

# LEWIS-BASE ADDUCTS OF LEAD (II) COMPLEXES. CRYSTAL STRUCTURES OF Pb (BIPY) (H<sub>2</sub>O) (NO<sub>3</sub>)<sub>2</sub> AND Pb (PHEN) (H<sub>2</sub>O) (NO<sub>3</sub>)<sub>2</sub>

A. A. Soudi<sup>1</sup>, J. McB. Harrowfield<sup>2</sup>, H. Miyamae<sup>3</sup> and A. H. White<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Zanjan University, Zanjan, Islamic Republic of Iran  
<sup>2</sup>Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Perth, W. A., 6009, Australia

<sup>3</sup>Department of Chemistry, Faculty of Science, Josai University, Keyakidai, Sakado, Saotama 350-02, Japan

## Abstract

Reactions of equimolar amounts of lead (II) nitrate and 2, 2'- bipyridine or 1, 10-phenanthroline in aqueous methanolic solution yield crystals of Pb (bipy)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub> (1) or Pb (phen) (H<sub>2</sub>O) (NO<sub>3</sub>)<sub>2</sub> (2) respectively. Their structures were determined by X-ray crystallography. The method and structure determination is described.

## Introduction

As part of the continuing structural and synthetic studies of Pb (II)- nitrogen donor ligands [1-6], we wish to report the preparation and X-ray structures of two complexes of lead (II)- nitrate with the bidentate cyclic amines 2, 2'- bipyridine and 1, 10- phenanthroline.

There are two of several known complexes of lead (II) with these ligands. Other species with 1:2, 1:3 and even 1:4 stoichiometries as well as 1:1 have been prepared and practically characterized [7].

monohydrate: To a solution of 2, 2'- bipyridine (0.078 g, 0.5 mmol) in hot methanol was added a hot aqueous solution of Pb (NO<sub>3</sub>)<sub>2</sub> (0.16 g, 0.5 mmol). The volume of the solution was decreased by half, and the complex precipitated by vapor diffusion of methanol over 24 hours at room temperature. Fine, colourless needles were obtained, m. p. 220°C (Found: C, 23.75; H, 1.98; N, 11.08. Calc. for C<sub>10</sub>H<sub>8</sub>N<sub>4</sub>O<sub>7</sub>Pb: C, 23.71; H, 1.97; N, 11.08%).

## Experimental Section

Synthesis of lead (II) nitrate- 2- 2'- bipyridine

Lead (II) nitrate- 1, 10- phenanthroline monohydrate was prepared by the same molar ratio and the same method, m. p. 270°C (Found: C, 27.18; H, 1.9; N,

10.56. Calc. for C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O<sub>7</sub>Pb: C, 27.20; H, 1.89; N, 10.58%).

## Structure Determinations and Discussion

(1): Crystal of approximate dimensions, 0.3 × 0.6 × 0.2 mm was mounted on a CAD-4 diffractometer, using graphite- monochromated Mo K α radiation 4832. Reflections were measured (2 θ ≤ 65°, h 0 to 9, k 0 → 14, and 1-30 to 29) of which 3443 unique reflections with I ≥ 3σ (I) were considered. «observed».

(2): Crystal used for diffraction was approximate dimensions of 0.90 × 0.25 × 0.18 mm 4316. Reflections were measured (2 θ ≤ 60°, h 0 to 10, k 0 to 14, and 1-29 to 29) of which 3596 independent reflections were I ≥ 3σ (I). Other conditions were the same as mentioned for (1). For absorption correction, A\* min. and max. = 4.65 and 12.62.

The structure (1) was solved by direct method, and (2) by heavy atom method. They were refined by block-diagonal least- squares using the XTAL program [8] system of a SUN computer.

Hydrogen atoms were located from calculation except for water and set their isotropic thermal parameters 5/4 of their mother carbon atoms. Complex neutral atom scattering factor used was published in [9]. Pertinent results are given in Tables I-III, and figures 1 and 2.

