Direct Synthesis of the Novel 2-D Mixed-ligands Lead(II) Complex, Crystal Structure of [Pb(4,4′-bpy)(NO$_3$)(SCN)]$_n$ (4,4′-bpy = 4,4′-bipyridine): (A New Polymeric Compound with Three Bridged Ligand and Inactive Lone Pair)

A. Morsali and A. R. Mahjoub*
Chemistry Department, Tarbiat Modarres University, Tehran, Iran

(Received July 22, 2003; CL-030665)

A lead(II) complex with three ligands, 4,4′-bipyridine (4,4′-bpy), nitrate, and thiocyanate, has been synthesized and characterized by CHN elemental analysis, IR-, ^{1}H-, ^{13}C- and ^{207}Pb NMR spectroscopy. The single-crystal X-ray data of [Pb(4,4′-bpy)(NO$_3$)(SCN)]$_n$ compound shows that the complex to be two dimensional polymeric and the Pb atom has an eight-coordinate geometry. The lone pair of electrons on lead(II) is inactive in this complex.

In relation with work on mixed-ligands lead(II) complexes[1–5] described in earlier papers, it is hardly surprising to find further examples of these complexes with Pb^{2+} ion. The 4,4′-bpy ligand,[6–8] thiocyanate,[10] and nitrate[3,10] anions are widely used for the synthesis of polynuclear complexes with extended structures. The lead(II) complexes are frequently discussed in considering of the coordination and stereoactivity of heavy metals.[11] Since the presence of lone pair is not directly detected but recognized on the basis of the spatial distribution of atoms assumed to be donors to the central ion, the identification of these donor atoms is fundamental to the analysis of any particular system. Interestingly, this is not a straightforward process. Building new molecular species and modifying their architectures in order to control their physical properties, have been a topic for many research groups. Different ligands have been used to study the lead(II) complexes.[10,11] The bridge ligands such as 4,4′-bpy because of forming of polynuclear complexes are also a very good candidate for the investigation of the "stereochemical activity" of valence shell electron lone pairs in the polymeric and supramolecular compounds.

The [Pb(4,4′-bpy)(NO$_3$)(SCN)]$_n$ complex was prepared by the following method (the branch tube method): 4,4′-bpy (0.156 g, 1 mmol) was placed in one arm of the branched tube and a mixture of lead(II) nitrate (0.331 g, 1 mmol) and potassium thiocyanate (0.097 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60 °C while the other was at ambient temperature. After 10 days, white crystals (mp = 220 °C), had deposited in the cooler arm which were filtered off, washed with acetone and ether and air dried (0.242 g, yield 50%), Found: C, 27.87; H, 1.29; N, 11.25%. Calcd for $C_{11}H_8N_4O_3PbS$: C, 27.30; H, 1.65; N, 11.58%. IR(cm^{-1}) selected bands: 718(s), 800(s), 1060(m), 1365(vs), 1585(s), 2040(s), 3035(w). ^{1}H NMR (DMSO, δ): 7.8 ppm (m, 2H) and 8.75 ppm (m, 2H). ^{13}C{^{1}H} NMR (DMSO, δ): 123.20 (S^{13}CN), 124.30, 139.30, 144.50, 149.30. ^{207}Pb NMR (DMS, δ) −2369.44 ppm.

