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Complexation of lead(II) by L-aspartate: crystal structure of polymeric Pb(aspH)(NO_3)

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Abstract

Two lead compounds containing the aspartate ligand are described, with compositions Pb(aspH)NO_3 and Pb(asp). The crystal structure of the first shows it is a three-dimensional polymer in which each lead atom is coordinated to six oxygen atoms, five from carboxyl groups and one from a nitrate ion. For Pb(asp), spectroscopic data suggest the presence of Pb–NH_2 interaction.

Keywords: Lead(II); Aspartate; Structures

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 the kidneys and the brain, and also that it interferes with many steps in the biosynthesis of heme [1–3]. However, the critical interactions of this metal with specific biomolecules have not yet 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 aspartic and glutamic residues. This fact, together with the lack of studies of interactions of lead with simple biomolecules, motivated the present work, in which two different lead complexes with aspartate were obtained, Pb(aspH)(NO_3) (**I**) and Pb(asp) (**II**). Since lead can present a wide 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, the structural analysis of this pair of complexes proved to be interesting in itself.

2. Experimental

Lead nitrate and lead oxide (litharge) were purchased from Merck, L-aspartic acid and L-aspartic acid monosodium salt hydrate were from Sigma Chemical Co., and all were used without further purification. Elemental analyses were carried out by Desert Analytics, Tucson, AZ. IR spectra were recorded in the 4000–400 cm^{-1} region using both KBr pellets and HCBD suspension in a Nicolet 540 spectrophotometer. The far IR spectra were recorded in a Nicolet 740 FTIR in the 700–70 cm^{-1} region using polyethylene pellets. Amino group protons were interchanged by deuterium by soaking samples in D_2O for 24 h.

The ^{13}C CP-MAS spectra were recorded on a Varian Unity-plus 300 MHz spectrometer operating at 75.429 MHz, and 30° pulse was used. A 7 mm diameter silicon nitride rotor

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with kel-F caps was used. The rotor spin rate was kept between 3.5 and 4.5 kHz for all experiments, with a delay time of 7 s, and between 128 and 516 transients accumulated. Adamantane was used as external reference.

2.1. Preparation of Pb(aspH)(NO_3) (I)

3.31 g (10 mmol) of lead nitrate were dissolved in 50 ml water and combined with 1.55 g (10 mmol) of monosodium aspartate hydrate also in 50 ml of water. The pH was adjusted to 4.0 with 0.1 M NaOH and the solution left to crystallise. Colourless needles were collected the next day. *Anal*. Calc. for Pb($C_4H_6O_4N$)(NO_3): C, 11.97; H, 1.49; N, 6.98. Found: C, 12.11, H, 1.55, N, 6.84%.

2.2. Preparation of Pb(asp) (II)

1.33 g (10 mmol) aspartic acid were dissolved in 300 ml water. To this solution, 2.23 g PbO powder (litharge) were added. The reaction vessel was placed in an ultrasound bath for 15 min during which the yellow powder dissolved and a white precipitate formed. *Anal*. Calc. for Pb($C_4H_5O_4N$): C, 14.20, H, 1.47, N, 4.1. Found: C, 14.10; H, 1.42, N, 3.98%.

2.3. Crystallography

Pertinent crystal data are collected in Table 1, and complete crystallographic information is deposited as a CIF file. The structure was solved and refined using standard procedures [13–15]. On the final difference map, a maximum peak of 1.81 e Å^{-3} close to the heavy atom was attributed to the fact that the crystal was larger than the X-ray beam and to the difficulty in applying a suitable absorption correction. H atoms were omitted because of their small contribution to the structure factors.

