

Hydrothermal synthesis and crystal structure of a novel lead(II) phosphonate containing trifunctional phosphonate anions: $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$

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Abstract

Hydrothermal reaction of lead(II) acetate with proline-*N*-methyl-phosphonic acid, namely, (*S*)-HO₃PCH₂-NHC₄H₇-CO₂H at 180 °C has resulted in a novel layered compound, Pb₄O[O₃PCH₂-NC₄H₇-CO₂]₂ **1**. The novel compound has been characterized by single-crystal X-ray diffraction, elemental analysis, infrared spectroscopy and thermogravimetric analysis. The compound features a layered structure in *ab* plane, and the layers have an inorganic ‘core’ with the organic part of the phosphonate anion being directed into the interlayer region.

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Metal phosphonates belonging to the class of inorganic-organic hybrid materials have received a great deal of attention in recent years due to the possibility to form interesting structures with potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry [1–4]. The organic moieties of the phosphonate ligand RPO₃²⁻ can be modified by other functional groups such as amino, hydroxy and carboxylate. The introduction of these functional groups may not only result in new structure types of metal phosphonates, but also bring interesting functionalities. Furthermore, the ability to functionalize metal phosphonates would extend their versatility to lead to new and more selective applications as shape recogni-

tion, and more importantly, in stereoselectivity when chiral linkers are used [5,6].

During the past few years, the use of bi- and trifunctional phosphonic acids in the synthesis of metal phosphonates has resulted in the formation of 2D or 3D open-framework. In the point of view of structural construction of inorganic-organic hybrid compounds, phosphonic acids with additional carboxylic functional groups are useful ligands, because they could together provide various kinds of coordination modes under different reaction conditions which may result in various interesting structures. [7–9]. Recently, an enantiomerically pure proline-*N*-methyl-phosphonic acid, namely, (*S*)-HO₃PCH₂-NHC₄H₇-CO₂H with two functional groups (–COOH and –PO₃H₂) has been used as a ligand to synthesis of open-frameworks, Co₃(O₃PCH₂NHC₄H₇CO₂)₂ · 5H₂O [10] and Zn₂[(*S*)-O₃PCH₂NHC₄H₇CO₂]₂ [11]. We have also been interested in exploring novel open-framework metal

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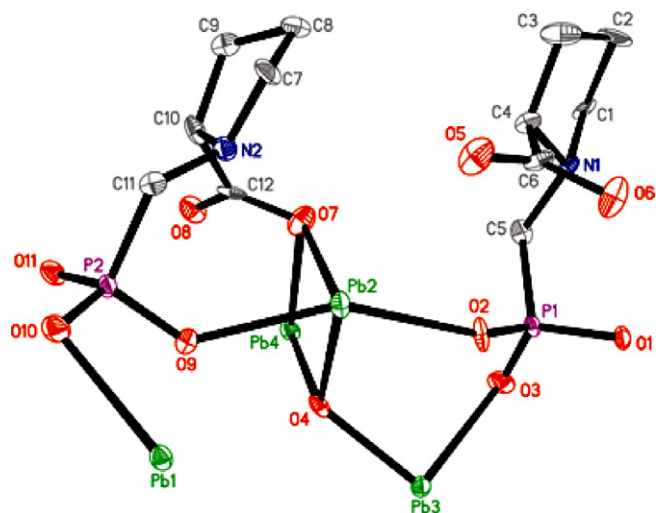


