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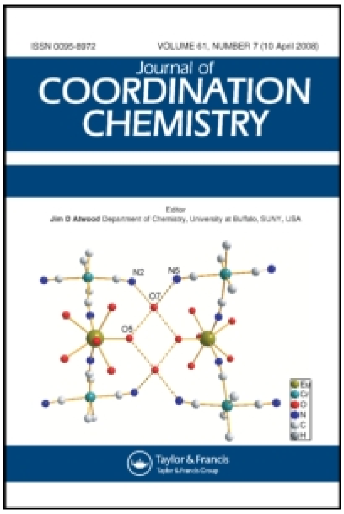

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Unusual bridging modes for percholorate in a 2D polymeric lead(II) complex, $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$

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Unusual bridging modes for percholorate in a 2D polymeric lead(II) complex, $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$

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A lead(II) complex containing 2,2′-bipyridine (bpy), acetate and perchlorate ligands, $[Pb(bpy)(CH_3COO)(ClO_4)]$ has been synthesized and characterized by elemental analysis, IR-, ^{1}H NMR-, ^{13}C NMR spectroscopy. Single crystal X-ray data show the complex is two dimensional polymeric as a result of an unusual perchlorate bi- and unidentate bridging with repeating dimeric $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$ units. The Pb atom has an unsymmetrical eight-coordinate geometry with a coordination gap around the Pb(II) ion, possibly occupied possibly by a stereo-active lone pair of electrons on lead(II).

Keywords: Perchlorate, Lead(II); Crystal structure; Mixed-anion complexes; 2,2′-bipyridine

1. Introduction

Lead is a toxic environmental contaminant with neurological and/or hematological effects [1–2]. The design of drugs to counteract the effects of lead poisoning requires establishing preferred ligands for lead, resulting in a resurgence of interest in the coordination chemistry of Pb(II). In recent years numerous reports concerning coordination chemistry of lead(II) with chelating ligands [3–5] have been discussed in regard to the coordination and stereo-activity of the valence shell lone electron pairs. Mixed ligand complexes such as $[Pb(bpy)(ClO_4)(CH_3COO)]_n$, whose difference is only in one part of the coordination sphere are interesting. The importance of the mixed-anions lead(II) complexes is due to the influence of different ligands on

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the structure and lone pair activity of the complexes, in which case, the main section of the coordination sphere remain the same.

Recently, we reported the syntheses and the crystal structures of 1 : 1 adducts of [Pb(phen)(O_2CCH_3)(O_2ClO_2)] [6], [Pb(phen)(O_2CCH_3)(O_2NO)] [7], [Pb(phen)(O_2CCH_3)(NCS)] [8], [Pb(bpy)(O_2CCH_3)(NCS)] [9] and 1 : 2 adducts of [$Pb(phen)_2$(CH_3COO)]X (X = NCS^-, NO_3^- and ClO_4^-) [10]. As a continuation of this work, in the present article we report the synthesis and crystal structure of the new 1 : 1 adduct containing 2,2′-bipyridine (bpy), acetate and perchlorate ligands as a new 2D polymeric compound with Pb $\cdots$ O(perchlorate) $\cdots$ Pb scaffolding in two dimension, $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-RAPID.

2.2. *Preparation of [Pb(bpy)(ClO_4)(CH_3COO)]*

2,2′-bipyridine (0.156 g, 1 mmol) was placed in one arm of a branched tube reactor and a mixture of lead(II) acetate (0.36 g, 1 mmol) and sodium perchlorate (0.123 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C, while the other was at ambient temperature. After 8 d, white crystals, (m.p. 235°C) had deposited in the cooler arm. Yield: 0.260 g, 50%. (found C: 27.30; H: 2.50; N: 5.70, whereas the calculated for $C_{12}H_{11}ClN_2O_6Pb$ are C: 27.61; H: 2.20; N: 5.37%). IR (cm^{-1}) selected bonds: 622(s), 850(s), 1110(vs), 1430(s), 1585(s), 1640(s), 2980(w), 3140(w). ^1H NMR (DMSO; δ): 1.65 (s, 3H), 7.80 (t, 2H), 8.25 (q, 2H), 8.70 (d, 2H), and 7.78 (d, 2H). $^{13}C\text{-}\{^1H\}$ NMR (DMSO; δ): 27.30 ($^{13}CH_3\text{–}COO$), 178.60 ($CH_3\text{–}^{13}COO$), 117.50, 124.20, 127.60, and 1141.60.