**Key words:** Lead (II) Nitrate, Heterocycle Bases

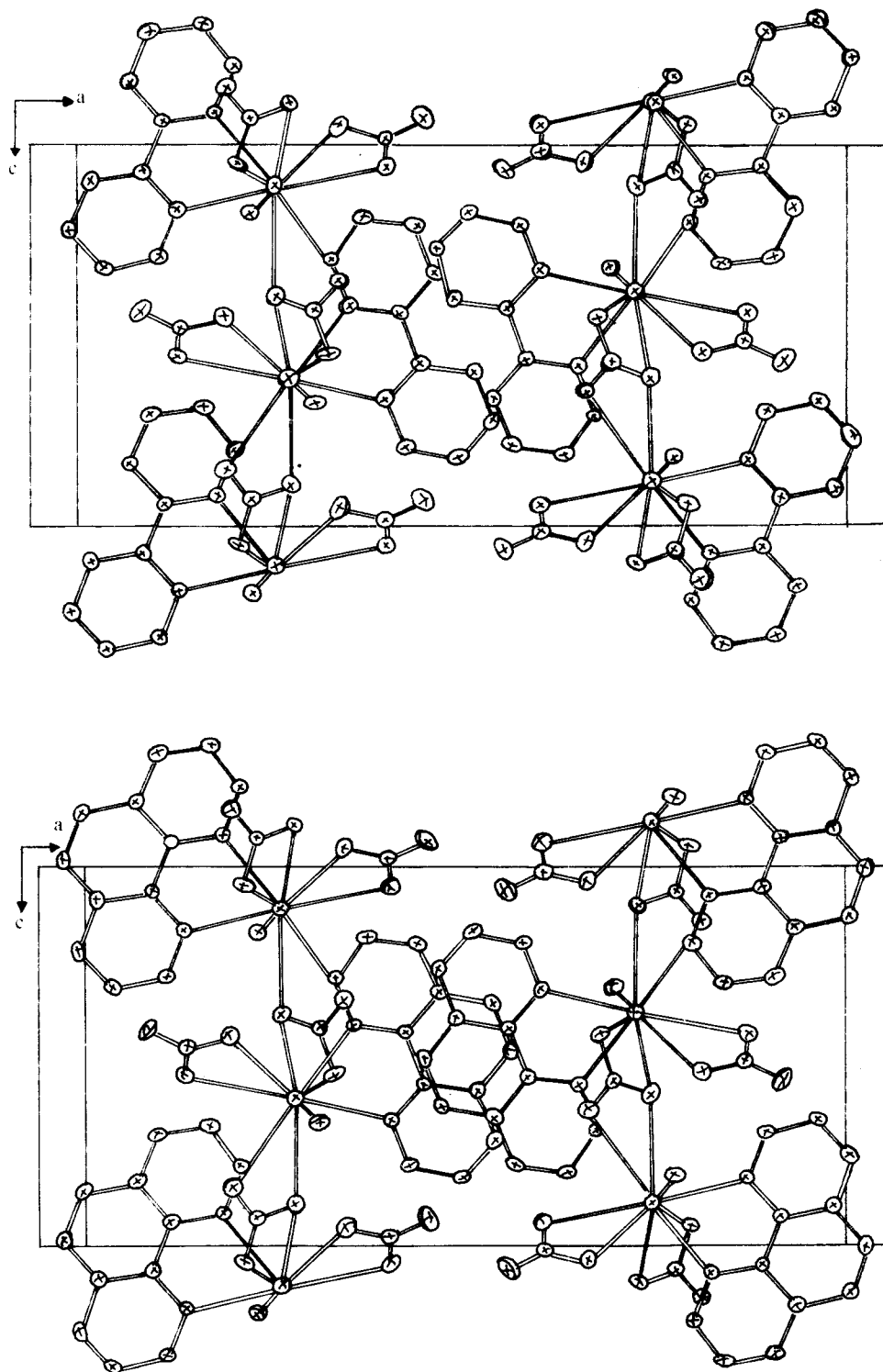
Table I. Crystallographic Data for 1 and 2<sup>a</sup>