Fig. 1. Asymmetric unit of $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms are omitted for clarity. Pb(1)–O(1)#1, 2.373(11) Å; Pb(1)–O(3)#2, 2.459(11) Å; Pb(1)–O(10), 2.513(13) Å; Pb(1)–O(6)#1, 2.699(11) Å; Pb(2)–O(9), 2.452(11) Å; Pb(2)–O(7), 2.511(12) Å; Pb(2)–O(2), 2.554(10) Å; Pb(2)–O(4), 2.598(11) Å; Pb(3)–O(4), 2.189(12) Å; Pb(3)–O(3), 2.510(11) Å; Pb(3)–O(11)#3, 2.616(11) Å; Pb(3)–O(5)#1, 2.643(13) Å; Pb(3)–O(8)#3, 2.637(12) Å; Pb(4)–O(4)#3, 2.290(10) Å; Pb(4)–O(4), 2.324(10) Å; Pb(4)–O(9)#3, 2.504(11) Å; Pb(4)–O(7), 2.647(14) Å. Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $x, y + 1, z$; #3 $-x + 1, -y + 1, -z + 1$.

phosphonate compounds based on proline-*N*-methyl-phosphonic acid. In this paper, we report the synthesis [12] of a novel 2D inorganic-organic hybrid compound, Pb_4O

$[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ **1** by hydrothermal technique, using (*S*)- $\text{HO}_3\text{PCH}_2\text{-NHC}_4\text{H}_7\text{-CO}_2\text{H}$ as ligand. The compound structure was characterized by single crystal X-ray diffraction [13], elemental analysis, infrared spectroscopy and thermogravimetric analysis. However, in the structure of **1**, the proline moiety proved to be racemized during the hydrothermal reaction, resulting in no chirality of the framework.

The crystal structure of $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ contains 31 non-hydrogen atoms in the asymmetric unit, all in general positions (Fig. 1). There are four crystallographically independent leads. Pb1, Pb2, and Pb4 are four-coordinated by four oxygen atoms with bond distances between 2.290(10) and 2.699(11) Å, whereas Pb3 is five-coordinated by five oxygen atoms with bond distances between 2.189(12) and 2.643(13) Å. So the coordination geometries around Pb1, Pb2 and Pb4 can be described as Ψ - PbO_4 tetragonal pyramid and Pb3 can be described as Ψ - PbO_5 distorted octahedron.

There are two proline-*N*-methyl-phosphonic acids in an asymmetric unit. All the oxygen atoms of the proline-*N*-methyl-phosphonic acid ligand are coordinated by metal ions. In comparison to $\text{Co}_3(\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2)_2 \cdot 5\text{H}_2\text{O}$ [10], in the structure of compound **1**, the coordination of the proline-*N*-methyl-phosphonic acid ligand to the lead atom through the phosphonate group and the carboxylate group leaves nitrogen atom uncoordinated and the amino group free, and the functionality of the material is thus retained. Addition, there is one bridging oxygen atom (O4), coordinated four lead atoms (Pb2, Pb3 and 2