3. Results and discussion

3.1. Spectroscopic results

3.1.1. IR spectra

For the free ligand, in its monosodium salt form, asymmetric and symmetric stretching absorptions of the carboxylate group appear at 1582 and 1415 cm^{-1} respectively, while for the lead complex **I**, the first absorption shifts to 1560 cm^{-1} and the second is obscured by the nitrate ion absorption, which displays a quite intense band at 1385 cm^{-1}. Even though the crystal structure shows each lead atom has a nitrate ion coordinated in unidentate mode, the IR spectrum displays the characteristic band of free nitrate, which appears practically at the same wavenumber in Pb(NO_3)$_2$, suggesting a rather weak interaction, mainly of electrostatic nature. To rule out the possibility that coordination of nitrate to lead had been broken during the fabrication of the KBr pellet, the spectrum was recorded in HCBD, which is transparent in the 1565–1170 cm^{-1} region, and showed no difference. In the N–H region, three weak bands in the 2920–3150 cm^{-1} interval are consistent with the presence of the –NH_3^+ group.

Table 1
Crystal data

Empirical formula	$C_4H_6N_2O_7Pb$
Formula weight	401.30
Crystal system	Orthorhombic
Colour, habit	colourless, regular needle
Crystal size (mm)	0.74×0.16×0.06
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	4.5894(5)
b (Å)	11.6164(9)
c (Å)	15.476(2)
Z	4
Absorption coefficient (mm^{-1})	20.467
Radiation	Mo Kα ($\lambda=0.71073$ Å)
2θ Range (°)	3–55
Reflections collected	1472
Independent reflections [a]	1335 ($R_{int}=3.33\%$)
Transmission factors (min., max.)	0.0113, 0.0373
Final R indices (1269 $I>2\sigma(I)$) (%)	$R_1=3.83$, $wR_2=9.77$
Final R indices (all data) (%)	$R_1=4.27$, $wR_2=10.76$
Goodness-of-fit, S	1.175
Data-to-parameters ratio	1335/128

[a] R_{int}, R_1, wR_2 and S are defined as follows:

$$R_{int}=\frac{\sum|F_o{}^2-\langle F_o{}^2\rangle|}{\sum F_o{}^2},\quad R_1=\frac{\sum||F_o|-|F_c||}{\sum|F_o|},$$

$$wR_2=\sqrt{\frac{\sum w(F_o{}^2-F_c{}^2)^2}{\sum w(F_o{}^2)^2}},\quad S=\sqrt{\frac{\sum w(F_o{}^2-F_c{}^2)^2}{m-n}}.$$

The IR spectrum for complex **II**, however, is very different in the latter region. It has two very well defined bands with moderate intensity at 3301 and 3233 cm^{-1}, indicative of a coordinated –NH_2 group [16,17]. The assignment of these two bands was confirmed by deuterium exchange upon which they shift towards 2464 and 2379 cm^{-1} respectively.

The asymmetric stretching absorption of the carboxylate in this complex is located at 1532 cm^{-1}, 28 cm^{-1} lower than for the Pb(aspH)NO_3 complex. The symmetric stretching absorption can be observed in complex **II** at 1347 cm^{-1}. The difference ($\Delta\nu$) between ν_a and ν_s is 185 cm^{-1}, which is very close to the $\Delta\nu$ of the free amino acid or its sodium salt (vide supra, 167 cm^{-1}), and this is in agreement with a bridging carboxylate [16,17].

3.1.2. Far IR spectra

Pb(asp) has an important band at 325 cm^{-1}, not present in the far IR spectrum of Pb(aspH)NO_3. Since it shifts to 313 cm^{-1} in the deuterated sample, it could be indicative of a Pb–NH_2 vibration.

3.1.3. NMR spectra

Table 2 shows chemical shifts in ^{13}C solid state NMR for both the reported complexes as well as for the acid and monobasic forms of the ligand. While δ (ppm) values for aliphatic carbon atoms in both lead complexes are very sim-

Table 2
^{13}C NMR chemical shifts (ppm)

Nucleus	$AspH_2$	NaAspH	$Pb(AspH)NO_3$	Pb(Asp)
COOα	176.32	174.24	181.54	188.7
CH	54.11	48.9	56.80	56.60
CH_2	38.26	34.85	44.02	42.34
COOβ	175.25	174.24	177.48	181.8

ilar, those for the carboxylate groups of Pb(asp) are significatively shifted to lower fields, suggesting a qualitatively different interaction with lead atoms.

