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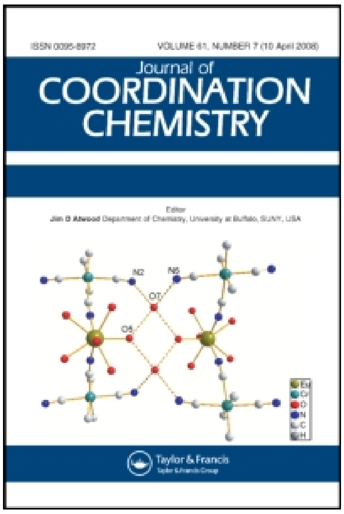

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Syntheses and characterization of some new mixed-ligand lead(II) complexes, Pb(en)(CH_3COO)X (X = NCS^-, or); Crystal Structure of [Pb(en)(CH_3COO)(NO_3)]*_n* (en = ethane-1,2-diamine)

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SYNTHESES AND CHARACTERIZATION OF SOME NEW MIXED-LIGAND LEAD(II) COMPLEXES, Pb(en)(CH_3COO)X ($X = NCS^-$, ClO_4^- OR NO_3^-); CRYSTAL STRUCTURE OF $[Pb(en)(CH_3COO)(NO_3)]_n$ (en = ETHANE-1,2-DIAMINE)

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Lead(II) complexes with ethane-1,2-diamine (en) containing two different anions, [Pb(en)(CH_3COO)X] ($X = NCS^-$, ClO_4^- or NO_3^-), have been synthesized and characterized by CHN elemental analysis, IR, ^1H NMR, ^{13}C NMR and ^{207}Pb NMR spectroscopy. Single crystal X-ray data for [Pb(en)(NO_3)(CH_3COO)] show the complex to be polymeric. The Pb atom has an unsymmetrical five-coordinate geometry and the weak interaction of lead(II) with oxygen atoms of adjacent molecule produces polymeric units in the solid state. The en ligand and counter ions in this complex exhibit a coordination gap around the Pb(II) ion, occupied possibly by a stereoactive lone pair of electrons on lead(II), that may be affected by intermolecular hydrogen bonding.

Keywords: Lead; Crystal structure; Mixed-anion complexes; Lone pair activity

INTRODUCTION

Recent structural studies on lead(II) compounds [1] have provided a basis for detailed analysis of coordination sphere distortions as a consequence of the stereoactivity of the valence shell lone-pair electrons. Weak interactions such as crystal packing, inter-ligand repulsions [2] and hydrogen bonding may affect the lone pair in the coordination sphere. Mixed-ligand complexes such as [Pb(en)(CH_3COO)X] ($X = NCS^-$, ClO_4^- or NO_3^-) differ only in one part of the coordination sphere, the main coordination sphere being the same. Recent reports of the crystal structures of 1 : 1 adducts, [Pb(phen)(O_2CCH_3)(O_2ClO_2)] [3], [Pb(phen)(O_2CCH_3)(O_2NO)] [4] and [Pb(phen)(O_2CCH_3)

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(NCS)] [5] and 1 : 2 adducts of [Pb(phen)$_2$(CH$_3$COO)]X (X = NCS$^-$, NO$_3^-$ or ClO$_4^-$) [6], [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$) [7] and [Zn(bpy)$_2$(CH$_3$COO)](ClO$_4$) [8] describe the presence of bridging acetate and its influence upon the coordination stereochemistry of lead(II). In the present paper, we report the syntheses and characterization of new 1 : 1 adducts of ethane-1,2-diamine (en), Pb(en)(CH$_3$COO)X (X = NCS$^-$, ClO$_4^-$ or NO$_3^-$).

EXPERIMENTAL

Physical Measurements

IR spectra are recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses are carried out using a Heraeus CHN-O- Rapid analyzer. Melting points are measured on an Electrothermal 9100 apparatus and are uncorrected. The ^{207}Pb solution NMR spectra are recorded on a Bruker DRX-500 AVANCE spectrometer at 104.6 MHz using a 5 mm broad-band probe. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using PbPh$_4$ ($\delta_{Pb} = -178.0$ ppm, saturated in CDCl$_3$) as an external standard (0.01 M) at 25°C. Each lead spectrum is acquired in 3–10 h.