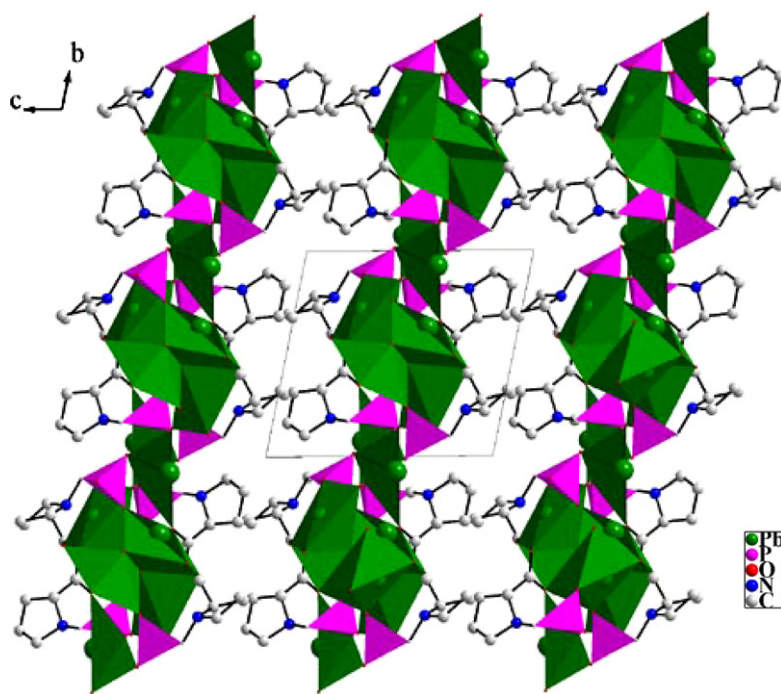


Fig. 2. The layered structure of $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ viewed along *a*-axis direction, showing helical chains formed by alternately arranged PbO_4 , PbO_5 and O_3PC polyhedra. The purple tetrahedral are O_3PC . The green polyhedra are PbO_4 and PbO_5 . All H atoms have been omitted for clarity. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)

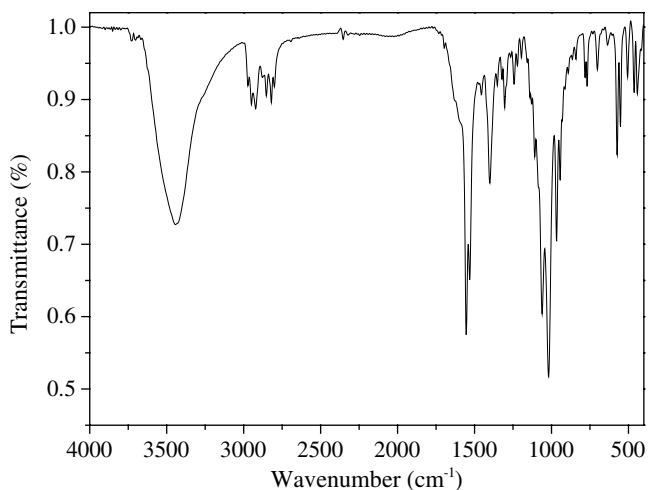


Fig. 3. The IR spectrum of $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$.

Pb4), and the bridging oxygen atom (O4) should carry two negative charges. Based on the charge balance, the two proline-*N*-methyl-phosphonic acids should carry six negative charges, in other words, all the ligands should be fully deprotonated to balance the charges of four Pb (II) ions.

This compound is layered, and the layer (*ab* plane) is built up of proline-*N*-methyl-phosphonic acid groups that link the lead atoms. The structure is similar to other layered phosphonate materials in that the layers have an inorganic 'core' with the organic part of the phosphonate anion being directed into the interlayer region. As shown in Fig. 2, compound **1** consists of helical chains formed by alternately arranged PbO_4 , PbO_5 and O_3PC polyhedra. These chains are interconnected through the $[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]^{3-}$ ions building a two-dimensional framework structure, and the layers are only held together by weak van-der-Waals interactions. Perhaps, the most unusual aspect of this compound is the chirality of the proline-*N*-methyl-phosphonic acid. The acid used in the synthetic procedure is chirally pure. In the product however, the proline moiety was racemized during the hydrothermal reaction, resulting in no chirality of the framework.

The IR spectrum [14] of compound **1** was recorded in the region from 4000 to 400 cm^{-1} (Fig. 3). The weak band at 2820 and 2921 cm^{-1} can be attributed to the asymmetric and symmetric C–H stretching vibrations of the $-\text{CH}_2$ groups. No band is seen at *ca.* 1715 cm^{-1} corresponding to $\nu(\text{C}=\text{O})$ for the free acid ($-\text{COOH}$). However, there are two pairs of strong bands centered at 1553, 1531 and 1452, 1400 cm^{-1} , which are assigned to the asymmetrical and symmetrical stretching vibrations of C–O groups when present as COO^- moieties [15]. The weak band at 1304 cm^{-1} is characteristic of the C–N stretching vibration. The $\text{P}=\text{O}$ and $\text{P}-\text{O}$ stretching and bending bands appear in the region of 1100–900 cm^{-1} . Additional intensive and sharp bands at low energy (573, 505, and 463 cm^{-1}) are found. These bands are probably due to bending vibrations of the tetrahedral O_3PC groups and $\text{Pb}-\text{O}$ stretching vibrations.