Further experiments were carried out to measure ^1H relaxation times by observing the change in signal intensity for cross-polarisation ^{13}C solid state spectra, as a function of time [18,19] (Fig. 1(a,b)). For $Pb(AspH)NO_3$ a value of 3.60 ± 0.16 s was obtained, whereas for Pb(asp) the value was 12.37 ± 0.68 s. Since these values are a measure of the rigidity of the molecules, the latter is consistent with the chelate formation suggested by the IR spectrum. For both forms of the ligand, relaxation times are assumed to be less than 1 s, which is the minimum waiting time allowed by the apparatus, since signal intensity was constant at all times measured up to 70 s.

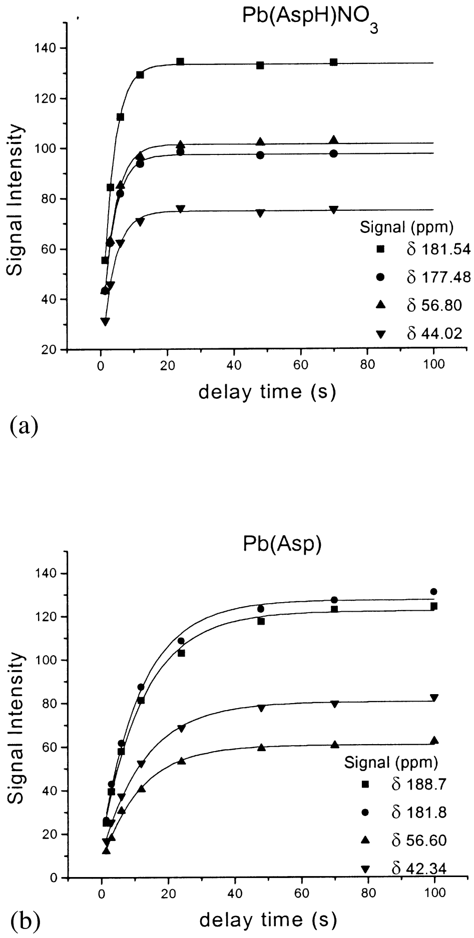

Fig. 1. Determination of ^1H relaxation times for (a) Pb(aspH)(NO_3) and (b) Pb(asp).

3.2. Crystal structure

The crystal structure shows this compound forms a three-dimensional network, owing to the nature of the aspartate ligand which can coordinate to two different lead atoms through each carboxylate, together with the fact that a single oxygen atom in a carboxylate can bridge two metal atoms. The three-dimensional network has chains running along the three axes of the orthorhombic cell. A remarkable feature is the formation of 18-membered rings containing three Pb ions and three ligand molecules with weak metal–metal interactions: Pb···Pb 4.589 and 4.706 Å (Fig. 2).

The overall geometry around each Pb can be considered a distorted square pyramid, with the apex occupied by the two oxygen atoms from the chelating β-carboxylic group (Fig. 3) with a bite angle O1–Pb–O2 = 49.8° and with bond lengths C1–O1 = 1.264(19) and C1–O2 = 1.24(2) Å. The difference in the two Pb–O distances for this group, Pb–O1 = 2.706(12) and Pb–O2 = 2.500(11) Å, is consistent with the

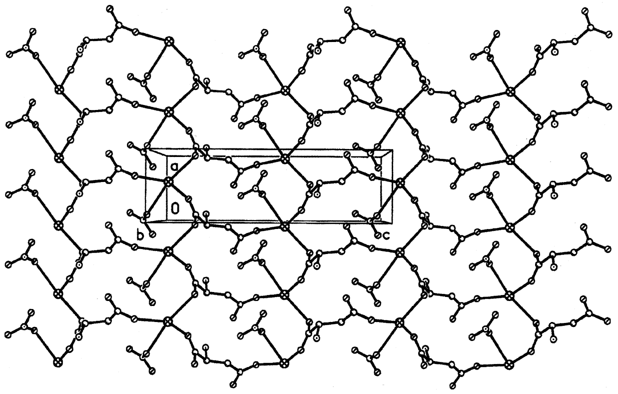

Fig. 2. 18-membered rings containing three Pb ions and three ligand molecules.