	1	2
formula	C <sub>10</sub> H <sub>8</sub> N <sub>4</sub> O <sub>7</sub> Pb	C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O <sub>7</sub> Pb
Space Group	P2 <sub>1</sub> /C	P2 <sub>1</sub> /C
a, Å	7.244(9)	7.168(2)
b, Å	9.872(2)	9.972(1)
c, Å	20.355(5)	21.069(3)
β, deg	109.08(7)	99.47(1)
v, Å <sup>3</sup>	1378.3	1485.5
ρ <sub>calc</sub> g.cm <sup>-3</sup> (Z)	2.44	2.37
μ <sub>Mo</sub> , cm <sup>-1</sup>	121	112
Z	4	4
R, R <sub>w</sub>	0.048, 0.053	0.034, 0.039

<sup>a</sup> Both compounds are monoclinic, space group, λ = 0.71069 Å, T = 295K.

Table II. Selected Bond Lengths (Å) and Angles (deg.) for 1 and 2

1		2	
Pb-N1	2.411(2)	Pb-N1	2.481(1)
Pb-N2	2.418(2)	Pb-N2	2.478(6)
Pb-011	2.549(4)	Pb-011	2.681(2)
Pb-012	2.580(4)	Pb-012	2.701(4)
Pb-014	2.861(6)	Pb-014	2.882(6)
Pb-015	2.842(1)	Pb-015	2.851(2)
Pb-021	3.091(7)	Pb-021	3.088(8)
Pb-022	3.023(4)	Pb-022	3.031(4)
Pb-01W	2.401(4)	Pb-01W	2.398(4)
N1-Pb-N2	61.42(2)	N1-Pb-N2	61.85(4)
011-Pb-012	59.28(5)	011-Pb-012	58.96(5)



**Figure 1.** Unit cell contents of (a top) 1 and (b bottom) 2, projected down b in each case, 20% thermal ellipsoids are shown for the no. of hydrogen atoms in each case.

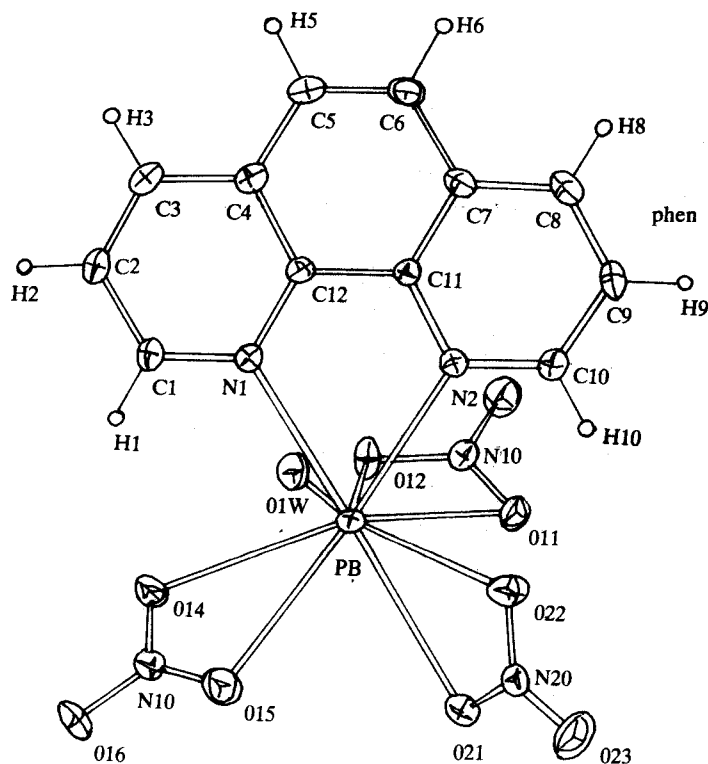
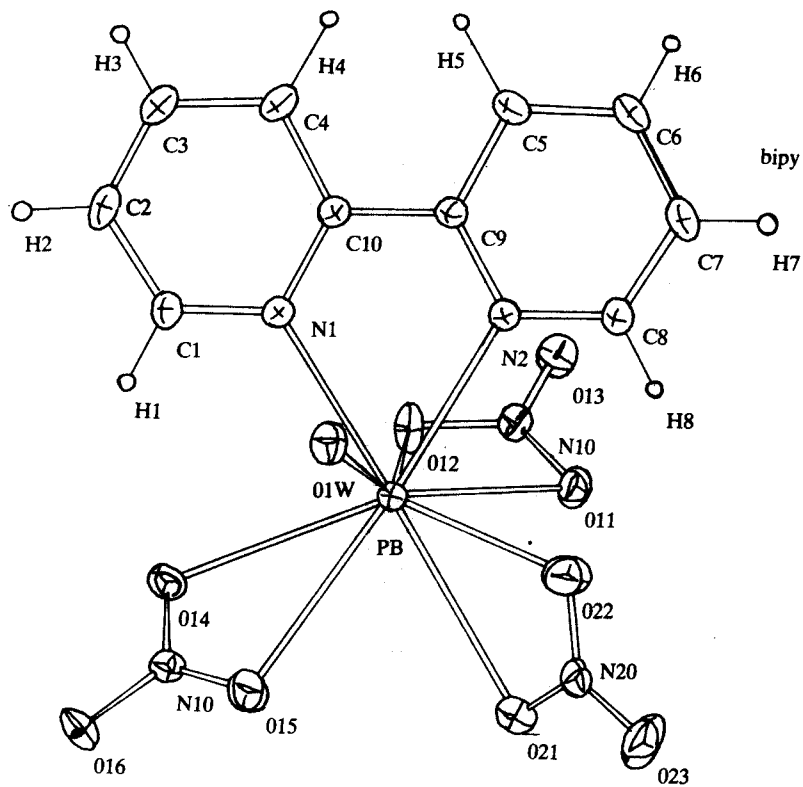


