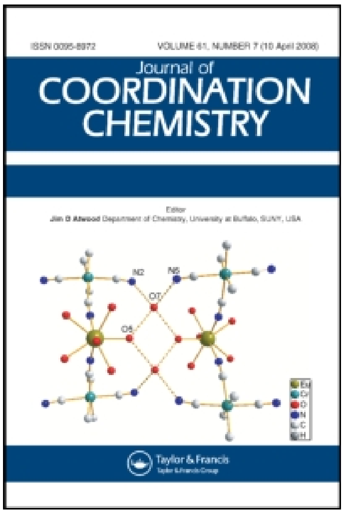

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Lead(II) complexes of proline

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Three new proline (pro) lead(II) complexes were synthesized and characterized by elemental analyses, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Single crystal X-ray structural analysis of $[Pb(pro)(H_2O)]_n$ shows the complex to be a novel 1D chain polymer as a result of water bridging. Coordination number of Pb(II) is six, with a 'stereo-chemically active' electron lone pair, and the coordination sphere is hemidirected. The chains interact with each other via weak $Pb \cdots O$ intractions and hydrogen bonding to create a 2D framework.

Keywords: Crystal structure; Lead(II); Proline

1. Introduction

Knowledge of the toxicity of lead goes back to ancient times. Recent clinical studies have established that it affects several organs such as kidneys and brain, and that it also interferes with many steps in the biosynthesis of heme [1–3]. However, critical interactions of this metal with specific biomolecules have not been elucidated. For instance, it is known that it binds strongly to sulfhydryl groups, acting as a soft acid, but also that it accumulates in the oxygen rich sites of bone, where it replaces calcium, a typical hard acid, and that its toxic effects are more serious for patients who are calcium deficient [4, 5]. Recent studies strongly suggest that Pb(II) finds its way into the organism by binding to a calcium transport protein known as ICBP or calbindine [6]. The amino acid sequence of this protein has been determined and it is known that the calcium binding site is rich in proline residues. This fact, together with the lack of studies of interactions of lead with simple biomolecules, motivated the present work, in which three different lead complexes with proline were obtained. Since lead has a variety of coordination numbers and geometries [7] and since the crystal structures of several metal complexes with aspartate [8–12] show the coordination versatility of this ligand, study of the interaction between lead and amino acids may be useful in understanding the action of metal ions in organisms. Recently complexes of lead(II) with valine, aspartate and nitrate, $[Pb(val)_2(H_2O)_2(NO_3)_2]$ and $[Pb(aspH)(NO_3)]$ were reported [13, 14]. In this article we report the synthesis and crystal structure of the first amino acid lead(II) complexes involving proline.

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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 analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

2.2. *Preparation of [Pb(pro)$_2$(H$_2$O)]$_n$ (1)*

1 was prepared by dissolving lead(II) nitrate (0.331 g, 1 mmol) in distilled water and methanol and adding a mixture of proline (0.115 g, 1 mmol) and sodium hydroxide solution 1 M (1 mL, 1 mmol) in methanol. The resulting solution was stirred and allowed to stand for some days at room temperature. Slow evaporation of the solvent at room temperature yielded suitable crystals for X-ray analysis (m.p. 258°C). The crystals were washed with acetone and air dried. Anal. Calcd for $C_{10}H_{18}N_2O_5Pb$: C, 26.46; H, 3.97; N, 6.17; found: C, 26.36; H, 3.70; N, 6.35. IR (cm^{-1}) bands: 3300–3400 m, 2976 w, 2938 w, 1596 vs, 1376 s, 1323 m, 1038 m, 938 m, 707 m. ^{1}H NMR (DMSO): δ: 4.39 (t, 1H), 3.34 (m, 2H), 2.45 (m, 2H), 1.85 (m, 2H) ppm. ^{13}C NMR (DMSO): δ: 24.84, 31.50, 46.58, 61.76 and 183.20 ppm.

2.3. *Preparation of [Pb(phen)(pro)(NO$_3$)] (2)*

1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube [15] and mixtures of lead(II) nitrate (0.331 g, 1 mmol) in distilled water and proline (0.115 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 3 days, yellow crystals were deposited in the cooler arm, which were filtered off, washed with ether and air dried (yield 54%), m.p.: 243°C. Anal. Calcd for $C_{17}H_{16}N_4O_5Pb$: C, 36.23; H, 2.84; N, 9.95; found: C, 36.51; H, 2.78; N, 6.13%. IR (cm^{-1}) bands: 3200–3400 m, 3062 w, 2984 w, 1600 s, 1576 vs, 1515 s, 1486 m, 1450 m, 1369 vs, 1100 m, 1038 m, 853 m, 730 m. ^{1}H NMR (DMSO): δ: 1.50 (2H, m, CH of pro), 1.95 (2H, m, CH of pro), 2.96 (2H, m, CH of pro), 4.10 (1H, t, CH of pro), 7.87 (2H, m, CH of phen) 8.05 (2H, s, CH of phen) 8.59 (2H, m, CH of phen), and 9.17 (2H, m, CH of phen). ^{13}C NMR (DMSO): δ: 24.94, 31.84, 46.34, 61.62, 124.58, 127.28, 129.50, 139.23, 144.56, 149.32 and 182.90 ppm.

