

COMPLEXES OF LEAD(II)*: CRYSTAL STRUCTURES OF $L_2Pb(NO_3)_2$ AND $L_2Pb(SCN)_2$ $L=2$ -(AMINOMETHYL) PYRIDINE

A. A. Soudi

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

Abstract

The reactions of $Pb(NO_3)_2$ and $Pb(SCN)_2$ with 2-(aminomethyl)pyridine ($C_6H_8N_2 = L$) yielded colourless crystals of $L_2Pb(NO_3)_2$ (**1**) and $L_2Pb(SCN)_2$ (**2**), respectively. Their structures were determined by X-ray crystallography. Crystal data: **1**, monoclinic, $P2_1/c$, $a = 9.263$ (4) Å, $b = 7.783$ (2) Å, $c = 6.692$ (3) Å, $\beta = 101.26$ (2)°, $Z = 2$, Mo $K\alpha$, 1540 observed ($I > 2.5 \sigma(I)$) data (22°C), $R = 0.038$; **2**, monoclinic $P2_1/c$, $a = 10.010$ (3) Å, $b = 8.212$ (10) Å, $c = 8.010$ (5) Å, $\beta = 94.26$ (5)°, $Z = 2$, Mo $K\alpha$ 1856 observed ($I > 2.5 \sigma(I)$) data (22°C), $R = 0.040$.

Introduction

The coordination chemistry of Pb(II) is very extensive, and even the limited range of structural studies of lead(II) complexes have revealed a remarkable variety of coordination numbers and stereochemistry [1, 2]. In particular, only limited information is available concerning the complexes of lead(II) with amines and N-bonded heterocyclic ligands [3-9], especially when comparison is drawn with transition metal analogues. Here the synthesis and structural characterisation of 1:2 adducts of lead(II) nitrate and thiocyanate with 2-(aminomethyl)pyridine is reported.

Experimental Section

Materials

2-(Aminomethyl)pyridine and $Pb(NO_3)_2$, were obtained from Aldrich and used without further purification. $Pb(SCN)_2$ was synthesised by the

addition of a hot aqueous solution of NaSCN to a boiling aqueous solution of $Pb(NO_3)_2$.

Physical Measurements

Elemental analyses were carried out on a Heraeus elemental analyser, CHN-O-RAPID. Infrared spectra were obtained as KBr disks (4000-600 cm^{-1}) with a Perkin-Elmer IR-297 spectrophotometer.

Preparation of $L_2Pb(NO_3)_2$ (**1**) and $L_2Pb(SCN)_2$ (**2**)

1 mmol of $Pb(NO_3)_2$ or $Pb(SCN)_2$ fine powder was placed at the bottom of a branched glass tube and a solution of 2 mmol 2-(aminomethyl)pyridine in 25 ml of ethanol was poured into the tube. The end of the tube containing $Pb(NO_3)_2$ or $Pb(SCN)_2$ was kept in an oil bath at 333 K and the other end kept at ambient temperature (ca. 292-294 K). After a few days, crystals grew in the lower temperature region which were filtered off and washed with ethanol and ether and air dried.

$L_2Pb(NO_3)_2$ (**1**): yield = 73%, m.p. = 218°C, Anal. Calcd for $C_{12}H_{16}N_6O_6Pb$: C, 26.32; H, 2.92; N, 15.36.

Keywords: Synthesis and molecular structures of L_2PbX_2 ($L = 2$ -(Aminomethyl) pyridine, $X = NO_3, SCN$)

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Found: C, 26.41; H, 2.89; N, 15.40%.

L₂Pb(SCN)₂ (2): yield = 81%, m.p. = 238°C, Anal.
Calcd for C₁₄H₁₆N₆S₂Pb: C, 31.17; H, 2.97; N, 15.58. Found: C, 31.13; H, 2.80; N, 15.61%.

X-Ray Structural Determinations

Colourless crystals of **1** and **2** were attached to the end of a glass fiber and mounted on a CAD4 diffractometer, employing graphite-monochromated Mo-K α radiation. Unit cell dimensions of **1** and **2** at

22°C were obtained by least-squares fits of the setting angles of 30 reflections, respectively. The structures were solved via Patterson and Fourier synthesis. Hydrogen atoms were found from different Fourier maps calculated after isotropic refinement. Refinement was by full-matrix least-squares techniques based on F^2 to minimise the quantity of $\sum_w (|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$ using XTAL program [10]. Scattering factors for all atoms were taken from Reference 11. Pertinent results are given in Tables I-IV and Figure 1.