Preparation of [Pb(en)(CH$_3$COO)(NO$_3$)]

[Pb(en)(NO$_3$)(CH$_3$COO)] was prepared by the following method (the branch tube method): ethane-1,2-diamine (0.120 g, 2 mmol) was placed in one arm of the branched tube and a mixture of lead(II) acetate (0.72 g, 2 mmol) and sodium nitrate (0.170 g, 2 mmol) in the other. Methanol was added carefully 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 15 d white crystals (m.p. 185°C) were deposited in the cooler arm. Yield: 0.174 g, 45%. (Found: C, 13.70; H, 2.45; N, 10.30. Calculated for C$_4$H$_{11}$N$_3$O$_5$Pb: C, 12.372; H, 2.83; N, 10.82%). IR (cm^{-1}) selected bonds: 723(s), 850(s), 1370(vs), 1435(s), 1594(s), 1640(s), 2980(w), 3240(s). ^{1}H NMR (DMSO; δ): 1.70 (s, 3H), 3.20 (s, 4H), 3.50 (s, 4H). ^{13}C–{^{1}H} NMR (DMSO; δ): 26.51 (^{13}CH$_3$–COO), 178.11 (CH$_3$–^{13}COO) and 42.60 (NH$_2$–^{13}CH$_2$–). ^{207}Pb NMR (DMSO, δ): −1127.06 ppm.

Preparation of [Pb(en)(CH$_3$COO)X] (X = NCS$^-$ or ClO$_4^-$)

Complexes [Pb(en)(CH$_3$COO)X] (X = NCS$^-$ or ClO$_4^-$) were prepared similarly to [Pb(en)(NO$_3$)(CH$_3$COO)] complex.

[Pb(en)(CH$_3$COO)(NCS)]

The reactant materials used were en, lead(II) acetate, potassium thiocyanate, (2 : 1 : 2). (White crystals) m.p. 225°C. Yield: 0.250 g, 65%. (Found: C, 15.30; H, 2.40; N, 10.70; Calculated for C$_5$H$_{11}$N$_3$O$_2$SPb: C, 15.58; H, 2.85; N, 10.91%.). IR (cm^{-1}) selected bonds: 780(s), 1420(s), 1575(s), 1645(s), 2020(vs), 2980(w), 3245(s). ^{1}H NMR (DMSO; δ): 1.70 (s, 3H), 3.20 (s, 4H), 3.53 (s, 4H). ^{13}C–{^{1}H} NMR (DMSO; δ): 26.51 (^{13}CH$_3$–COO), 178.11 (CH$_3$–^{13}COO), 132.15 (N^{13}CS) and 42.50 (NH$_2$–^{13}CH$_2$–). ^{207}Pb NMR (DMSO, δ): −1250.00 ppm.

[Pb(en)(CH_3COO)(ClO_4)]

The reactant materials were en, lead(II) acetate, sodium perchlorate (2.5 : 1 : 2). (White crystals 0.234 g, yield 55%), m.p. 280°C. (Found: C, 11.40; H, 2.40; N, 6.45. Calculated for $C_4H_{11}ClN_2O_6Pb$: C, 11.25; H, 2.58; N, 6.56%). IR (cm^{-1}) selected bonds: 620(s), 1110(vs), 1425(s), 1565(s), 1645(s), 2975(w), 3245(s) and 3270(s). ^1H NMR (DMSO; δ): 1.72 (s, 3H), 3.25 (s, 4H) and 3.50 (s, 4H). ^{13}C–{^1H} NMR (DMSO; δ): 27.05 ($^{13}CH_3$–COO), 177.50 (CH_3–^{13}COO) and 42.50 (NH_2–$^{13}CH_2$–). ^{207}Pb NMR (DMSO, δ): −1109.25 ppm.

Crystal Structure Determination

Crystallographic measurements were made at 293(2) K using a Siemens R3m/V diffractometer. Intensity data were collected within the range $2.68 \leq \theta \leq 27.10°$ using graphite monochromataed 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 2471 unique reflections were measured, from which 1642 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 the hydrogen atoms were idealized and included in the calculation of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter. Final $R1$, $wR2$ (with goodness of fit on F^2 1.043) were $R1 = 0.0505$, $wR2 = 0.1125$. The final difference density map showed a maximum peak and hole of 1.672 and −2.133 e Å^{-3}. Corrections for Lorentz and polarization effects as well as the empirical absorption correction using the SADABS programs were applied. All structural calculations were carried out with a PDP – 11/23+ computer using the SDP-PLUS program package [9,10].