2.3. *Crystallography*

2.3.1. Determination of the structure. Crystallographic measurements were made at 298(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $2.81 \leq \theta \leq 30.07°$ using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 4204 unique reflections were measured, from which 3168 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. R, R_w with goodness of fit on F^2 1.015 $R = 0.0443$, $R_w = 0.1094$. The final difference density map showed a maximum peak and hole of 2.401 and -2.378 e Å^{-3}. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using the Sadabs programs were applied. All structural calculations were carried out with a PDP – 11/23+ computer using the SDP – PLUS program package [11, 12].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in unit cells are shown in figures 1 and 2.

3. Results and discussion

3.1. *Synthesis*

Reaction between 2,2′-bipyridine (bpy) and an equimolar mixture of lead(II) acetate with sodium perchlorate, gave $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$. The IR spectrum shows absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600 cm^{-1} range and $\nu(ClO_4)$ at 1110 cm^{-1}. The characteristic bands of the acetate anions appear about 1640 $\upsilon_{as(C\text{-}O)}$ and 1430 $\upsilon_{sym(C\text{-}O)}$ cm^{-1}. The Δ value $(\upsilon_{as} - \upsilon_{sym})$ indicates that the acetate anions coordinate to the Pb^{II} center in bridging mode [13–15].

Table 1. Crystal data and structure refinement for $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

Empirical formula	$C_{24}H_{22}Cl_2N_4O_{12}Pb_2$
Formula weight	1043.74
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 11.679(2)$ Å; $\alpha = 90.00°$ $b = 16.358(3)$ Å; $\beta = 93.16(3)°$ $c = 15.793(3)$ Å; $\gamma = 90.00°$
Volume	3012.8(10) $Å^3$
Z	4
Density (calculated)	2.301 $Mg\,m^{-3}$
Absorption coefficient	11.407 mm^{-1}
F(000)	1952
Crystal size	$0.40 \times 0.30 \times 0.25\,mm^3$
Theta range for data collection	2.81 to 30.07.
Index ranges	$0 \le h \le 13$, $0 \le k \le 23$, $-22 \le l \le 22$
Reflections collected	4204
Independent reflections	4013 [*R*(int) = 0.0655]
Completeness to theta = 30.07	90.6%
Absorption correction	Ψ-scan
Max. and min. transmission	0.1627 and 0.0920
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4013/1/201
Goodness-of-fit on F^2	1.015
Final *R* indices for 3168 ref1. [$I > 2\text{sigma}(I)$]	$R1 = 0.0443$, $wR2 = 0.1094$
R indices (all data)	$R1 = 0.0593$, $wR2 = 0.1184$
Largest diff. Peak, hole	2.401, −2.378 e $Å^{-3}$

Table 2. Selected bond lengths and angles for the $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

Bond lengths (Å)		Bond angles (°)	
Pb(1)–N(1)	2.423(6)	O(2)–Pb(1)–N(1)	79.7(2)
Pb(1)–N(2)	2.466(6)	O(2)–Pb(1)–N(2)	75.9(2)
Pb(1)–O(1)	2.657(7)	N(1)–Pb(1)–N(2)	66.6(2)
Pb(1)–O(1)[a]	2.791(8)	O(2)–Pb(1)–O(1)	50.8(2)
Pb(1)–O(2)	2.359(6)	N(1)–Pb(1)–O(1)	89.2(2)
Pb(1)–O(3)	2.991(8)	N(2)–Pb(1)–O(1)	125.1(2)
Pb(1)–O(5)	2.950(8)	O(1)–Pb(1)–O(2)	51.90(12)
Pb(1)–O(6)	3.259(8)	N(1S)–Pb(1)–O(2)	76.43(15)
Pb(1)–Pb(1)[a]	4.5502(9)	N(7)–Pb(1)–O(2)	129.06(13)
		N(1)–Pb(1)–O(2)[a]	119.68(13)
		O(1)–Pb(1)–O(2)[a]	134.82(12)
		N(1S)–Pb(1)–O(2)[a]	67.95(14)
		N(7)–Pb(1)–O(2)[a]	123.99(12)
		N(1)–Pb(1)–O(2)[a]	141.92(13)
		O(1)–Pb(1)–O(2)[a]	85.7(13)
		O(2)–Pb(1)–O(1)[a]	115.7(2)
		N(1)–Pb(1)–O(1)[a]	86.3(2)
		N(2)–Pb(1)–O(1)[a]	148.8(2)
		O(1)–Pb(1)–O(1)[a]	66.8(3)
		O(2)–Pb(1)–C(11)	25.4(2)
		N(1)–Pb(1)–C(11)	85.5(2)
		N(2)–Pb(1)–C(11)	100.9(2)
		O(1)–Pb(1)–C(11)	25.4(2)
		O(2)–Pb(1)–O(5)	143.4(2)
		N(1)–Pb(1)–O(5)	69.38(19)
		N(2)–Pb(1)–O(5)	74.2(2)
		O(1)–Pb(1)–O(5)	143.5(2)
		O(1)–Pb(1)–O(5)[a]	82.1(2)
		C(11)–Pb(1)–O(5)	154.3(2)
		O(2)–Pb(1)–O(3)	84.9(3)
		N(1)–Pb(1)–O(3)	147.5(2)
		N(2)–Pb(1)–O(3)	82.1(2)
		O(1)–Pb(1)–O(3)	102.8(3)
		O(1)–Pb(1)–O(3)[a]	126.1(3)
		C(11)–Pb(1)–O(3)	92.7(3)
		O(5)–Pb(1)–O(3)	111.1(3)
		O(2)–Pb(1)–O(6)	149.9(3)
		N(1)–Pb(1)–O(6)	109.9(2)
		N(2)–Pb(1)–O(6)	81.8(4)
		O(1)–Pb(1)–O(6)	152.3(4)
		O(1)–Pb(1)–O(6)[a]	93.8(4)
		C(11)–Pb(1)–O(6)	164.0(2)
		O(5)–Pb(1)–O(6)	41.6(2)