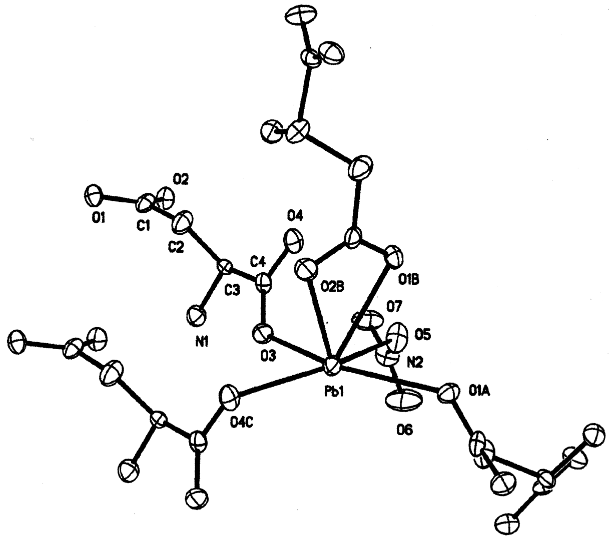

Fig. 3. The coordination environment of lead atoms in Pb(aspH)(NO_3) with the labelling scheme. Symmetry codes used to generate equivalent atoms are the following: A $-x-1/2$, $-y+2$, $z+1/2$; B $-x-1$, $y-1/2$, $-z+3/2$; C $x+1$, y, z. Thermal ellipsoids are at 30% probability level. H atoms were not included in the refinement.

bridging role of O1 between two symmetry related Pb ions (Table 3).

The lead atom lies 0.13 Å above the base of the pyramid, which is defined by four oxygen atoms from four different ligand moieties. Two of these oxygen atoms are from α-carboxylates in two symmetry related ligands, with similar distances, Pb–O3 = 2.493(12) and Pb–O4′ = 2.563(12) Å.

The third position in the base of the pyramid is occupied by the oxgen atom O1A, which forms part of a β-carboxylate that chelates a neighbouring Pb atom. An oxygen atom from the nitrate anion is coordinated at the fourth position in the base of this pyramid in unidentate mode, with the expected distance Pb1–O5 = 2.730(17) Å, only slightly shorter than the Pb–O distance in lead nitrate (2.81 Å [20]), which is in agreement with the apparent ionic behaviour of this nitrate observed in the IR spectrum.

The α-carboxylic groups are disymmetric, as noted from bond lengths C4–O3 = 1.20(2) and C4–O4 = 1.257(19) Å, in line with a localisation of the negative charge on O3. This is confirmed by the fact that Pb–O3 is the shortest coordination distance (2.493(12) Å).

This geometry leaves a wide space below the base of the pyramid containing the lead atom, which can be thought of as occupied by the ‘inert pair’ of electrons on Pb(II).

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) [7]. They classify lead complex coordination as holodirected or hemidirected. Holodirected refers to complexes in which the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed throughout only part of the coordination sphere, leaving a void or gap in the distribution of bonds to the ligand. The latter, present in all Pb(II) compounds with coordination numbers 2 to 5, is quite common in Pb(II) complexes with coordination numbers 6, 7 and 8, and does not exist in lead 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 void *trans* to the chelating β-carboxylate, quite similar to what Clegg et al. found for lead crotonate [21].