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

DISCUSSION

Synthesis

The reaction between ethane-1,2-diamine (en) and mixtures of lead(II) acetate with potassium thiocyanate, sodium nitrate or sodium perchlorate provided crystalline material analyzing as Pb(en)(CH_3COO)X (X = NCS^-, ClO_4^- or NO_3^-). The IR spectrum of the Pb(en)(CH_3COO)(NCS) shows ν(NCS) at 2020 cm^{-1}, with ν(COO) at 1420 and 1575 cm^{-1}; Pb(en)(CH_3COO)(NO_3) shows ν(NO_3) at 1370 cm^{-1}, and ν(COO) at 1435 and 1594 cm^{-1}; Pb(en)(CH_3COO)(ClO_4) shows ν(ClO_4) at 1110 cm^{-1}, and ν(COO) at 1425 and 1565 cm^{-1}. The characteristic bands of the acetate anions appear about 1575 (υ_{as}(C–O)) and 1420 (υ_{sym}(C–O)) cm^{-1} for lead(II) complexes. The Δ value (υ_{as}–υ_{sym}) indicates that the acetate anions coordinate in a bridging mode [7,8]. Attempts to isolate Pb$(en)_2$(CH_3COO)X (X = NCS^-, ClO_4^- or NO_3^-) were not successful, in each case only the 1 : 1 adduct was isolated.

TABLE I Crystal data and structure refinement for [Pb(en)(CH_3COO)(NO_3)]

Empirical formula	$C_4H_{11}N_30_5Pb$
Formula weight	388.35
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions, Å, °	$a = 5.578$ (3), $\alpha = 90.00$ $b = 22.947$ (12), $\beta = 99.16$ $c = 7.569$ (4), $\gamma = 90.00$
Volume, $Å^3$	956.5 (8)
Z	4
Density (calculated), $mg\,m^{-3}$	2.697
Absorption coefficient, mm^{-1}	17.637
$F(000)$	712
Crystal size, mm^3	0.5 × 0.4 × 0.3
Theta range for data collection, °	3.25–28.06
Index ranges	$-1 \leq h \leq 7$, $-3 \leq k \leq 30$, $-10 \leq l \leq 9$
Reflections collected	2471
Independent reflections	2230 [$R(\text{int}) = 0.0550$]
Completeness to theta = 30.060, %	95.7
Absorption correction	Empirical
Max. and min. transmission	0.0602 and 0.0177
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2230/0/118
Goodness-of-fit on F^2	1.043
Final R indices for 1642 ref1. [$I > 2\sigma(I)$]	$Rl = 0.0505$, $wR2 = 0.1125$
R indices (all data)	$R1 = 0.0855$, $wR2 = 0.1245$
Largest diff. Peak, hole, $e\,Å^{-3}$	1.672, −2.133

Crystal Structure of [Pb(en)(CH_3COO)(NO_3)]$_n$

The crystal structure of [Pb(en)(CH_3COO)(NO_3)]$_n$ consists of polymeric units (Fig. 1). Each lead atom is chelated by two nitrogen atoms of en with Pb–N distances of 2.368 and 2.408 Å, an acetate anion with Pb–O distances of 2.392 and 2.798 Å and also oxygen atoms of a nitrate anion with Pb–O distances of 2.722, 3.307 Å. The weak interaction of lead(II) with oxygen atoms of adjacent molecules produce polymeric units in the solid state. Each Pb in this structure, along with five normal bonds, forms three "weak" Pb···O bonds and the exact distances are Pb···O2 3.307, Pb···O3$(x+1, y, z)$ 3.040 and Pb···O1$(x+1, y, z)$ 3.446 Å (Table II). The presence of a lone pair on lead is apparently the reason that the bridging interactions are long. If the stereochemically active lone pair was not present, more interactions should exist between lead(II) and the neighboring oxygen atoms of nitrate. The coordination number in this complex is seven (two from 'en', two from acetate and also three from nitrate anions). The interaction of lead(II) with oxygen atoms of nitrates from adjacent molecules produces polymeric units in the solid state. The compound is a rarely observed 1D framework type with three ligands simultaneously coordinated.

