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Synthesis and characterization of a three-dimensional open-framework lead(II) carboxyethylphosphonate, $Pb_3(O_2CCH_2CH_2PO_3)_2$

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The hydrothermal synthesis and single crystal XRD characterization of a three-dimensional open-framework lead(II) carboxyethylphosphonate, $Pb_3(O_2CCH_2CH_2PO_3)_2$, is described; the structure contains PbO_3, PbO_4 and PbO_5 polyhedra, each with stereochemically active lone pairs of electrons, and exhibits several types of channels.

The unique features of organic and inorganic compounds complement each other in hybrid materials leading to new solid state structures and materials with composite or even new properties. Metal oxide meso-structures, which are formed with the aid of organic surfactants, provide striking examples of such materials.[1] The metal phosphonate family is illustrative of hybrid materials, which contain a PO_3/metal–inorganic core that is separated by a tunable organic moiety bound to phosphorus.[2] Di-, tri- and tetra-valent metal phosphonates have been investigated widely in recent years due to their potential use as sorbents, ion-exchangers and catalysts. The layered structures formed by many of these materials are particularly interesting.[3–6] Alkyl phosphonic acids have been used as ligands to synthesize novel tin(II) phosphonates,[7,8] and the synthesis and characterization of several three-dimensional metal carboxyethylphosphonates have been reported in the recent literature.[3,9–14] There are, however, very few reports on lead containing phosphonates, though the lead derivatives of hydroxyethylidene diphosphonic and phenyl phosphonic acids are known.[15,16] In this communication, we describe the synthesis and characterization of a lead carboxyethylphosphonate where the ligand is bifunctional and the open-framework structure has an interesting channel architecture.

The compound $Pb_3(O_2CCH_2CH_2PO_3)_2$ was synthesized hydrothermally by reacting 2-carboxyethylphosphonic acid with lead nitrate solution.[17] The single crystal structure[18] was solved by direct methods using SHELXS-86 and difference Fourier syntheses.[19] The asymmetric unit contains 21 non-hydrogen atoms and is shown in Fig. 1a. The structure of $Pb_3(O_2CCH_2CH_2PO_3)_2$ consists of three crystallographically independent lead atoms having quite different coordination geometries: Ψ-tetrahedral PbO_3, Ψ-trigonal bipyramidal PbO_4, and Ψ-octahedral PbO_5 (the lone pairs occupying the fourth, fifth and sixth coordination sites, respectively). In Fig. 1b, we show the three-, four- and five-coordinated lead atoms, respectively, along with the Pb–O bond lengths. There are two units of 2-carboxyethylphosphonic acid in the asymmetric unit, the first (–COOH) unit is monodentate in nature and the second is bidentate. The oxygens of the carboxylate groups act both as the chelating as well as the bridging unit, as can be seen from Fig. 2a.

The complex connectivities give rise to an interesting three-dimensional open framework, the structure of which can be described as follows. A complex double-layered arrangement exhibiting several different ring features is obtained by connecting chains of the three-, four- and five-coordinated lead atoms through 2-carboxyethylphosphonate groups [Fig. 2(a)]. The three-dimensional network [Fig. 2(b)] is then achieved *via* the fifth coordination of Pb2, which connects the layers (the fifth Pb–O distance being 2.719 Å). The edge- and corner-sharing arrangement of polyhedra results in several distinct narrow channels. One is found along [001] within the double-layers [Fig. 2(b)] and two others (along [100] and [001]) are formed as a result of the connection between the double-layer channels. Interestingly, there is no structure-directing agent present in the compound, in contrast to many open-framework structures.