[a] $-x+1$, $-y+1$, $-z+1$.

3.2. *Crystal structure of* $[Pb(bpy)(ClO_4)(CH_3COO)]_n$

The crystal structure of this compound consists of polymeric units of $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$. Each lead is chelated by two nitrogen atoms of bpy with Pb–N distances of 2.423 and 2.466 Å, acetate anions with Pb–O distances of 2.359, 2.657 and 2.791 Å, and also oxygen atoms of perchlorate with Pb–O distances of 2.991, 2.950 and 3.259 Å (table 2). The coordination number in this complex is eight (two of "bpy" ligand, three of acetate and also three of perchlorate anions); and interaction of lead(II) with oxygen atoms of perchlorate of adjacent molecules produce polymeric units. The compound is a rarely observed 2D framework with

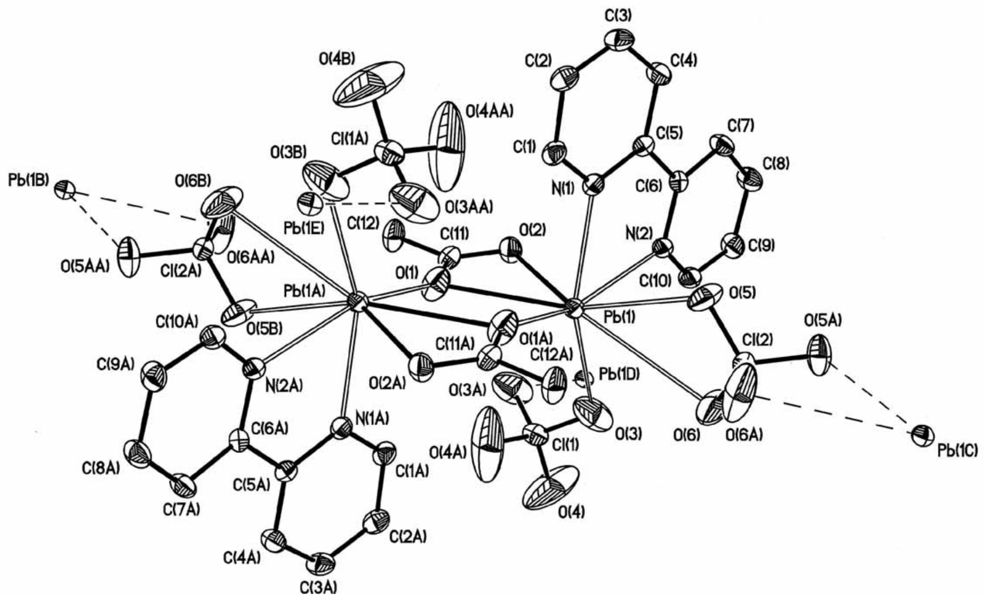

Figure 1. ORTEP diagram and a view of the Pb_2O_2 rhomb forming the basic link of the repeating dimeric units in $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