The arrangement of en, acetate and nitrate anions suggests a gap or hole in the coordination geometry around the metal ion [O(1)–Pb–O(4) 148.9°], occupied possibly by a stereoactive lone pair of electrons on lead(II). The observed shortening of the Pb–O bonds opposite to the putative lone pair (2.392 Å compared with 2.798 Å adjacent to the lone pair) supports this hypothesis [11]. Hence, the geometry of the nearest coordination environment of every lead atom is likely to be affected by the geometrical

TABLE II Selected bond lengths (Å) and angles (°) for the [Pb(en)(CH$_3$COO)(NO$_3$)]

Pb(1)–N(1)	2.408(9)	O(4)–Pb(1)–N(2)	83.1(3)
Pb(1)–N(2)	2.368(10)	N(1)–Pb(1)–N(2)	71.8(3)
Pb(1)–O(1)	2.722(10)	O(4)–Pb(1)–N(1)	80.6(3)
Pb(1)–O(4)	2.392(8)	N(2)–Pb(1)–O(1)	81.5(4)
Pb(1)–O(5)	2.798(9)	O(4)–Pb(1)–O(1)	148.9(3)
Pb(1)–O(2)	3.307(13)	N(1)–Pb(1)–O(1)	69.0(3)
Pb(1)–O(3) #1	3.040(10)	N(2)–Pb(1)–O(5)	126.8(3)
Pb(1)–O(1) #1	3.446(15)	O(4)–Pb(1)–O(5)	49.3(2)
O(1)–N(3)	1.241(12)	N(1)–Pb(1)–O(5)	77.5(3)
O(2)–N(3)	1.225(13)	O(1)–Pb(1)–O(5)	125.6(4)
O(3)–N(3)	1.238(12)	N(2)–Pb(1)–O(3) #1	69.4(3)
O(1)–O(3)	2.118(13)	O(4)–Pb(1)–O(3) #1	98.4(2)
O(1)–O(2)	2.143(16)	N(1)–Pb(1)–O(3) #1	140.9(3)
O(3)–O(2)	2.152(15)	O(1)–Pb(1)–O(3) #1	101.2(4)
		O(5)–Pb(1)–O(3) #1	130.7(3)
		N(2)–Pb(1)–O(2)	88.8(3)
		O(4)–Pb(1)–O(2)	165.0(2)
		N(1)–Pb(1)–O(2)	108.8(3)
		O(1)–Pb(1)–O(2)	40.2(3)
		O(5)–Pb(1)–O(2)	142.8(3)
		O(2)–Pb(1)–O(3) #1	66.9(2)
		N(2)–Pb(1)–O(1) #1	59.6(3)
		O(4)–Pb(1)–O(1) #1	61.9(3)
		N(1)–Pb(1)–O(1) #1	120.1(3)
		O(1)–Pb(1)–O(1) #1	129.1(5)
		O(5)–Pb(1)–O(1) #1	104.6(3)
		O(3) #1–Pb(1)–O(1) #1	37.5(2)
		O(2)–Pb(1)–O(1) #1	103.1(3)
		O(2)–N(3)–O(3)	121.8(11)
		O(2)–N(3)–O(1)	120.8(12)
		O(1)–N(3)–O(3)	117.4(10)

#1 $x+1$, y, z #2 $-x$, $-y+1$, $-z+1$.

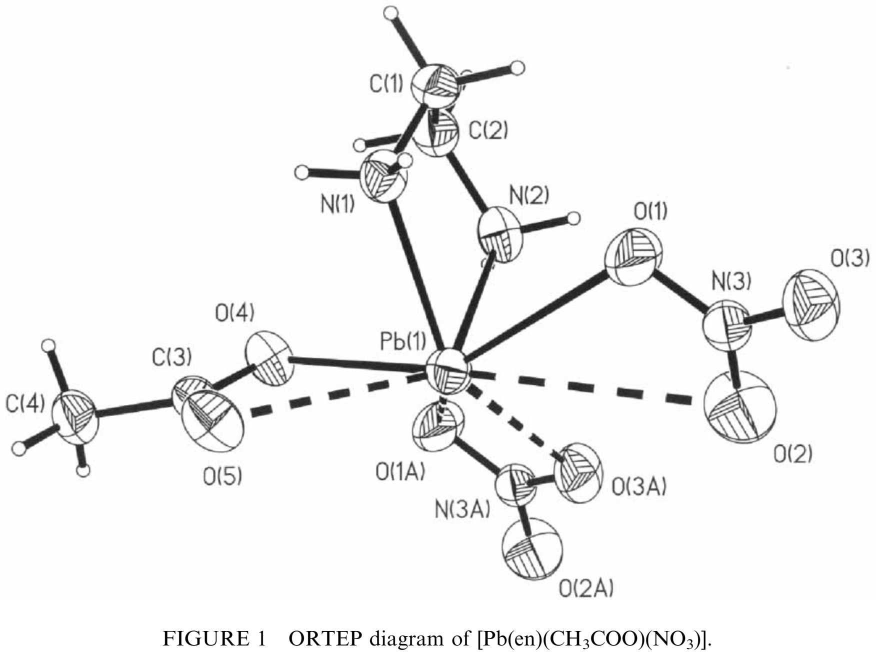


FIGURE 1 ORTEP diagram of [Pb(en)(CH$_3$COO)(NO$_3$)].