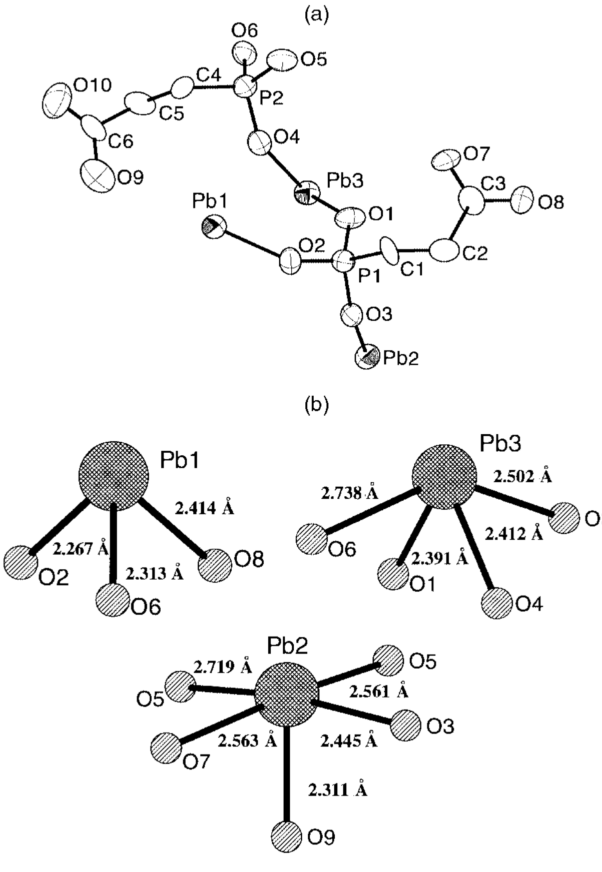

Fig. 1 (a) Asymmetric unit of $Pb_3(O_2CCH_2CH_2PO_3)_2$. (b) Lead atoms having three-, four- and five-coordination geometries.

Turning to the details of the structure, the three-coordinated lead (Pb1) atom has two oxygens (O2 and O6) from $-PO_3$ groups (O6 is three-coordinated) and one oxygen (O8) from a carboxylic acid group. The four-coordinated lead (Pb3) is surrounded by oxygens from four $-PO_3$ groups, which results in