Table I. Crystallographic data

formula	C ₁₂ H ₁₆ N ₆ O ₆ Pb (1)	C ₁₄ H ₁₆ N ₆ S ₂ Pb (2)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.263 (4)	10.010 (3)
<i>b</i> , Å	7.783 (2)	8.212 (10)
<i>c</i> , Å	6.692 (3)	8.010 (5)
β , deg	101.26 (2)	94.26 (5)
<i>V</i> , Å ³	1443 (6)	1478 (2)
<i>Z</i>	2	2
<i>d</i> _{calcd} , g/cm ³	2.16 (4)	2.21 (4)
cryst size, mm	0.3×0.48×0.53	0.39×0.56×0.62
temp, °C	22	22
μ (Mo K α), cm ⁻¹	98.3	96.8
radiation (graphite monochromated)	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)
range of transmission factors	0.18-0.41	0.24-0.53
scan method	ω	θ -2 θ
data collcn range (2θ), deg	1 - 45	3 - 70
no. of reflcns measd	1783	1876
no. of unique data ($I > 2.5 \sigma(I)$)	1540	1856
<i>R</i> , <i>R</i> _w	0.038, 0.045	0.040, 0.036

Table II. Non-hydrogen atom coordinates of **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pb	0	0.16810	1/4
		Nitrate	
N(5)	0.19891(6)	0.58785(4)	0.38481(2)
O(1)	-0.11875(2)	0.60530(7)	0.23511(3)
O(2)	-0.18541(4)	0.53831(2)	0.31568(6)
O(3)	0.28324(8)	0.62603(3)	0.31315(4)
		Ligand	
N(1)	0.865(6)	0.3103(3)	0.2102(11)
N(2)	0.1289(8)	0.3906(7)	0.4381(7)
C(1)	0.1681(2)	0.2091(11)	0.5183(3)
C(2)	0.2138(4)	0.2896(6)	0.6021(3)
C(3)	0.1923(9)	0.4831(2)	0.4306(4)
C(4)	0.0531(7)	0.3184(9)	0.3228(2)
C(5)	0.0432(9)	0.5712(6)	0.3224(8)
C(6)	0.0821(4)	0.3289(9)	0.4871(4)