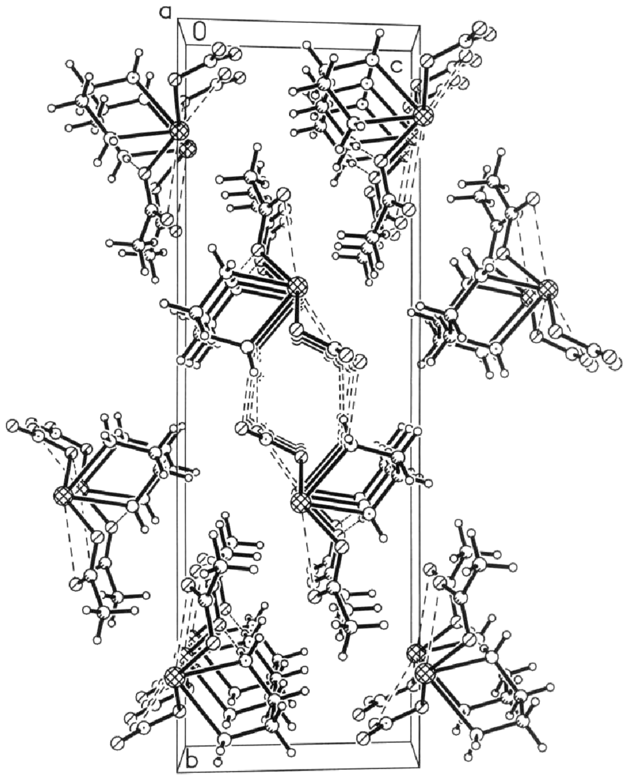


FIGURE 2 The unit cell and showing hydrogen bonding between en ligand in [Pb(en)(CH$_3$COO)(NO$_3$)]$_n$.

TABLE III Hydrogen bond parameters (distances (Å) and angles (°)) for [Pb(en)(CH$_3$COO)(NO$_3$)]

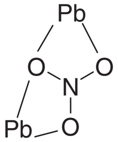
D–H	*d*(*D–H*)	*d*(*H*···*A*)	*d*(*D*···*A*)	<(*DHA*)	*A*
N(1)–H (8A)	0.900	2.170	3.022(12)	157.74	O(5) [x, $-y+3/2$, $z+1/2$]
N(1)–H (8B)	0.900	2.080	2.967(11)	168.34	O(4) [$x-1$, y, z]
N(2)–H (6A)	0.900	2.130	3.014(13)	166.87	O(3) [$-x$, $-y+1$, $-z+1$]
N(2)–H (6B)	0.900	2.316	3.037(13)	136.97	O(1) [$x+1$, y, z]
N(2)–H (6B)	0.900	2.481	3.100(14)	126.30	O(2) [$-x+1$, $-y+1$, $-z+1$]

constraints of coordinated en, acetate and nitrate anions and by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom.

The complexes are linked by intermolecular hydrogen bonding. The coordinated ethane-1,2-diamine molecule is involved in hydrogen bonding; it acts as a hydrogen-bond donor with coordinated oxygen atoms of adjacent nitrate and acetate anions being potential hydrogen-bond acceptors. The hydrogen bond parameters {distances (Å), *d*(D–H), *d*(H···A), *d*(D···A) and angles (°), <(DHA)} are given in Table III. As shown in Fig. 2, hydrogen bonding between the oxygen atoms of the nitrate anions produces dimeric units, and weak interactions of the lead atoms with oxygen atoms of adjacent nitrate anions along with hydrogen bonding between oxygen atoms of the acetate yield infinite chains parallel to the crystallographic vector *a*.

