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Letter

Cyclic acetate dimers formed by C–H···O hydrogen bonds in an open-framework zinc phosphate-acetate

Ayi A. Ayi,[a] Amitava Choudhury,[a,b] Srinivasan Natarajan[a] and C. N. R. Rao*[a,b]

[a] *Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in*
[b] *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

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A novel three-dimensional zinc phosphate-acetate, formed by acetate dimers with C–H···O bonds, has been synthesized for the first time under mild conditions.

As part of our investigations of inorganic open-framework structures, we were interested in synthesizing a metal phosphate-acetate, analogous to the metal phosphate-oxalates reported in the last few years.[1,2] The idea was that, in a phosphate-acetate, the acetate unit would connect the metal phosphate layers, just as the oxalate does in the phosphate-oxalates, thereby creating a channel. We have been able to prepare such a zinc phosphate-acetate, with the composition, $[CH_3CH_2CH_2NH_3]_4[Zn_3Zn(CH_3COO)(PO_4)(HPO_4)_3(H_2PO_4)(CH_3COO)]$, **I**, under non-hydrothermal conditions at 60 °C. What is especially noteworthy about this compound is that the acetate units bridging the phosphate layers form symmetric cyclic dimers through nearly linear C–H···O hydrogen bonds. To our knowledge, this is the first case of such a C–H···O bonded acetate dimer, comparable to the carboxylic acid dimers in the O–H···O hydrogen bonded systems. In addition, this is also a good example of a system where C–H···O bonds are involved in determining the three-dimensional architecture of an inorganic solid.

The zinc phosphate-acetate **I**, prepared at 60 °C in the presence of propylamine,† was characterized by single crystal X-ray diffraction using a Siemens SMART-CCD diffractometer.‡ The asymmetric unit contains 53 non-hydrogen atoms, of which four Zn and five P atoms are crystallographically independent (Fig. 1a). The structure of **I** consists of macroanionic layers built up from ZnO_4, $ZnO_3(OAc)$ and PO_4 tetrahedra. Charge compensation is achieved by the presence of a free acetate group and protonated propylamine molecules situated in between the layers. The ZnO_4 and PO_4 tetrahedra are connected so as to form a layer with 4-, 6- and 8-membered apertures, as shown in Fig. 1b. The acetate group bonded to Zn(4) points into the inter-lamellar space between the zinc phosphate layers, and interacts with the acetate group of the adjacent layer (Fig. 2a). The most striking aspect of the positions of these acetate units is that they form C–H···O hydrogen bonds between the methyl group hydrogens and carbonyl oxygens, as shown in Scheme 1.

The C···O and H···O distances in the dimer are 3.49 and 2.53 Å, respectively. This H···O distance is at the lower end of the range of distances reported in the literature for C–H···O hydrogen bonded systems.[3] The C–H···O bond angle in the acetate dimer is 179°, making it nearly linear. A majority of the C–H···O bonds appear to have H···O distances in the 2.5–3.0 Å range, with a C–H···O angle of 140 ± 25°. On the basis of the plot of the C–H···O angle against the H···O distance given by Desiraju,[3] we consider the hydrogen bond in **I** to be particularly strong. The acetate dimer in **I** is quite different from the other dimeric C–H···O hydrogen bonded structures, such as *N*,*N*-dimethylnitroamine, 4-(*N*,*N*-dimethylamino)benzoic acid and *N*,*N*-dimethylformamide dimers,[3–5] the hydrogen bonding between the methyl hydrogen and the carbonyl oxygen being a new feature. The dimeric structure is probably favored by the pillaring role of the acetate ions, linked to adjacent zinc phosphate layers. Besides the unique hydrogen bond structure, the acetate dimer also plays a key role in forming a 14-membered channel along the *a* axis (Fig. 2a). Along the *b* axis, a 10-membered channel results from similar interactions.

The Zn–O distances in the ZnO_4 tetrahedra of **I** are in the range 1.900(5)–1.999(5) Å (av. 1.946 Å) and the O–Zn–O bond angles in the range 96.2(3)–123.4° (av. 109.2°). Of the four Zn atoms, three [Zn(1), Zn(2) and Zn(3)] are connected to P through four Zn–O–P linkages, while the fourth [Zn(4)] makes only three bonds and possess one terminal oxygen. The