Figure 2. Structure and numbering scheme for 1 (top) and 2 (bottom). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

Table III. Non- Hydrogen Atom Coordinates of 1 and 2.

atom	1			2		
	x	y	z	x	y	z
Pb	0.16823(2)	0.38930(4)	0.26824(3)	0.16803(8)	0.38620(1)	0.26911(1)
O(1)W	0.48980(3)	0.32040(5)	0.32550(1)	0.49223(2)	0.32054(5)	0.31580(3)
N(1)	0.16526(3)	0.33131(2)	0.38510(6)	0.16539(2)	0.32784(8)	0.38703(4)
N(2)	0.23826(3)	0.56928(2)	0.35566(3)	0.23940(4)	0.57954(3)	0.34453(6)
C(1)	0.13728(1)	0.20481(7)	0.40789(6)	0.13670(1)	0.20596(2)	0.40840(6)
C(2)	0.14496(3)	0.17548(4)	0.47368(5)	0.14492(3)	0.17558(3)	0.47378(5)
C(3)	0.18871(4)	0.27355(2)	0.51779(6)	0.18869(3)	0.27356(2)	0.51782(6)
C(4)	0.22224(4)	0.40529(2)	0.49751(6)	0.22225(3)	0.40528(5)	0.49753(3)
C(5)	0.26993(1)	0.51239(7)	0.54135(2)	0.26995(1)	0.51242(6)	0.54139(3)
C(6)	0.29921(2)	0.63561(5)	0.52085(3)	0.29923(2)	0.63566(8)	0.52088(3)
C(7)	0.28950(1)	0.66375(5)	0.45363(4)	0.28952(3)	0.66379(5)	0.45366(4)
C(8)	0.32171(2)	0.79160(4)	0.42964(5)	0.32173(2)	0.79164(3)	0.42968(8)
C(9)	0.31328(2)	0.81109(3)	0.36476(6)	0.31331(6)	0.81110(3)	0.36481(8)
C(10)	0.27390(3)	0.70165(1)	0.32445(3)	0.27387(2)	0.70172(8)	0.32440(3)
C(11)				0.24567(2)	0.55910(8)	0.40864(3)
C(12)				0.20860(1)	0.42705(4)	0.43078(2)
N(10)	-0.19990(6)	0.56875(7)	0.27790(4)	-0.19991(4)	0.56876(2)	0.27793(6)
O(11)	-0.10975(2)	0.60530(4)	0.23511(3)	-0.10980(2)	0.60535(3)	0.23513(7)
O(12)	-0.18444(4)	0.44732(5)	0.29520(6)	-0.18445(4)	0.44740(7)	0.29519(5)
O(13)	-0.29720(8)	0.64608(3)	0.30325(4)	-0.29726(4)	0.64600(6)	0.30328(5)
O(14)	-0.13721(4)	0.68237(3)	0.25467(2)	-0.13524(3)	0.65894(2)	0.23985(7)
O(15)	-0.28231(7)	0.71232(4)	0.29895(3)	-0.28312(2)	0.73113(3)	0.31212(7)
O(16)	-0.32211(4)	0.62342(3)	0.27982(4)	-0.30814(3)	0.61987(2)	0.25621(2)
N(20)	0.29323(1)	0.51780(3)	0.14178(5)	0.29323(4)	0.51772(2)	0.14175(8)
O(21)	0.15358(2)	0.44422(4)	0.13031(3)	0.15264(2)	0.44417(5)	0.13042(2)
O(22)	0.36033(5)	0.54539(2)	0.19959(7)	0.36037(3)	0.54537(2)	0.19956(8)
O(23)	0.36750(3)	0.56492(8)	0.09773(5)	0.36746(2)	0.56501(5)	0.09782(3)