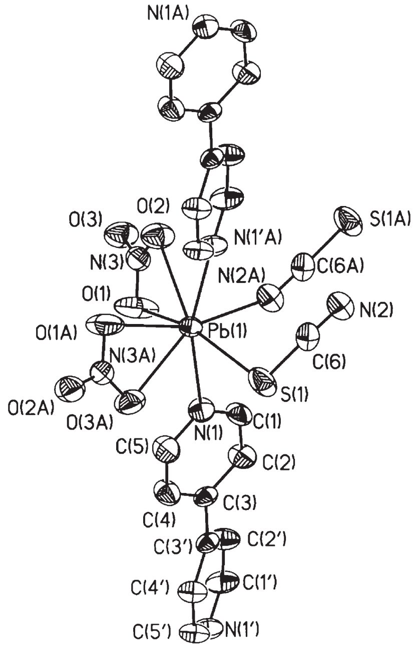

Figure 1. The ORTEP diagram of the [Pb(4,4′-bpy)(NO$_3$)(SCN)]$_n$. Selected bond lengths [Å] and bond angles [°]: Pb(1)–N(1) 2.664(5), Pb(1)–N(2)#1 2.461(6), Pb(1)–N(1′)#2 2.702(5), Pb(1)–O(1) 2.724(6), Pb(1)–O(2) 2.802(6), Pb(1)–O(3)#3 2.815(6), Pb(1)–O(1)#3 2.842(6), Pb(1)–S(1) 2.909(2), N(1)–Pb(1)–N(2)#1 82.4(2), N(2)#1–Pb(1)–N(1′)#2 84.4(2), N(1)–Pb(1)–N(1′)#2 162.4(2), N(2)#1–Pb(1)–O(1) 87.7(2), O(1)–Pb(1)–N(1) 72.7(2), N(1′)#2–Pb(1)–O(1) 118.47(18), N(2)#1–Pb(1)–O(2) 76.9(2), O(2)–Pb(1)–N(1) 114.67(18), N(1′)#2–Pb(1)–O(2) 73.33(17), O(1)–Pb(1)–O(2) 45.57(16), N(2)#2–Pb(1)–O(3)#3 152.9(2), N(1)–Pb(1)–O(3)#3 78.02(17), N(1′)#2–Pb(1)–O(3)#3 109.96(19), O(1)#2–Pb(1)–O(3)#3 104.0(2), O(2)–Pb(1)–O(3)#3 128.59(18), N(2)#1–Pb(1)–O(1)#3 159.3(2), N(2)–Pb(1)–O(1)#3 118.25(18), N(1′)–Pb(1)–O(1)#3 75.42(19), O(1)–Pb(1)–O(1)#3 97.68(3), O(2)–Pb(1)–O(1)#3 92.6(2), O(3)#3–Pb(1)–O(1)#3 44.42(15), N(2)#1–Pb(1)–S(1) 85.47(16), N(1)–Pb(1)–S(1) 84.37(15), N(1′)#2–Pb(1)–S(1) 82.96(15), O(1)–Pb(1)–S(1) 156.75(16), O(2)–Pb(1)–S(1) 151.52(12), O(3)#3–Pb(1)–S(1) 74.11(14), O(1)#3–Pb(1)–S(1) 96.50(17). #1 $-x+1$, $-y+1$, $-z$ #2 $x+1$, $y-1$, z #3 $-x+1$, $y-1/2$, $-z+1/2$.

Single crystal X-ray diffraction analysis of the complex was carried out (Figure 1).[12] The crystal structure of [Pb(4,4′-bpy)(NO$_3$)(SCN)]$_n$ consists of two dimensional polymeric units of [Pb(4,4′-bpy)(NO$_3$)(SCN)]. The nitrogen atoms of 4,4′-bipyridine ligand and the oxygen atoms of nitrate anion are linked to different lead atoms and also the sulfur and nitrogen atoms of thiocyanate anion are bridged to two lead atoms. Each lead atom is linked by the nitrogen atoms of 4,4′-bipyridine ligand with a Pb–N distances of 2.664(5), and 2.702(5) Å, the oxygens of nitrate anions with Pb–O distances of 2.724(6), 2.802(6), 2.815(6), 2.842(6) Å, the nitrogen of thiocyanate anion with a Pb–N distance of 2.461(6) Å and also the sulfur atom of thiocyanate anion with a Pb–S distance of 2.909(2) Å. The coordination number in this complex is eight (two 4,4′-bipyridine ligands, four nitrate anions, two thiocynate anions) and the lead atoms are bridged by 4,4′-bipyridine, nitrate and thiocyanate ligands and produce polymer units in the solid state. Since the inversion center is not located at the middle of the C(3)–C(3′) bond, the aromatic rings of 4,4′-bipyridine are not coplanar. The two 4,4′-bipyridine ligands are trans and the N(1)–Pb(1)–N(1′A) angle is 162.4°, but the thiocyanate and also nitrate ligands are cis. The nitrate anion could be chelated as bidentate and also could be bridged and indeed, one of oxygen atoms of this anion is linked to two difference lead atoms.