2.4. *Preparation of [Pb(phen)$_2$(pro)(NO$_3$)] (3)*

1,10-Phenanthroline (0.4 g, 2 mmol) was placed in one arm of a branched tube [15] and mixtures of lead(II) nitrate (0.331 g, 1 mmol) in distilled water and and proline (0.115 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 3 days, yellow crystals deposited in the cooler arm, which were filtered off, washed with ether and air dried (yield 44%), m.p.: 275°C. Anal. Calcd for $C_{29}H_{24}N_6O_5Pb$: C, 46.80; H, 3.23; N, 11.30; found: C, 46.63; H, 3.41; N, 11.12%. IR (cm^{-1}) bands: 3200–3350 m, 3058 w, 2992 w, 1566 vs, 1523 s, 1486 m, 1431 m, 1376 vs, 1323 s, 1284 s, 1107m, 861 m, 738 m. ^1H NMR (DMSO): δ: 1.51 (2H, m, CH of pro), 1.82 (2H, m, CH of pro), 2.87 (2H, m, CH of pro), 4.03 (1H, t, CH of pro), 7.92 (4H, m, CH of phen) 8.05 (4H, s, CH of phen) 8.64 (4H, m, CH of phen), and 9.13 (4H, m, CH of phen). ^{13}C NMR (DMSO): δ: 25.84, 31.56, 46.48, 61.86, 124.87, 127.59, 129.91, 138.60, 145.11, 150.42 and 182.73 ppm.

2.5. *X-ray crystallography*

X-ray measurements were made at 120(2) K using a Bruker SMART 1000CCD area detector. The intensity data were collected within the range $3.61 \le \theta \le 27.98°$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved using SHELXTL [16]. The molecular plots were prepared by using SHELXTL and ORTEP III [17].

Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in table 2. Fragment of the coordination polymer and a perspective view of supramolecular assemblies are shown in figures 1 and 2, respectively.

Table 1. Crystal data and structure refinement for **1**.

Identification code	$[Pb(pro)_2(H_2O)]_n$
Empirical formula	$C_{10}H_{18}N_2O_5Pb$
Formula weight	453.45
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2
Unit cell dimensions (Å, °)	
a	19.570(3)
b	5.8871(9)
c	5.4254(8)
α	90
β	90.788(2)
γ	90
Volume (Å^3)	624.99(16)
Z	2
Density (Calcd) ($Mg\,m^{-3}$)	2.410
Absorption coefficient (mm^{-1})	13.513
$F(000)$	428
Crystal size (mm^3)	0.7 × 0.3 × 0.05
Theta range for data collection (°)	3.61 to 27.98
Index ranges	$-25 \le h \le 25$, $-7 \le k \le 7$, $-7 \le l \le 7$
Reflections collected/unique	2997/1354 [$R_{(int)} = 0.0790$]
Completeness to $\theta = 28.00$	95.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.139 and 0.011
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1354/1/83
Goodness-of-fit on F^2	1.003
Final R indices [1821 rfls with $I > 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.0903$
R indices (all data)	$R_1 = 0.0405$, $wR_2 = 0.0904$
Absolute structure parameter	0.03(3)
Largest diff. peak, hole (e Å^{-3})	2.482 and −2.509

Table 2. Selected bond lengths (Å) and angles (°) for $[Pb(pro)_2(H_2O)]_n$ (**1**).

Pb1–O1^{i}	2.347(7)	Pb1–N1^{i}	2.49(1)
Pb1–O1	2.347(7)	Pb1–N1	2.49(1)
Pb1–O1W	2.928(4)	Pb1 $\cdots$ O2^{i}	3.297(9)
Pb1 $\cdots$ O2	3.297(9)		
O1^{i}–Pb1–O1	88.6(4)	O1^{i}–Pb1–N1^{i}	69.0(3)
O1^{i}–Pb1–N1	73.0(3)	O1–Pb1–N1^{i}	73.0(3)
O1–Pb1–N1	69.0(3)	N1–Pb1–N1^{i}	126.0(4)

i: $-x+1$, y, $-z-2$.

