A Dimeric Mixed-Anions Lead(II) Complex: Synthesis and Structural Characterization of $[Pb_2(BTZ)_4(NO_3)(H_2O)](ClO_4)_3$ {BTZ = 4,4'-Bithiazole}

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The reaction of mixture $Pb(ClO_4)_2$ and $Pb(NO_3)_2$ with 4,4'-bithiazole ligand yielded white crystals of $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$. In this complex the cationic part is in fact binuclear and contains two PbL_2 groups linked via bridging NO_3^- anion. It also contains a water molecule and as well as 4,4'-bithiazole ligands in all cases are coordinated via nitrogen atoms. Three perchlorate anions are uncoordinated to lead(II) and the lone pair of valence electrons of the lead(II) ions appears to be stereochemically active. The coordinated water molecule is involved in hydrogen bonding acting as hydrogen-bond donors with two O atoms of perchlorate ions as potential hydrogen-bond acceptors.

The coordination chemistry of lead(II) with N-donor ligands has been investigated in the past decade and frequently discussed in considering the coordination and stereoactive of valence shell lone electron pairs.[1–8] Extensive recent structural studies of lead(II) compounds[9,10] in particular have provided a basis for rather detailed analysis of the evidence for coordination sphere distortions which may be a consequence of the presence of such pairs. We want to show the nature of adducts formed between mixed-anions lead(II) complex and aromatic *N,N'*-bidentate ligand of which 4,4'-Bithiazole (BTZ).

The 4,4'-bithiazole ligand was prepared from 1,4-dibromobutane-2,3-dione and thioformamide by method of Erlenmeyer and Ueberwasser (mp 170 °C).[11] The $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$ complex was prepared by the reaction of a solution of 4,4'-bithiazole (2 mmol) in hot acetonitrile (5 mL) and a hot aqueous solution of lead(II) nitrate (0.5 mmol) and lead(II) perchlorate trihydrate (0.5 mmol) (10 mL), the final solution being brought to the boil and allowed to cool slowly overnight, depositing white crystals (mp 290 °C) (Found: C, 22.00; H, 1.60; N, 9.90%. Calcd for $C_{28}H_{24}Cl_3N_{11}O_{16}Pb_2S_8$: C, 21.70; H, 1.55; N, 9.95%). The IR spectrum of the solid complex shows $\nu(NO_3)$ at 1380 cm^{-1} consistent with unidentate or unsymmetrical bidentate nitrate coordination and. $\nu(ClO_4)$ at 1090 cm^{-1}. Single-crystal X-ray diffraction analysis of the complex was carried out.[12] Crystal Data: $C_{28}H_{24}Cl_3N_{11}O_{16}Pb_2S_8$, M_r 1547.79, monoclinic, Space group $P2(1)/n$, $a = 14.177(3)$, $b = 22.638(5)$, $c = 14.891(3)$Å, $\beta = 98.206(4)^\circ$, $V = 4730.2(17)$ Å^3, D_c ($Z = 4$) = 2.173 Mg/m^3, $F(000)$ 2960. Specimen: 0.40 × 0.30 × 0.30 mm; $R(wR) = 0.0347(0.0809)$ for 11924 reflections with $I > 2.0\sigma(I)$. The title structure (Figure1) is very interesting for the presence of unequally bridging NO_3 ion. The structure consists of a binuclear $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$ complex, being a dimer, the two lead(II) ions being more closely linked by the nitrate and NO_3^- is asymmetrically coordinated to two different Pb^{2+} ions, so that the bridging unit is the Pb–O–N–O–Pb and the Pb–O(NO_3) distances are 2.870 [Pb(1)–O(1)], and 2.738 Å [Pb(2)–O(2)]. The bridging oxygen of nitrate ion increases the coordination number of both lead(II) ions. The environmental in two lead atoms is different, the coordination number in Pb(1) is five (four Pb–N and one Pb–O nitrate ion), whereas in another lead(II) ion [Pb(2)] is six (four Pb–N and two Pb–O: water molecule and nitrate ion).