The coordination chemistry of Pb(II) in aqueous media has not yet been widely explored, but at the present time both solution equilibria and structural studies suggest a low affinity of lead for nitrogen donors, particularly aliphatic amines. In most cases, pH values needed to deprotonate these donors promote metal hydrolysis and precipitation of $Pb(OH)_2$, which is why the compound Pb(asp) described in this work cannot be found in aqueous solution. This suggests that under physiological conditions, amine residues in proteins or

Table 3
Bond lengths (Å) and bond angles (°) for complex **I**

Pb(1)–O(3)	2.493(12)	Pb(1)–O(2)#1 [a]	2.500(11)
Pb(1)–O(4)#2	2.536(12)	Pb(1)–O(1)#1	2.706(12)
Pb(1)–O(5)	2.730(17)	Pb(1)–O(1)#3	2.743(10)
C(1)–O(2)	1.24(2)	C(1)–O(1)	1.264(19)
C(1)–C(2)	1.53(2)	C(2)–C(3)	1.52(2)
C(3)–N(1)	1.47(2)	C(3)–C(4)	1.56(2)
C(4)–O(3)	1.20(2)	C(4)–O(4)	1.257(19)
O(1)–Pb(1)#4	2.706(11)	O(1)–Pb(1)#5	2.743(10)
O(2)–Pb(1)#4	2.500(11)	O(4)–Pb(1)#6	2.536(12)
N(2)–O(6)	1.19(2)	N(2)–O(7)	1.25(2)
N(2)–O(5)	1.289(19)		
O(3)–Pb(1)–O(2)#1	91.4(4)	O(3)–Pb(1)–O(4)#2	79.2(4)
O(2)#1–Pb(1)–O(4)#2	77.8(4)	O(3)–Pb(1)–O(1)#1	99.2(4)
O(2)#1–Pb(1)–O(1)#1	49.8(4)	O(4)#2–Pb(1)–O(1)#1	127.6(4)
O(3)–Pb(1)–O(5)	73.5(4)	O(2)#1–Pb(1)–O(5)	112.9(5)
O(4)#2–Pb(1)–O(5)	150.7(3)	O(1)#1–Pb(1)–O(5)	68.3(4)
O(3)–Pb(1)–O(1)#3	155.3(4)	O(2)#1–Pb(1)–O(1)#3	99.0(4)
O(4)#2–Pb(1)–O(1)#3	124.8(4)	O(1)#1–Pb(1)–O(1)#3	71.7(3)
O(5)–Pb(1)–O(1)#3	81.8(4)		
O(2)–C(1)–O(1)	123.0(15)	O(2)–C(1)–C(2)	119.8(14)
O(1)–C(1)–C(2)	117.1(16)	C(3)–C(2)–C(1)	113.0(14)
N(1)–C(3)–C(2)	110.0(13)	N(1)–C(3)–C(4)	112.5(14)
C(2)–C(3)–C(4)	107.5(13)	O(3)–C(4)–O(4)	128.5(14)
O(3)–C(4)–C(3)	117.2(14)	O(4)–C(4)–C(3)	114.3(13)
C(1)–O(1)–Pb(1)#4	88.3(10)	C(1)–O(1)–Pb(1)#5	122.9(9)
Pb(1)#4–O(1)–Pb(1)#5	119.5(4)	C(1)–O(2)–Pb(1)#4	98.7(9)
C(4)–O(3)–Pb(1)	117.6(11)	C(4)–O(4)–Pb(1)#6	122.3(9)
O(6)–N(2)–O(7)	122.0(18)	O(6)–N(2)–O(5)	119.5(18)
O(7)–N(2)–O(5)	118.0(17)	N(2)–O(5)–Pb(1)	127.9(12)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x-1, y-1/2, -z+3/2$; #2 $x+1, y, z$; #3 $-x-1/2, -y+2, z+1/2$; #4 $-x-1, y+1/2, -z+3/2$; #5 $-x-1/2, -y+2, z-1/2$; #6 $x-1, y$, z.

peptides do not contribute in a significant manner to lead assimilation.

Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), deposition number CCDC 133354.

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