The comparison of mode of acetate coordination in this complex with some reported analogues containing acetate ligands illustrates the influence of hydrogen bonding on the structural geometry. There is a correlation between strength of the ligands in the coordination sphere of lead(II) complexes and the chelating ability of acetate. [Pb(phen)(O_2CCH_3)(O_2ClO_2)] [3] and [Pb(phen)(O_2CCH_3)(O_2NO)] [4] are polymeric, [Pb(phen)(O_2CCH_3)$_2$] [12] and [(phen)Pb(O_2CCH_3)(NCS)] [5] are dimeric and [Pb(phen)$_2$(CH_3COO)](ClO_4) [6] is monomeric. The Pb_2O_2 rings share edges with PbOCO quadrilaterals to make a dimeric core similar to the central Pb_2O_2 rings of dimeric [Pb(phen)(O_2CCH_3)$_2$] [6], [Pb(phen)(O_2CCH_3)(NCS)] and polymeric [Pb(phen)(O_2CCH_3)(O_2ClO_2)] and [Pb(phen)(O_2CCH_3)(O_2NO)]; the long edge of the rings in [Pb(phen)(O_2CCH_3)(O_2NO)]$_n$, [Pb(phen)(O_2CCH_3)(O_2ClO_2)]$_n$, [Pb(phen)(O_2CCH_3)(NCS)]$_2$ and [Pb(phen)(O_2CCH_3)$_2$]$_2$ are 2.804, 2.736, 3.190 and 3.366 Å, respectively. This is consistent with the assumption that nitrate should be a stronger ligand than perchlorate and a weaker ligand than thiocyanate and acetate, ($CH_3COO^- > NCS^- > NO_3^- > ClO_4^-$). When strong ligands like CH_3COO^- and NCS^- are coordinated to lead(II) in [Pb(phen)(O_2CCH_3)X] ($X = CH_3COO^-$ or NCS^-), the structures are dimeric and the acetate ligand bridges only one side, however when weaker ligands, such as NO_3^- or ClO_4^-, coordinate to the lead(II) ion in the [Pb(phen)(O_2CCH_3)X] ($X = NO_3^-$ or ClO_4^-), the structures are polymeric and acetate ligands bridge two sides. Thus the acetate ligand in all reported 1 : 1 lead(II) complexes can bridge one or two sides; in [Pb(phen)(CH_3COO)(NO_3)] it bridges two sides. In [Pb(en)(CH_3COO)(NO_3)], the acetate ligand is not bridging, perhaps because of intermolecular hydrogen bonding between the hydrogen atoms of the en ligand of an adjacent molecule and oxygen atoms of acetate anions, thus decreasing the coordination ability of the acetate.

The obvious similarities between the two mixed-anion lead(II) complexes, [Pb(L)(CH_3COO)(NO_3)] (L = en or phen) are that both are polymeric and the coordination number around lead is eight. Despite the similarities, the significant differences show the influence of different ligands on the geometry, although the main coordination sphere remains the same. In [Pb(phen)(O_2CCH_3)(O_2NO)], both acetate oxygen atoms are bridging, forming polymeric units and the nitrate anion is asymmetrically bidentate towards the lead atom but does not appear to be involved in further bridging interactions. In [Pb(en)(NO_3)(CH_3COO)], the acetate oxygen atoms are not bridging and the interaction of lead(II) with the oxygen atoms of the nitrate of adjacent molecules produces polymeric units in the solid state. Indeed, two oxygen atoms of the nitrate are chelated and two are linked to two different lead atoms forming a one-dimensional polymeric structure, as shown below.



The three N–O bond lengths and three angles for the nitrate anion in the [Pb(en)(NO_3)(CH_3COO)]$_n$ complex are different, [N(3)–O(1) 1.241, N(3)–O(2) 1.225, N(3)–O(3) 1.238 Å, O(2)–N(3)–O(3) 121.8, O(2)–N(3)–O(1) 120.8 and O(1)–N(3)–O(3) 117.4°]; also the O–O distances are different, [O(1)–O(3) 2.118, O(1)–O(2) 2.143 and O(2)–O(3) 2.152 Å], showing the bridging between the two lead atoms.

Two factors, lone pair activity and hydrogen bonding, control the coordination sphere of this complex. The question is whether lone pair activity has stretched the coordination geometry to result in hydrogen bonding or whether the hydrogen bonding has imposed a gap in the coordination sphere. The effect of the lone pair in most lead(II) complexes, especially 1 : 1 adducts, is appreciable, resulting in a smaller gap, suggesting that lone pair activity may be the most important factor and have an effect on hydrogen bonding; the weak intra- and inter-molecular hydrogen bonding may help to increase the 'gap' in coordination geometry around Pb(II). The weak hydrogen bond can play a significant and predictable role in structure.

Acknowledgment

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Supplementary Material

Complete tables of bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge, UK CB2 1EZ on request, quoting the deposition number 208609 for $[Pb(en)(CH_3COO)(NO_3)]_n$.

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