. Crystal data for (1) and (2)

	(1)	(2)
formula	$(C_{20}H_{16}N_4)$ $Pb(ClO_4)$ (CH_3CO_2)	$(C_{20}H_{16}N_4)$ $Pb(ClO_4)_2$
fw	678.07	718.57
space group	$P1(2)$	$P2_1/n(14)$
a, Å	7.384(2)	6.883(5)
b, Å	12.824(3)	13.010(4)
c, Å	10.622(6)	10.710(5)
β, deg	80.98(2)	91.26(2)
V, Å^3	1005.82(2)	959.06(5)
Z	2	2
dcalc, g/cm^3	1.87(3)	1.91(2)
crst. size mm^3	0.29 x 0.31 x 0.38	0.36 x 0.28 x 0.40
μ, cm^{-1}	95.9	97.2
radiation(monochromated in incident beam)	Mo kα (λ= 0.71073 Å)	Mo kα (λ= 0.76181 Å
temp, °C	20±2	20±2
transm factors: max, min	0.998, 0.829	0.968, 0.812
R	0.033	0.048
R_w	0.045	0.041

Table II. The final positional parameters for $(MeCO_2)$ $Pb(bipy)_2$ (O_2ClO_2)

Atom	x	y	z	x	y	z
Pb	0.2261(2)	0.01231(3)	0.06351(5)			
	2,2'bipyridine ligands					
	Ligand 1= 1				Ligand 1= 2	
N(1a)	0.12118(5)	0.08231 (2)	0.2189(8)	0.2903(8)	0.1211(9)	0.3621
C(1a1)	0.106(2)	0.231(1)	0.248(2)	0.298(1)	0.249(2)	0.451(2)
C1(1a2)	0.024(1)	0.282(2)	0.323(1)	0.319(2)	0.331(1)	0.528(2)
C(1a3)	-0.042(2)	0.231(1)	0.340(1)	0.343(2)	0.256(1)	0.652(1)
C(1a4)	-0.025(1)	0.112(2)	0.292(1)	0.348(1)	-0.105(2)	0.613(2)
C(1a5)	0.059(1)	0.029(2)	0.238(1)	0.341(2)	-0.038(1)	0.521(1)
C(1b5)	0.082(1)	-0.091(1)	0.169(2)	0.357(1)	0.108(2)	0.383(1)
C(1b4)	0.017(1)	-0.168(2)	0.189(1)	0.391(1)	0.173(2)	0.431(1)
C1(1b3)	0.030(1)	-0.298(2)	0.132(2)	0.412(1)	0.323(2)	0.351(1)
C(1b2)	0.117(1)	-0.341(1)	0.081(2)	0.398(1)	0.363(2)	0.195(1)
C(1b1)	0.186(2)	-0.285(2)	0.083(2)	0.351(1)	0.290(2)	0.123(2)
N(1b)	0.1599(4)	-0.1618(7)	0.1471(8)	0.3438(6)	0.1866(9)	0.1939(6)
	Perchlorate					
C1	0.4152(8)	-0.3126(6)	0.1462(12)			
O(1)	0.3912(7)	-0.2856(12)	0.0899(6)			
O(2)	0.5334(6)	-0.3673(9)	0.2231(8)			
O(3)	0.4731(8)	-0.1326(12)	0.1123(7)			
0(4)	0.3941(2)	-0.2319(8)	0.0961(8)			
	Acetate					
C(1)	0.1841(4)	0.3431(6)	-0.5143(6)			
O(5)	0.3329(7)	0.2376(8)	-0.2039(2)			
O(6)	0.2931(2)	0.3114(10)	-0.0926(8)			
C(2)	0.1948(10)	0.3662(12)	-0.2633(8)			

and the mixture allowed to stand. The crystals of the adduct were deposited overnight and were filtered off, washed with methanol and air-dried. Found: C, 38.89; H, 2.82; N, 8.30. $C_{22}H_{19}N_4O_6PbCl$ requires C, 38.93; H, 2.80; N, 8.26%. The compound (**2**) was prepared by the same method while the amount of lead(II) perchlorate hexa hydrate was used two folded (0.51 g, 1 mmol), therefore lead(II) acetate was not used.

Found: C, 33.12; H, 2.25; N, 7.75 $C_{20}H_{16}N_4O_8PbCl_2$ requires C, 33.40; H, 2.23; N, 7-79%.

Structure Determination

Colorless crystals of the adducts were attached to the end of a glass fiber and mounted on a CAD4 diffractometer, employing graphite monochromated Mo Kα radiation. Unit cell dimensions at 20°C were obtained by least-squares fits of the setting angles of 30 reflections. The structures were solved via Pattersons heavy atom method using SHELXS-86 [4]. Hydrogen atoms were found from different Fourier maps calculated after anisotropic refinement. Refinement was by full-matrix least-squares 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 system on a SUN computer [5]. Scattering factors of all atoms were taken from reference 6. The final atomic parameters for (**1**) are given in Table II. Selected bond lengths and angles are given in Table III.

Results and Discussion

The reaction of "bipy" with a mixture of $Pb(ClO_4)_2$, $6H_2O$ and $Pb(Ac)_2.3H_2O$ or $Pb(ClO_4)_2, 6H_2O$ in methanolic solution (2:1) was found to produce colorless crystals of (**1**) and (**2**), respectively (Figure 1). The infrared spectra of (**1**) and (**2**) clearly show that in the solid state the perchlorate and acetate ions are coordinated to the lead atom. Thus ν(Cl-O) stretching frequencies are observed at 1130(s), 1110(s), 1090(w), 1080(s) and 900(w) cm^{-1} while carboxylate (CO_2) at 1554 and 1420 cm^{-1}, indicating bidentate ClO_4 [7], and $MeCO_2$ [8] ions.