The dispositions of the two complexes within their respective unit cells are shown in Figure 1. The PbL units are linked by bridging NO<sub>3</sub> units, one NO<sub>3</sub> being crystallographically independent in each structure. The lead atom is nine - coordinate PbN<sub>2</sub>O<sub>7</sub>; two ligand nitrogen atoms, six nitrate oxygen atoms and a water molecule. Thus one of the nitrate bridged, bifurcated way to form one- dimensional polymeric array.

Each bidentate is unsymmetrically bonded. Pb-N distance of 2.4- 2.5 Å are normal value. Six of Pb-O (nitrate) are in a range of 2.5- 3.1 Å. The shortest bond distance of Pb-O (water) of 2.4 Å indicates that the water bonds too tight to replace by the other ligand. The bond might be replaced in the presence of the other bidentate nitrogen donor to form the Pb (NO<sub>3</sub>)<sub>2</sub>L<sub>2</sub> complexes [7]. Two complexes are isomorphous. The compound (1) was slightly decomposed during the data collection and shows somewhat high R value.

## References

1. L. M. Engelhardt, B. M. Furphy, J. McB. Harrowfield, J. M. Patrick, and A. H. White, *Inorg. Chem.*, **28**, 1410, (1989).
2. L. M. Engelhardt, J. M. Patrick, C. R. Walker, and A. H. White, *Aust. J. Chem.*, **40**, 2107, (1987).
3. L. M. Engelhardt, D. L. Kepert, J. M. Patrick, and A. H. White, *ibid.*, **24**, 329, (1989).
4. L. M. Engelhardt, J. M. Patrick, and A. H. White, *ibid.*, **42**, 335, (1989).
5. L. M. Engelhardt, B. M. Furphy, J. McB. Harrowfield, J. M. Patrick, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton Trans.*, **4**, 595, (1989).
6. D. L. Kepert, J. M. Patrick, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, **41**, 175, (1988).
7. Z. Anorg. Allgem. Chim., **133**, 239, 1938, *J. Inorg. Nucl. Chem.*, **9**, 211, 1959, and *Z. Anorg. Allgem. chim.*, **346**, 203, 1966, (cited in Gmelin Pb, 1971).
8. R. H. Hall and J. M. Stewart, XTAL Users Manual Version 2.4 U. W. A. press (1988).
9. *International Tables for X-ray Crystallography*. Birmingham, Kynosh press, Vol. IV, (1974).