The coordination around lead(II) continues to be a matter of interested,[10] especially the extent to which the lone pair is stereochemically active. The arrangement of the two 4,4'-bithiazole ligands and one NO_3^- anions suggests a gap (free space) in coordination geometry around the Pb(1) (angle N(8)–Pb(1)–N(13) is 135.7°) occupied, possibly by a stereoactive lone pair of electrons on the lead(II). The observed shortening of the Pb–N bonds on the side of the Pb^{2+}(1) ion in opposite to the position of the putative lone pair (2.424(4) and 2.481(4) compared with 2.530(4) and 2.630(4) Å adjacent to the lone pair) support the presence of this feature. Hence, the geometry of the nearest coordination environment of Pb(1) atom is likely caused by the geometrical constraints of coordinated 4,4'-bithiazole and NO_3^- and the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom which occupies one equatorial coordination site of pseudo octahedral. Such an environment leaves space for bonding of oxygen atoms ClO_4^- anions (Figures 1 and 2). The distances between the lead and oxygen atoms of ClO_4^-anions (2.9–3.2 Å) are typical for mainly ionic interaction (Table 1).

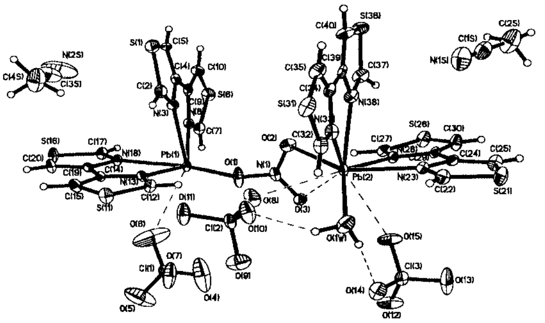

Figure 1. *ORTEP* diagram of $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$
Selected bond lengths [Å] and bond angles [°] for Pb(1) and Pb(2). Pb(1): Pb(1)-N(18) 2.424(4), Pb(1)-N(3) 2.481(4), Pb(1)-N(8) 2.530(4), Pb(1)-N(13) 2.630(4), Pb(1)-O(1) 2.870(4), N(18)-Pb(1)-N(3) 76.51(13), N(18)-Pb(1)-N(8) 81.54(12), N(3)-Pb(1)-N(8) 66.27(13), N(18)-Pb(1)-N(13) 65.91(12), N(3)-Pb(1)-N(13) 77.20(12), N(8)-Pb(1)-N(13) 135.77(12). Pb(2): Pb(2)-N(28) 2.530(3), Pb(2)-N(38) 2.575(4), Pb(2)-N(33) 2.628(4), Pb(2)-O(2) 2.738(3), Pb(2)-O(1w) 2.758(4), Pb(2)-N(23) 2.487(4), N(38)-Pb(2)-N(33) 63.72(12), N(23)-Pb(2)-O(2) 142.58(11), N(28)-Pb(2)-O(2) 79.64(11), N(38)-Pb(2)-O(2) 73.53(11), N(33)-Pb(2)-O(2) 110.96(11), N(23)-Pb(2)-O(1W) 78.20(12), N(23)-Pb(2)-N(28) 65.96(12), N(28)-Pb(2)-O(1W) 132.69(12), N(23)-Pb(2)-N(38) 83.40(13), N(38)-Pb(2)-O(1W) 131.71(12), N(28)-Pb(2)-N(38) 75.01(12), N(33)-Pb(2)-O(1W) 69.97(12), N(23)-Pb(2)-N(33) 83.15(12), O(2)-Pb(2)-O(1W) 138.86(11), N(28)-Pb(2)-N(33) 130.78(12).

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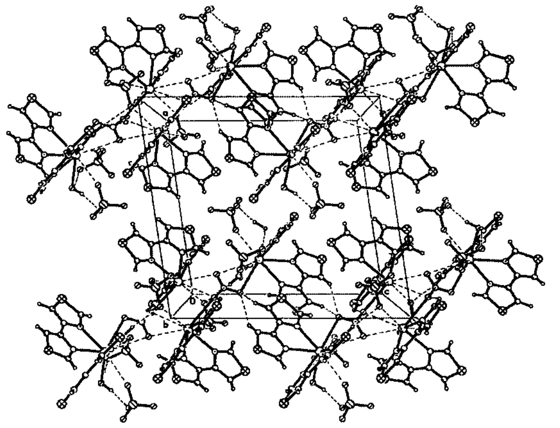

Figure 2. The unit cell of $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$.