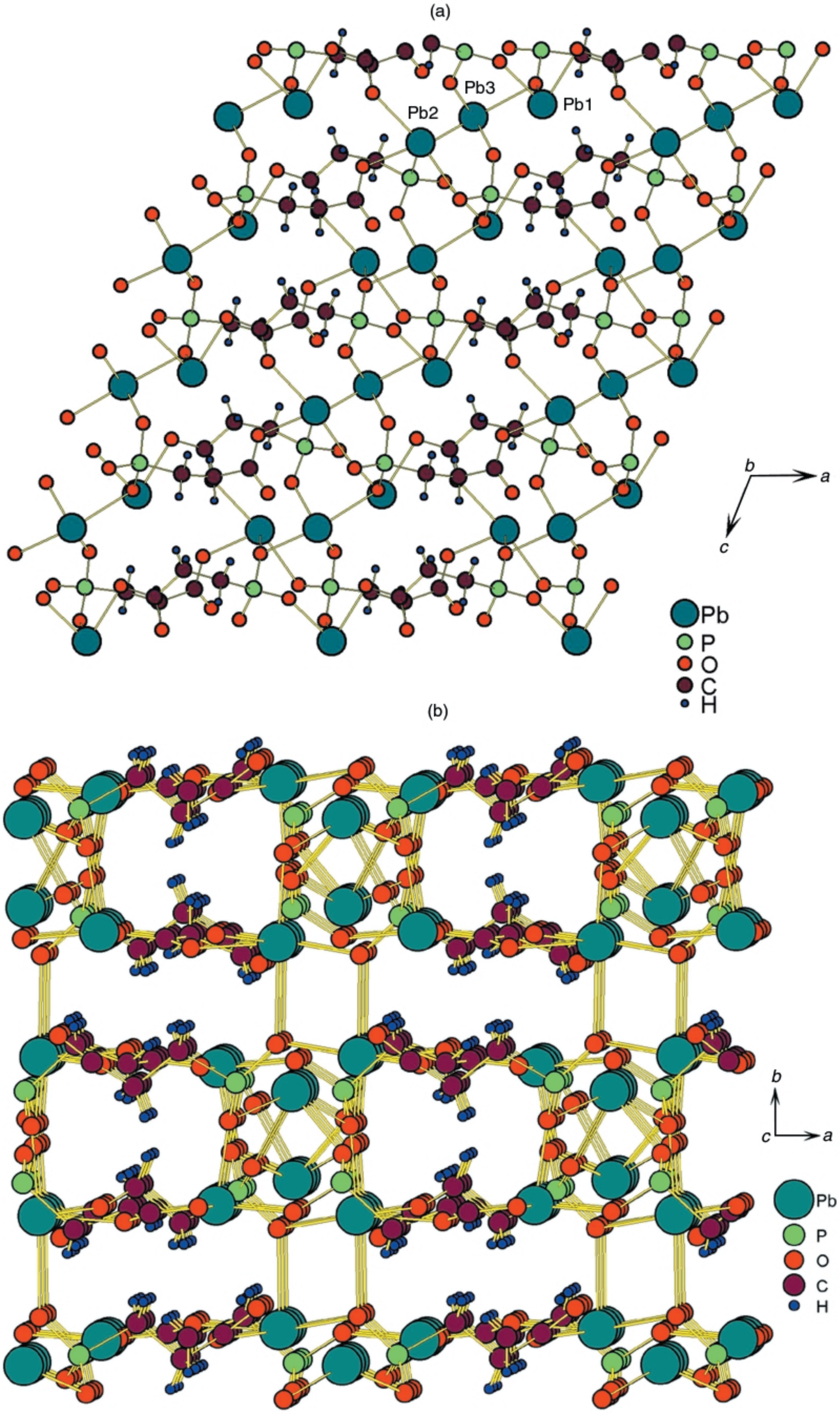

Fig. 2 (a) The layered arrangement (viewed along [010]) showing the mono- and bi-dentate nature of the carboxyethylphosphonic acid. The different lead atoms are labeled. (b) The three-dimensional structure of $Pb_3(O_2CCH_2CH_2PO_3)_2$ showing the channels along [001].

two three-coordinated oxygens, O3 and O6. Five-coordinated lead (Pb2) is surrounded by oxygens from three $-PO_3$ groups and two carboxylic acid groups. All three oxygens from $-PO_3$ groups (O3 and two O5) are three-coordinated. The valence electron counts around the lead atoms can be rationalized if we assume that each three-coordinated oxygen contributes two electrons rather than one. The Pb–O bond lengths vary from 2.267 to 2.738 Å, which are comparable to the values reported in other Pb(II) compounds.[13,14] Each phosphorus atom is tetrahedrally coordinated to three oxygens and a carbon atom.

There are two crystallographically independent P atoms and they have different local environments. In the first type, two oxygens are two-coordinated and the third oxygen is three-coordinated; it is classified as a [112] type phosphorus.[20] In the second type, one oxygen is two-coordinated and the remaining two oxygens are three-coordinated ([122] type phosphorus). It is interesting to compare the phosphorus environments in the title compound with some of the reported phosphonates, wherein the details were obtained mainly from NMR techniques.[20] The presence of both the [112] and [122] type phosphorus in $-PO_3$ groups is very unusual. The IR spectrum of the compound shows the asymmetric and symmetric vibrations of the carboxyl group at 1541 and 1419 cm^{-1}, respectively; the vibrations of the phosphonic group in the region 900–1100 cm^{-1} are in good agreement with previously reported values.[10]

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17 In a typical experiment, 1.655 g of lead nitrate and 0.77 g of 2-carboxyethylphosphonic acid were mixed with water in the ratio 1 : 1 : 55. The pH of the above solution was raised to 6, using 10 N NaOH. The starting mixtures were stirred to attain homogeneity, transferred to a 23 ml (fill-factor = 40%) PTFE bottle, then sealed in a stainless steel autoclave (Parr, USA) and heated at 150 °C for 48 h under autogenous pressure. The resulting product, which mainly contained crystals, was filtered and washed thoroughly with deionized water. The powder X-ray diffraction (XRD) pattern of the powdered crystals indicated that the product was a new material. Thermogravimetric analysis (TGA) was carried out in static air in the range between 25 and 900 °C. The results indicate that a sharp weight loss of 9.5% (calc. 9.9%) at around 400 °C corresponds to the loss of carbon, hydrogen and some oxygen. The powder XRD of the decomposed product at 400 °C confirms the presence of α-$Pb_3(PO_4)_2$ (JCPDS: 25-1394).

18 A suitable single crystal (0.01 × 0.2 × 0.1 mm) was carefully selected under a polarizing microscope. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 10 s per frame). The final unit cell constants were determined by a least squares fit of 1368 reflections in the range $3° < 2\theta < 46.5°$. Crystal data for $Pb_3(O_2CCH_2CH_2PO_3)_2$: monoclinic, space group $P2_1/c$, $a = 9.0559(10)$, $b = 14.5584(17)$, $c = 10.7154(12)$ Å, $\beta = 111.19(1)°$, $V = 1317.2(3)$ Å^3, $Z = 4$, $M = 923.63$, $\mu = 38.5$ mm^{-1}. Total data 10042 reflections; observed data 1368 relections; $R(\text{int}) = 0.116$. Final $R_F = 0.0446$, $wR_2 = 0.1046$, $S = 0.938$, for 190 parameters. CCDC reference number 186/1569.

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