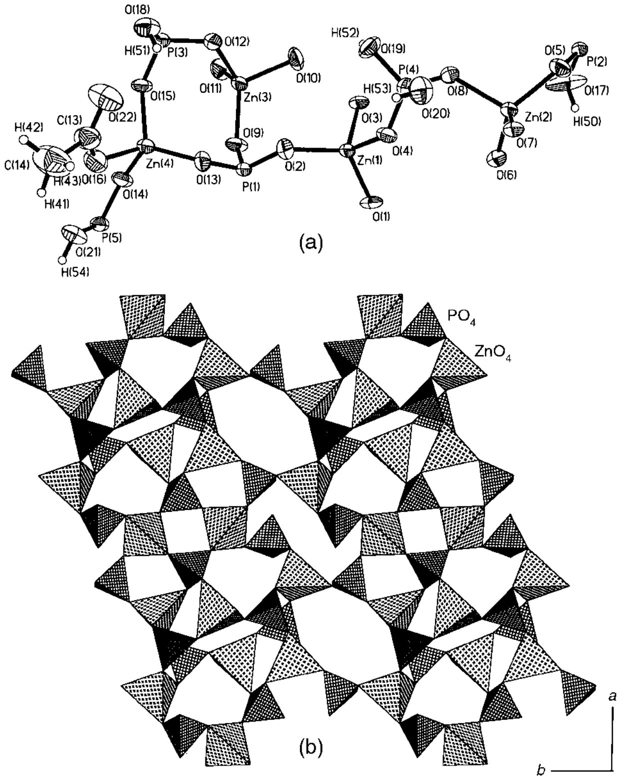


Fig. 1 (a) ORTEP plot of the framework in **I**, showing the labeling scheme. Thermal ellipsoids are given at 50% probability. (b) A polyhedral representation of the Zn phosphate layers in **I**. Note that the layers are formed with 4-, 6- and 8-membered apertures.

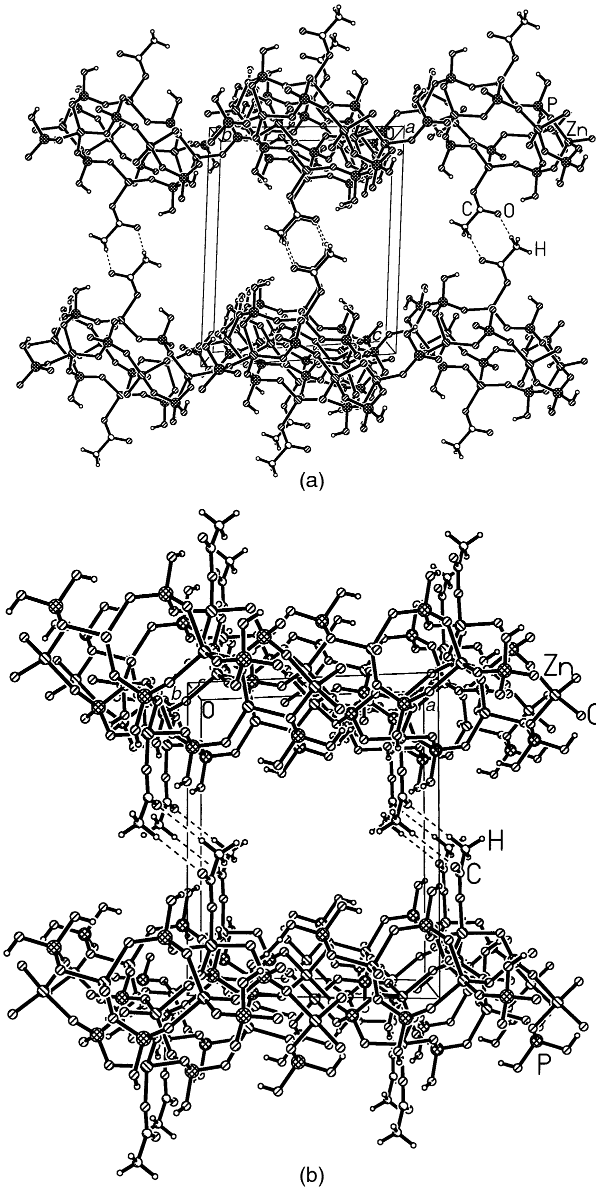
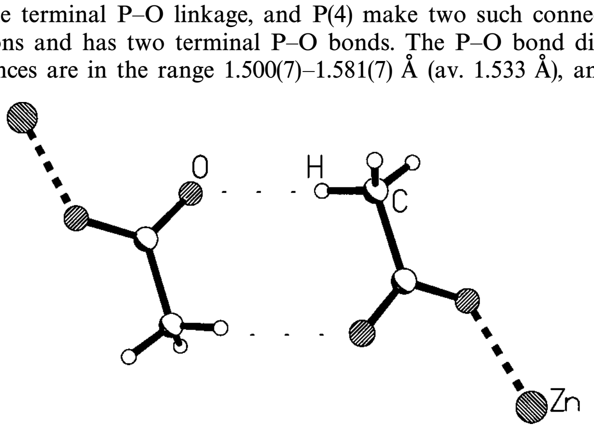