Thermogravimetric analysis [16] of compound **1** in the 50–800 °C temperature range in static air atmosphere revealed that it is thermally stable up to 327 °C. Above this temperature, a continuous weight loss was observed up to 520 °C, corresponding to the decomposition of the organic group, the weight loss (18.3%) is close to the calculated value (17.7%). The DTA curve exhibits a strong endothermic peak at approximately 422 °C, corresponding to the decomposition of the organic group.

In conclusion, a novel 2D inorganic-organic hybrid compound $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ has been hydrothermally synthesized from Pb (II) ion and proline-*N*-methyl-phosphonic acid and structurally characterized by single crystal X-ray diffraction analysis. The compound features a layered structure in that the layers have an inorganic 'core' with the organic part of the phosphonate anion being directed into the interlayer region. The proline moiety was racemized during the hydrothermal reaction, resulting in no chirality of the framework.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2006.07.022](https://doi.org/10.1016/j.inoche.2006.07.022).

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- [12] The title compound $\text{Pb}_4\text{O}[\text{O}_3\text{PCH}_2\text{-NC}_4\text{H}_7\text{-CO}_2]_2$ was synthesized by the hydrothermal reaction. $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ (0.25 mmol) and (*S*)- $\text{HO}_3\text{PCH}_2\text{-NHC}_4\text{H}_7\text{-CO}_2\text{H}$ (0.25 mmol) [10] were dissolved in H_2O (10 ml; 555.5 mmol), and then 40% tetrabutylammonium hydroxide aqueous solution was added with stirring to adjust the pH of the mixture. The mixture (pH \approx 8) was sealed in a Teflon-lined stainless steel autoclave, and then

heated at 180 °C for 3 days. Colorless needle crystals were obtained in *ca.* 63.6% yield based on Pb. Anal. Calcd. for C₁₂H₁₈N₂O₁₁P₂Pb₄: C, 11.47; H, 1.44; N, 2.23; P, 4.93; Pb, 65.9. Found: C, 11.31; H, 1.51; N, 2.29; P, 4.78; Pb, 65.75%.

- [13] *Crystal structure analysis*: The data were collected at a temperature of 293 ± 2 K on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program with $T_{\max} = 0.2923$ and $T_{\min} = 0.0186$. The structure was solved in the space group $P\bar{1}$ by Patterson method and refined by the full-matrix least-squares fitting on F^2 using SHELXTL-97 [17]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms of organic ligands were added theoretically, fixed isotropic thermal parameters, and included in the structure factor calculations. The final Fourier map had a minimum and maximum electron density of -5.313 and 5.238 e Å⁻³. The residuals were found near the Pb²⁺ ions. *Crystal data for 1*: C₁₂H₁₈N₂O₁₁P₂Pb₄, $M = 1256.98$, Triclinic, $P\bar{1}$, $a = 9.6982(10)$ Å, $b = 10.1104(11)$ Å, $c = 11.3940(12)$ Å, $\alpha = 99.0150$ (10)°, $\beta = 107.7430(10)$ °, $\gamma = 96.3720(10)$ °, $V = 1035.85$ (19) Å³, $Z = 2$,

$D_c = 4.030$ g cm⁻³. Data were collected on a single crystal with dimensions $0.60 \times 0.05 \times 0.05$ mm³. 5842 reflections were measured with ω -scans, in the range of $2.07^\circ \leq \theta \leq 26.50^\circ$ ($-12 \leq h \leq 10$, $-12 \leq k \leq 12$, $-7 \leq l \leq 14$), 4193 independent reflections ($R_{\text{int}} = 0.0249$). Final $R_1 = 0.0546$ [$I > 2\sigma(I)$], $wR_2 = 0.1569$, and the goodness-of-fit on F^2 is 1.049. CCDC reference no. is 295423. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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