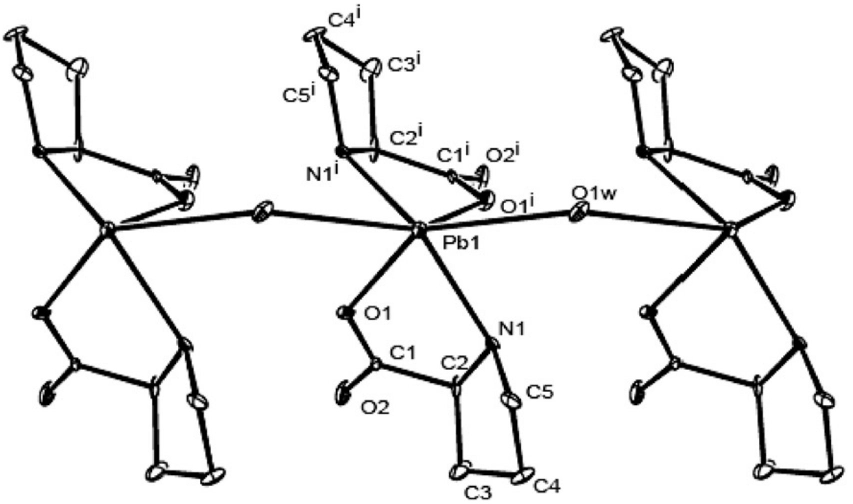

Figure 1. Fragment of the coordination polymer showing the 1D polymer.

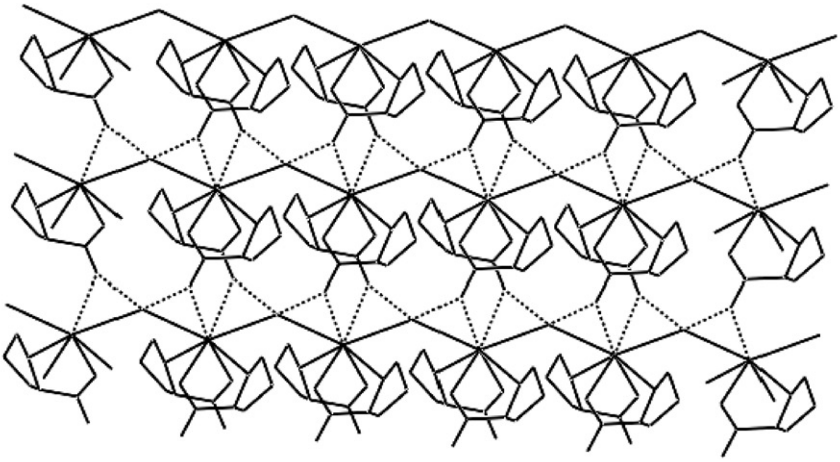

Figure 2. View of supramolecular assemblies in **1** via Pb $\cdots$ O intractions and hydrogen bonding.

3. Results and discussion

3.1. *Synthesis*

Reaction between lead(II) nitrate and mixtures of proline and sodium hydroxide in methanol provided the crystalline material $[Pb(pro)(H_2O)]_n$. The IR spectrum of this compound shows absorption bands resulting from skeletal vibrations of aliphatic ring between 2938 and 2976 cm^{-1}. The broad absorption band for ν(H–O) in **1** is at ca 3200–3400 cm^{-1}, attributable to coordinated water, hydrogen bonded, which is confirmed by the crystal structure. Reaction between 1,10-phenanthroline (phen) and mixtures of lead(II) nitrate with proline provided powdered materials analyzing as $[Pb(phen)(pro)(NO_3)]$ (**2**) and $[Pb(phen)_2(pro)(NO_3)]$ (**3**). The IR spectra of **2** and **3** show absorption bands resulting from skeletal vibrations of aromatic rings and nitrate anion in the 1400–1550 cm^{-1} and 1370 cm^{-1} ranges [18]. Strong bands in the IR spectra of **1** and **2** in the 1616–1570 and 1385–1370 cm^{-1} regions were assigned to the asymmetric and symmetric stretching modes of carboxylate groups, respectively [18, 19]. The separations between the asymmetric and symmetric stretching frequencies, $\Delta\nu(\nu_{asym}–\nu_{sym})$ range from 246 to 185 cm^{-1}, indicative of COO^- groups from proline with bridging O atoms [20]. But in the IR spectra of **3**, ν_{asym} and ν_{sym} of carboxylic group are in the 1566 and 1431 cm^{-1} respectively. The $\Delta\nu(\nu_{asym}–\nu_{sym})$ in the **3** is 135 cm^{-1}, that is significantly lower than the value of $\Delta\nu = 330\,cm^{-1}$ in **1** and **2**, indicate that the carboxylate group coordinates to the Pb in a bidentate fashion. The ^1H NMR spectrum of the DMSO solution of the three complexes displays four distinct absorption bands at 1.51–1.86, 1.82–2.45, 2.87–3.34, 4.03–4.39 ppm assigned to the aliphatic protons of proline. In complexes **2** and **3**, bands at 7.85–9.20 ppm are assigned to aromatic protons of phen. The ^{13}C NMR spectra of the DMSO solutions of the three complexes display distinct absorption bands at 182 ppm, assigned to the carboxylate carbons of proline and absorption bands at 124–151 and 24–62 ppm, assigned to the aromatic and aliphatic carbons, respectively. Because of the presence of two 'phen' ligands in the coordination sphere of lead(II) in **3**, and from the IR spectra, it is possible that **3** may be considered as mononuclear, but **1** and **2** are coordination polymers; this is confirmed by the crystal structure of **1**. Given the high coordination numbers and the inherently relatively weak bonding interaction of a metal such as Pb [21], this is perhaps unsurprising.