Table III. Selected bond lengths (Å) and angles (deg) for (**1**) and (**2**)

	(1)	(2)
Pb-N(1a)	2.52(2)	2.49(5)
Pb-N(1b)	2.56(1)	2.55(2)
Pb-N(2a)	2.50(2)	2.51(1)
Pb-N(2b)	2.48(2)	2.57(3)
Pb-O(1)	2.85(4)	2.83(2)
Pb-O(2)	2.87(1)	2.86(2)
Pb-O(5)	2.41(4)	2.88(4)
Pb-O(6)	2.43(2)	2.85(1)
N(1a)-Pb-N(1b)	68.1(4)	69.3(2)
N(2a)-Pb-N(2b)	67.4(2)	67.1(2)
O(1)-Pb-O(2)	62.4(3)	63.1(5)
O(5)-Pb-O(6)	57.8(2)	62.8(2)
O(1)-C1-O(2)	108.9(4)	
O(5)-C(1)-O(6)	115.8(6)	
O(5)-Pb-O(6)	71.9(4)	

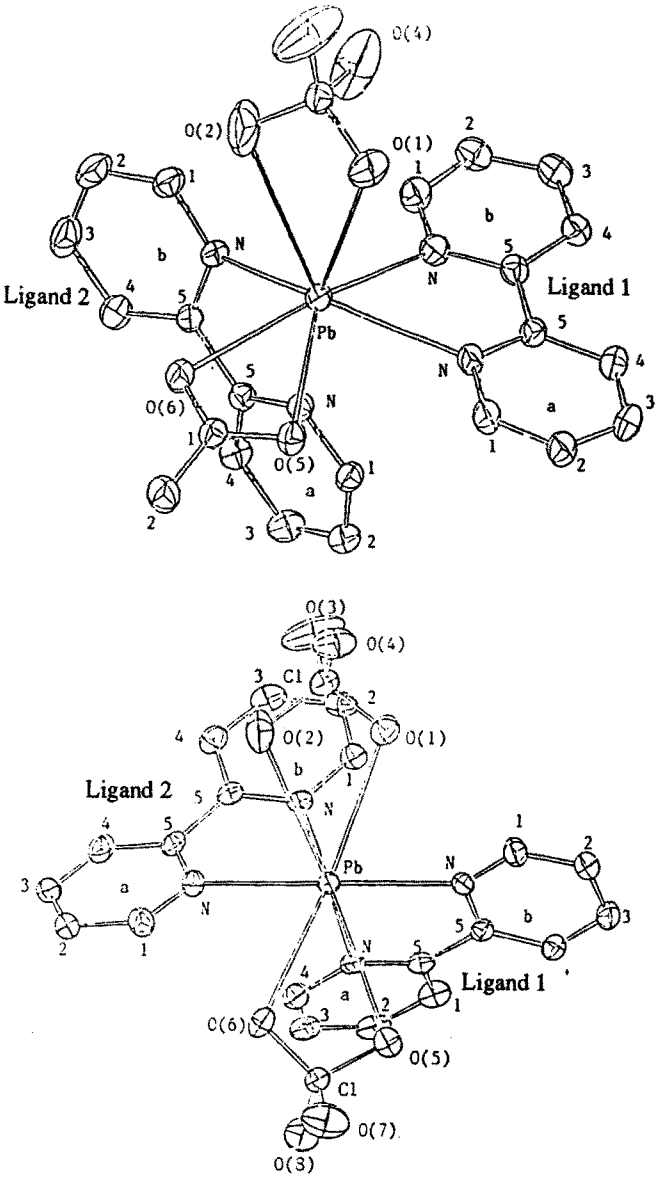

Figure 1. Prospective view and atom numbering of **1**(top) and **2**(bottom)

Description of the Crystal of Structure 1

The results of the structure determination by X-ray diffraction show that the complex is $(bipy)_2\ Pb(O_2ClO_2)(O_2CCH_3)$ (Figure 1). The lead atom is eight-coordinated with four of the coordination sites being occupied by a pair

of bidentate "bipy" moieties [Pb-N 2.48(2)-2.56(1)Å]. The remaining pairs of sites are occupied by a bidentate perchlorate [Pb-0(1) 2.85(4), Pb-0(2)2.87(1)Å] and acetate [Pb-0(5) 2.41(4), Pb-0(6) 2.43(2) Å] anions respectively.

Description of the Crystal of Structure 2

Crystals of **2** consist of $(bipy)_2$ $Pb(ClO_4)_2$ units (Figure 1). The lead atom is eight coordinate and from this point of view it resembles (**1**) except that the acetate ligand is replaced by the second perchlorate ion. The bond lengths and angles for (**2**) are shown in Table III.

It is evident from the projections shown and the data of Tables I and III that in the irregular coordination environments of (**1**) and (**2**) a considerable gap exists, this is consistent with the presence of sterically active lone pairs [3]. The lead atom deviates somewhat from two bipyridine planes (by 0.328 and 0.064 Å in (**1**) and 0.319 and 0.067 Å in (**2**)). Considering the Pb(II) center in the paper plane, the N_1, N_2, N_3 and N_4 nitrogen atoms form a plane below, while the oxygens O1, O2, O5, and O6 form a second plane above. The lone valence-electron pair then points perpendicular above the paper plane. If one assigns a stereochemical position to the lone pair of electrons on lead(II) it attains the coordination number 9 in both complexes.

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