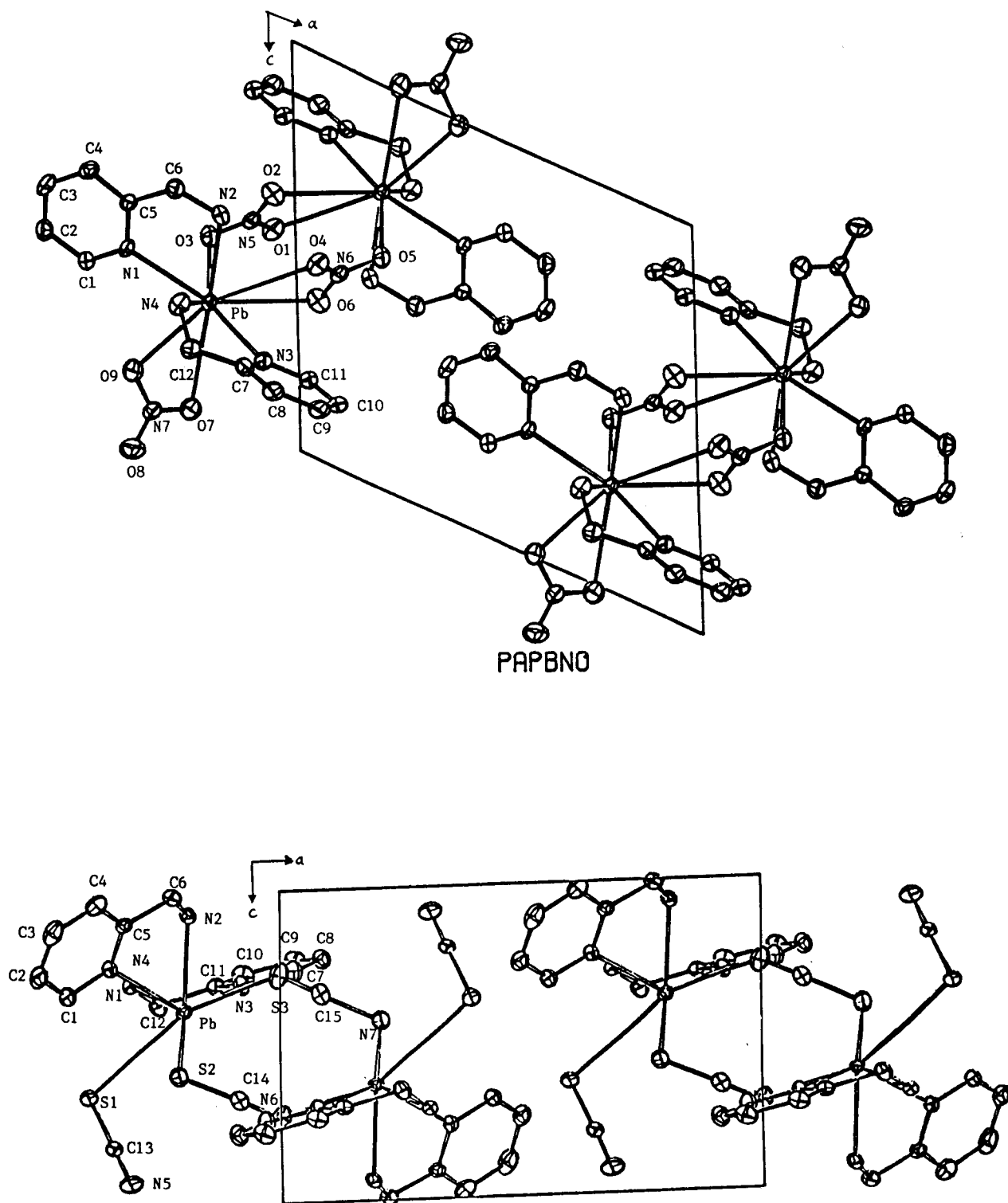


Figure 1. Unit cell contents and atom numbering of 1 (top) and 2 (bottom), projected down b in each case. 20% thermal ellipsoids are shown for the non-hydrogen atoms in each case.

Table III. Non-hydrogen atom coordinates of **2**

Atom	x	y	z
Pb	0	0.15438(4)	1/4
		Thiocyanate	
S(2)	0.1280(2)	0.1621(3)	-0.2116(5)
C(13)	0.1091(7)	0.1263(9)	-0.0965(4)
N(7)	0.0852(8)	0.0851(7)	0.1483(8)
		Ligand	
N(1)	0.0825(6)	0.3686(4)	0.5012(3)
N(2)	0.0982(7)	0.3884(2)	0.4498(6)
C(1)	0.0485(5)	0.4851(7)	0.2411(8)
C(2)	0.1022(5)	0.3139(4)	0.4412(6)
C(3)	0.1642(2)	0.4414(7)	0.5133(9)
C(4)	0.1046(5)	0.3232(8)	0.6127(6)
C(5)	0.1748(6)	0.2838(5)	0.4482(8)
C(6)	0.0961(9)	0.4818(4)	0.4731(7)

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

1		2	
Pb-N1	2.421(6)	Pb-N1	2.443(2)
Pb-N2	2.438(2)	Pb-N2	2.398(3)
Pb-O3	3.181(4)	Pb-N5	2.643(1)
Pb-O4	2.763(1)	Pb-S1	2.892(3)
Pb-O6	2.810(6)	Pb-S2	3.099(3)
N1-Pb-N2	62.40(2)	N1-Pb-N2	67.21(3)
O4-Pb-O6	58.91(6)	S2-Pb-N1	62.08(4)

Results and Discussion

The reaction of 2-(aminomethyl)pyridine (L) with $\text{Pb}(\text{NO}_3)_2$ or $\text{Pb}(\text{SCN})_2$ in ethanolic solution (2:1) was found to produce colourless crystals of **1** and **2**, respectively. These salts dissolve readily in water and the resulting solutions have a pH of approximately 7, indicating that the ligand L remains coordinated to lead(II) in solution. The infrared spectra of **1** and **2** clearly show that in the solid state the nitrate and thiocyanate anions, respectively, are also coordinated. Thus N-O stretching frequency of **1** was observed as a very strong, broad band centred at 1380 cm^{-1} , and in addition three weak bands at 1765 , 1745 and 1735 cm^{-1} , which are assigned to nitrate combination frequencies, have been detected in the infrared spectrum. The latter bands are particularly indicative of coordinated nitrate (monodentate and/or bidentate) [12]. The NCS bending and CS stretching vibrations at 483 and 820 cm^{-1} , respectively, in **2** were observed, consistent with coordination of SCN to the metal [13].