3.2. *Crystal structure of $[Pb(pro)_2(H_2O)]_n$ (1)*

Single crystal X-ray diffraction analysis of **1** was carried out (table 1). Selected bond lengths and angles are given in table 2. Determination of the structure of the **1** by X-ray crystallography showed the complex in the solid state (figure 1) to be polymeric unites. Each lead is chelated by two nitrogen atoms of 'pro' with Pb–N distances of 2.50(1) Å, oxygen atoms of 'pro' with Pb–O distances of 2.347(7) Å, and also oxygen atoms of water molecule with Pb–O distances of 2.928(4) Å (lead–oxygen separations ranging from 2.38–3.07 Å, for example, have been considered, on the basis of bond valence calculations, to be indicative of significant bonding interactions and there are numerous examples [22–24] of 'long' Pb $\cdots$ X contacts that are nonetheless much shorter than the next most distant contacts and thus have been taken as indicative of weak attractions). The coordination number in this complex is six (four from 'pro' ligand and two from water). Lead(II) atoms are bridged by water with a Pb $\cdots$ Pb distance in the

Table 3. Hydrogen bonding in crystals of **1**.

D–B···A	A···B (Å)	D···A (Å)	D–B···A (°)
N1–H1···O1 (x, y, $z+1$)	2.156(7)	2.98(1)	153.40
OW–H2W···O2 (x, $y-1$, z)	2.046(9)	2.74(1)	132.00
OW–H1W···O1 (x, y, $z+1$)	2.592(7)	3.30(1)	136.55

polymeric units of 5.425 Å. The arrangement of 'pro' ligand and water molecules suggests a gap or hole in coordination geometry around the metal ion [OWPb1OW angle is 135.79°], occupied possibly by a stereo-active lone pair of electrons on lead(II) [7]. The observed shortening of the Pb–O bonds on the side of Pb(II) ion opposite to the putative lone pair 2.347(7) Å compared with 2.928(4) Å adjacent to the lone pair) supports the presence of this feature [26]. To find any potential donor centre, it is necessary to extend the bonding limit. If a limit of 3.3 Å were to be placed upon Pb(II)-donor separation to be considered a coordinate bond, the Pb1 atoms are bonded by two oxygen atoms of 'pro' with distances of Pb1···O2 = 3.297(9) Å [21, 25], thus, the Pb^{II} coordination sphere is almost completed and led to a 2D framework. Here organized hydrogen bonding between the N–H of 'pro', O–H of water and oxygen of proline (the H···O distances range is 2.046 to 2.592 Å and the N–H···O and O–H···O angles 132.00 to 153.40°, table 3) contribute to formation of a supramolecular arrangement (figure 2).

Thus three factors, lone pair activity, Pb···O intractions and hydrogen bonding, may control the coordination sphere of **1**. The obvious question then is whether the lone pair activity has stretched coordinate bonds to result in hydrogen bonding or whether it is the hydrogen bonding, which has imposed a positioning of the donor atoms for forming gap in the coordination sphere. However, self-assembly of this coordination polymer is likely caused by lone pair activity, Pb···O intractions and hydrogen bonding.

Supplementary material

Crystallographic data for the structures reported in the article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC- 631012 for $[Pb(pro)_2(H_2O)]_n$. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033; Email: deposit@ccdc.cam.ac.uk).

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