Table 1. Pb···O distances [Å] with short contact for $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$

Pb(1)···O(1) (3-x, -y, 1-z)	3.227(4)	Pb(2)···O(3)	3.200(3)
Pb(1)···O(3) (3-x, -y, 1-z)	2.770(3)	Pb(2)···O(8)	2.946(14)
Pb(1)···O(4) (3-x, -y, 1-z)	2.997(5)	Pb(2)···O(15)	2.955(4)
Pb(1)···O(6)	2.985(4)		

Table 2. Hydrogen bond parameters (distances [Å] and angles [°]) for $[Pb_2(C_6H_4N_2S_2)_4(NO_3)(H_2O)](ClO_4)_3$

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	A
O(1W)-H(1W)	0.99	1.81	2.769	161	O(14)
O(1W)-H(1W)	1.05	2.07	2.914	136	O(10)

The coordination environment in Pb(2) atom is similar to Pb(1) atom (angle N(23)–Pb(2)–O(2) is 142.58˚), with this difference, that Pb(2) is coordinated by the one water molecule and the gap in coordination geometry around the Pb(2) shows that the lone pair in Pb(2) atom is also active.

Therefore the structure described here, coordination around the lead atoms is hemidirected[10] with a significant gap trans to the chelating 4,4'-bithiazole ligands. The unequally bridging NO_3^- ion is probably controled by lone pair activity and related with the position of O atoms rspect to lone pair.

The coordinated water molecule is involved in hydrogen bonding acting as hydrogen-bond donors with two O atoms of perchlorate as potential hydrogen-bond acceptors. As shown in Figure 1 the O(14) and O(10) atoms form hydrogen bonds with two hydrogen of water molecule (Table 2).

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References and Notes

1 R. D. Hancock, M. Shaikjee, S. M. Dobson, and J. C. A. Boeyens, *Inorg. Chim. Acta*, **154**, 229 (1988) .

2 P. Pyykkö, *Chem. Rev*., **88**, 563 (1988).

3 A. Bashall, M. Mcpartlin, B. P. Murphy, D. E. Fenton, S. J. Kitchen, and A. Tasker, *J. Chem. Soc., Dalton Trans*, **1990,** 505 and references therein.

4 P. Schwerdtheger, G. A. Heath, M. Dolg, and M. A. Bennett, *J. Am. Chem. Soc*., **114**, 7518 (1992).

5 K. Byriel, K. R. Dunster, L. R. Gahan, C. H. L. Kennard, J. L. Latten, I. L. Swann, and P. A. Duckworth, *Polyhedron*, **11**, 205 (1992).

6 A. Andres, A. Bencini, A. Garachalios, Bianchi, P. Dapporto, E. Garcia-Espna, P. Paoletti and P. Paoli, *J.Chem. Soc., Dalton Trans*., **1993**, 3507.

7 L. M. Engelhardt, J. M. Harrowfield, D. L. Kepert, H. Miyamae, J. M. Patrick, B. W.Skelton, A. A. Soudi, and H. White, *Aust. J. Chem*. **49**, 1111 (1996) .

8 A. K. Hall, J. M. Engelhard, A. Morsali, A. A Soudi, and A.Yanovsky, *Cryst. Eng. Comm*, **2000**, 13.

9 J. Parr, *Polyhedron*, **16** , 551 (1997).

10 L. Shimonni-Livny, J. P. Glusker, and C. W. Bock, *Inorg. Chem*., **37**, 1853 (1998) .

11 H. Erlenmeyer, and H. Ueberwasser, *Helv. Chim. Acta.,* **23**, 1268 (1940).

12 The intensity data were collected on a SIMENS SMART CCD difractometer with graphite-monochromated Mo Kα radiation at room-temprature. The crystal structure was solved by directed methods. Crystallographic details and complete listings have been deposited at the Cambridge Crystallographic(CCDC 162630).