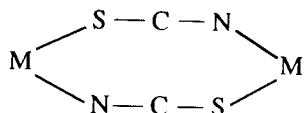
Description of the Crystal Structure of **1**

The lead atoms are nine coordinate, PbN_4O_5 ; four of the coordination sites are occupied by the nitrogen atoms of the bidentate ligands. The ligand coordination is almost planar with N-Pb-N angles ranging from 62.4 (**1**) to 67.2 (**2**). The four nitrogen atoms are clustered about two perpendicular planes. Away from the organic ligand, five coordination sites of the lead atom are occupied by O atoms of nitrates; these bridge the lead atoms by way of $\text{PbO}_3\text{N}_2\text{O}_3\text{Pb}$ units (Figure 1). The Pb-O distances range from 2.763 to 3.181 Å . These values can be compared to the lead-oxygen distances 2.805 Å in lead nitrate [14], and to those in N-bonded lead(II) nitrate complexes ($2.56 - 2.85 \text{ Å}$) [15].

Description of the Crystal Structure of **2**

Crystals of **2** comprise a binuclear species (Figure 1). The two lead atoms are seven coordinate, with five of the coordination sites occupied by a pair of

bidentate 2-(aminomethyl)pyridine moieties [Pb-N1 2.443(2), PbN2 2.398 (3)] together with a unidentate S-bonded thiocyanate [Pb-S2 3.099 (3)]. The remaining sites are occupied by bridging thiocyanate moieties which link the two lead atoms. Both thiocyanato (Pb-S-C-N) and isothiocyanato (Pb-N-C-S) modes of unidentate coordination are observed in **2**. This is consistent with the symmetric eight-membered ring motif, common in thiocyanate structures [16].



Successive Pb...Pb separation is 6.008(3)Å, which is typical in this category of lead(II) complexes [8]. In neither **1** nor **2** is there any suggestion of a sterically active lone pair e.g. by a large irregularity in the coordination sphere; in the present case, the maximum angle subtended by any pair of near neighbours in the coordination sphere does not exceed 70°C.

References

1. Kepert, D. L. *Inorganic stereochemistry*, pp. 64, 65, 194. Springer Verlag, Berlin, Heidelberg, (1982).
2. Wilkinson, G. *Comprehensive coordination Chemistry*, **3**, 188. Pergamon Books Ltd., (1987).
3. Engelhardt, L. M., Patrick, J. M., Walker, C. R. and White, A. H. *Aust. J. Chem.*, **40**, 2107, (1987).
4. Engelhardt, L. M., Kepert, D. L. Patrick, J. M. and White, A. H. *Ibid.*, **24**, 239, (1989).
5. Englehardt, L. M., Patrick, J. M. and White, A. H. *Ibid.*, **42**, 335, (1989).
6. Engelhardt, L. M., Furphy, B. M., Harrowfield, J. McB., Patrick, J. M., Skelton, B. W. and White, A. H. *J. Chem. Soc., Dalton Trans.*, **4**, 459, (1989).
7. Kepert, D. L., Patrick, J. M., Skelton, B. W. and White, A. H. *Aust. J. Chem.*, **41**, 175, (1988).
8. Englehardt, L. M., Furphy, B. M., Harrowfield, J. McB., patrick, J. M. and White, A. H., *Inorg. Chem.*, **28**, 1410, (1988).
9. Soudi, A. A. *J. Sci. I. R. Iran*, **5**, 343, (1990).
10. Hall, R. H. and Stewart, J. M., *XTAL. Users Manual Version 2.4* U. W. A., Press (1988).
11. *International Tables for X-ray Crystallography*, Kynoch: Birmingham, England, Vol. 4, (1974).
12. Addison, C. C., Logan, N., Wallwork, S. C. and Garner, C. D. *Q. Rev. Chem. Soc.*, **25**, 289, (1971).
13. Norbury, A H. *Adv. Inorg. Chem. Radiochem.*, **17**, 231, (1975).
14. Hamilton, W. C. *Acta Crystallogr.*, **10**, 103, (1957).
15. Lerner, E. I., Lippard, S. J. *Inorg. Chem.*, **16**, 1537, (1977).
16. Eg: Burmeister, J. L., *Coord. Chem. Rev.*, **3**, 225, (1968).