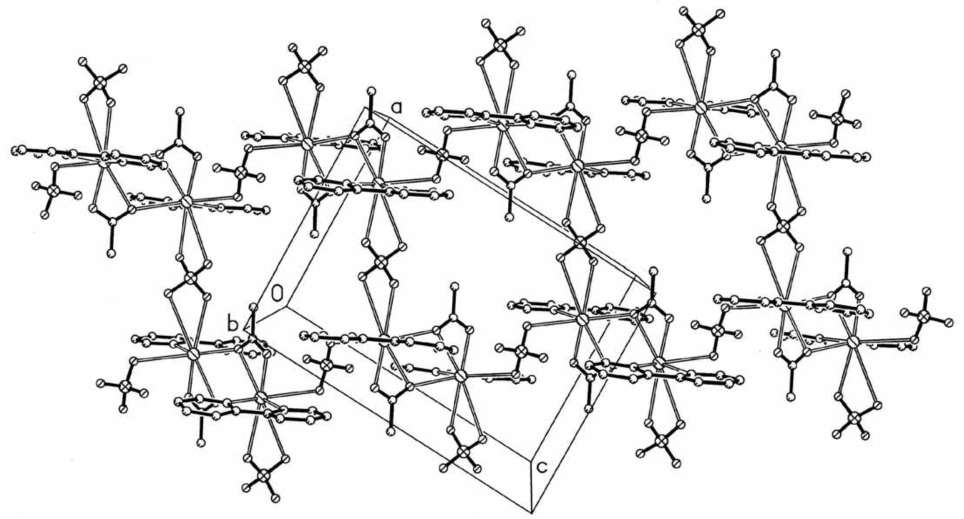

Figure 2. The unit cell and π–π stacking interaction between bipyridine ligands in $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

the basic repeating dimeric $[Pb_2(bpy)_2(\mu\text{-}OAc)_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)]$ moiety and, the structure may be considered a coordination polymer of lead(II) consisting of linear chains formed by bridging perchlorate anions. The OAc anions coordinate to Pb as a bidentate ligand and also bridge the two adjacent lead(II) ions, with a Pb–Pb distance in the dimeric units of 4.55 Å.

The arrangement of bpy, acetate and perchlorate suggest a gap or hole in coordination geometry around the metal ion [O(1)–Pb–N(2) angle is 125.1°], occupied possibly by a stereo-active lone pair of electrons on lead(II). The observed shortening of the Pb–O bonds on the side of Pb(II) ion opposite to the putative lone pair (2.359 Å compared with 2.657 Å adjacent to the lone pair) supports the presence of this feature [16]. Hence, the geometry of the nearest coordination environment of every lead atom is likely caused by the geometrical constraints of coordinated bpy ligand, acetate and perchlorate anions and by the influence of a stereo-chemically active lone pair of electrons in a hybrid orbital on the metal atom.

There are similarities in two mixed-anion lead(II) complexes, $Pb(L)(CH_3COO)(ClO_4)$ ($L = $ bpy and phen). Both complexes are polymeric and also the coordination number in both complexes is eight. Despite the similarities, there are significant differences between them, showing the influence of different ligands (here phen and bpy) on the structural geometry. In $[(phen)Pb(O_2CCH_3)(O_2ClO_2)]$, both acetate oxygen atoms are bridged, forming the polymeric units and the perchlorate anion is asymmetrically bidentate towards the lead atom but is not involved in further bridging interactions. In $[Pb(bpy)(ClO_4)(CH_3COO)]_n$, only one acetate oxygen is bridged producing dimeric units; interaction of lead(II) with oxygen atoms of perchlorate of adjacent molecules produce polymeric units. Two oxygen atoms of perchlorate anion are chelated and two are linked to two different lead atoms; in another dimension one of oxygen atoms of an adjacent perchlorate is chelated and one linked to two lead atoms (chart 1) forming the two-dimensional polymeric structure.

The percholorate anion is not usually coordinated to metal ions [17, 18], as a result of high symmetry and low dipole moment. In a recent report, the 1D helical coordination polymeric lead(II) complex with Pb···O(perchlorate)···Pb scaffoldings has been described [19]. In the present article, we manifest two different unusual bridging modes of perchlorate anions with Pb···O(perchlorate)···Pb scaffoldings in two dimensions, $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

The possible stereochemical activity of the lone pair in divalent Pb compounds has recently been discussed by Shimoni-Livny *et al.* [20] based on a thorough review of crystal data available in the *Cambridge Structural Database* (*CSD*) and by means of *ab initio* calculations. These authors classified lead coordination as 'holodirected' when the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, and as 'hemidirected' in cases where the bonds are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. The latter case, present in all Pb^{II} compounds with

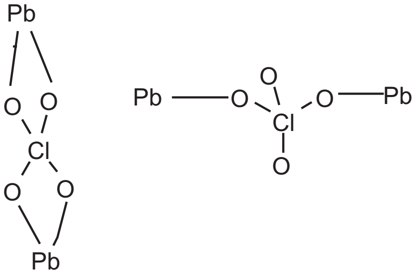

Chart 1

coordination numbers 2–5, is quite common in Pb^{II} complexes with coordination numbers 6, 7, and 8, but has not been found in Pb^{II} complexes with higher coordination numbers, where holodirected geometry is the rule. For the structure described here, coordination around the lead atoms is hemidirected with a significant gap trans to the chelating 2,2′-bipyridine.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 230241 for $\{[Pb(bpy)(\mu\text{-}OAc)]_2(\mu\text{-}O_2ClO_2)(\mu\text{-}OClO_2O)\}_n$.

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