The structure of $[Pb(4,4'\text{-bpy})(NO_3)(SCN)]_n$ compound is interesting in several aspects. The above-mentioned compound is a new rarely observed 2-D framework type and a new mixed-ligands complex containing three ligands that have simultaneously been bridged in its crystal structure and also the lone pair in this complex is inactive. The lone pair in the most of lead(II) complexes is active, and the structures with inactive lone pair were rarely observed.[11] The possible stereochemical activity of the lone pair in divalent lead compounds has recently been discussed by Shimoni–Livny et al. based on a thorough review of crystal data available in the Cambridge Structural Database (CSD).[11] They classify lead coordination as holodirected[11] which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of encompassing sphere, while hemidirected[11] refers to those cases in which the bonds to ligand atoms are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. The latter, presents in all Pb(II) compounds with coordination number 2 to 5, is quite common in Pb(II) compounds with coordination numbers 6, 7 and 8, and does not exist in lead complexes with higher coordination numbers, here holodirected geometry is the rule. For the structure described here, coordination around the lead atoms is holodirected and the arrangement of 4,4′-bipyridine (4,4′-bpy) and nitrate, thiocyanate anions do not suggest any gap or hole in coordination geometry around the metal, possibly lone pair of electrons on lead(II) is inactive. Whether the three bridged ligands help to inactivate the lone pair in the coordination geometry around the metal ion or whether inactiveness of the lone pair helps to form the three bridge, is not clear. As shown in Figure 2, the three bridged ligands yield infinite chains parallel to the crystallographic vectors *a* and *c*. There is π–π stacking interaction between the parallel aromatic rings belonging to adjacent chains in this complex parallel to the crystallographic vector *b*.

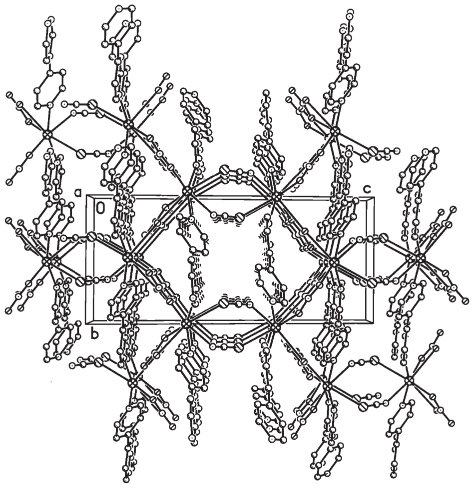

Figure 2. The unit cell of the $[Pb(4,4'\text{-bpy})(NO_3)(SCN)]_n$.

The Tarbiat Modarres University Research Council supported this work.

References and Notes

1 A. K. Holl, J. M. Harrowfield, A. Morsali, A. A. Soudi, and A. Yanovesky, *CrystEngComm*, **2000**, 13.
2 A. Morsali, M. Payheghader, and M. S. Salehi, *Z. Anorg. Allg. Chem.*, **628**, 12 (2002).
3 A. R. Mahjoub and A. Morsali, *Chem. Lett.*, **2001**, 1234.
4 A. R. Mahjoub and A. Morsali, *Z. Kristallogr. -New Cryst. Struct.*, **216**, 601 (2001).
5 A. R. Mahjoub and A. Morsali, *Polyhedron*, **21**, 1223 (2002).
6 M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen, and S. W. Ng, *Inorg. Chem.*, **37**, 2645 (1998).
7 Y.-C. Liang, M.-C. Hong, R. Cao, W.-P. Su, Y.-J. Zhao, and J.-B. Weng, *Polyhedron*, **20**, 2477 (2001).
8 Y. J. Shi, Y. Xu, Y. Zhang, B. Huang, D. R. Zhu, C. M. Jin, H. G. Zhu, Z. Yu, X. T. Chen, and X. Z. You, *Chem. Lett.*, **2001**, 678.
9 M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994).
10 J. M. Harrowfield, H. Miyamae, B. W. Skelton, A. A. Soudi, and A. H. White, *Aust. J. Chem.*, **49**, 1165 (1996) and references cited therein.
11 L. Shimonni-Livny, J. P. Glusker, and C. W. Bock, *Inorg. Chem.*, **37**, 1853 (1998).
12 Crystal Data: $C_{11}H_8N_4O_3PbS$, fw 483.46, monoclinic, Space group $P2_1/n$, $a = 9.2367(18)$, $b = 8.2303(16)$, $c = 19.0120(4)$ Å, $\beta = 103.13(3)$, $V = 1407.6(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 2.281$ Mg/m^3, $F(000)$ 896. Specimen: 0.40 × 0.30 × 0.30 mm; $R(wR) = 0.0326(0.0771)$ for 2441 reflections with $I > 2\sigma(I)$.

Published on the web (Advance View) December 20, 2003; DOI 10.1246/cl.2004.64