Fig. 2 (a) Structure of **I** along the *a* axis. Note the cyclic acetate dimers forming a 14-membered channel. (b) Structure of **I** along the *b* axis showing the 10-membered channel. The free acetate and the amine are not shown for clarity.

terminal oxygen belongs to the acetate group. An average Zn–O–P bond angle of 132.8° results from such linkages. All the P atoms are four-coordinate, forming typical tetrahedra with oxygens. While P(1) makes four P–O–Zn bonds, P(2), P(3) and P(5) form three P–O–Zn connections and possess one terminal P–O linkage, and P(4) make two such connections and has two terminal P–O bonds. The P–O bond distances are in the range 1.500(7)–1.581(7) Å (av. 1.533 Å), and O–P–O angles in the range 105.5(4)–113.2(3)° (av. 109.4°). The terminal P–O linkages, with P–O distances of 1.561(7) [P(2)–O(17)], 1.555(6) [(P(3)–O(18)], 1.524(5) [P(4)–O(19)], 1.571(6) [P(4)–O(20)] and 1.581(6) Å [P(5)–O(21)] are all –OH bonds. These structural parameters are consistent with bond valence sum calculations.[6] Apart from the C–H···O hydrogen bonding in the acetate dimer, there are other hydrogen bond interactions in **I**. Thus, the amine forms strong N–H···O (H···O, 2.0–2.4 Å) and weak C–H···O (H···O, 2.85 Å) bonds with the framework oxygens. The HPO_4 and H_2PO_4 groups form intramolecular O–H···O (H···O, *ca.* 2.6 Å) bonds as well.



Scheme 1

In conclusion, a zinc phosphate-acetate with a channel structure has been synthesized and characterized for the first time. Besides being a new type of open-framework structure, the phosphate-acetate has the novel feature wherein the phosphate layers are pillared by C–H···O hydrogen bonds. This acetate dimer constitutes an important addition to the family of C–H···O hydrogen bonded systems not only because of its unique structural features, but also because it is involved in forming a three-dimensional inorganic channel structure.

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Notes and references

† Compound **I** was synthesized from a THF–water mixture under non-hydrothermal conditions. 0.439 g of $Zn(COOCH_3)_2 \cdot 2H_2O$ was dispersed in a THF–H_2O mixture (75 : 25 v/v). To this, 0.26 ml of H_3PO_4 (88 wt.%) was added under constant stirring. The mixture was heated at 110 °C for 20 min to dissolve the ZnOAc, after which it was cooled and 0.5 ml of propylamine (PA) added at room temperature. The resulting white gel, with a composition of $Zn(COOCH_3)_2 \cdot 2H_2O : 2H_3PO_4 : 3PA : 20THF : 15H_2O$, was kept at 60 °C for 72 h. The product, a crop of rod-like colorless crystals was filtered under vacuum and washed with the minimum quantity of water and dried under ambient conditions. The sample was characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and infrared (IR) spectroscopic studies. Thermogravimetric analysis in the range room temperature to 700 °C showed two distinct mass losses. The first mass loss of 19.3% in the range 240–300 °C corresponds well with the loss of amine molecules (calc. 21.8%) and the second loss of 16.2% in the range 350–400 °C corresponds to the loss of both bonded and free acetate groups and hydroxyls of the $PO_3(OH)$ units (calc. 14.8%). The calcined sample is poorly crystalline and corresponds to condensed $Zn_2P_2O_7$ (JCPDS: 11.0026) and P_2O_5.

‡ A suitable single crystal was analyzed at 293 K; triclinic, space group $P\bar{1}$ (no. 2) with $a = 12.1830(6)$, $b = 12.9550(6)$, $c = 14.3375(7)$ Å, $\alpha = 85.988(1)$, $\beta = 89.019(1)$, $\gamma = 68.267(1)°$, $V = 2096.8(2)$ Å^3, $Z = 2$, $D_{calc} = 1.742$ g cm^{-3} and μ(Mo-Kα) = 2.534 mm^{-1}. A total of 8813 reflections were collected and were merged to give 5891 unique reflections ($R_{int} = 0.047$), of which 3983 were considered to be observed [$I > 2\sigma(I)$]. The structure was solved by direct methods using SHELXS-86,[7] and difference Fourier synthesis. Final R_1 (weighted, based on $|F^2|$) = 0.066, $wR_2 = 0.17$ and $S = 0.98$ values were obtained for 478 parameters. All the hydrogen atoms were located initially in the difference Fourier maps, and for the final refinement, hydrogen atoms for the framework were placed geometrically and held in the riding mode. The hydrogens on the amine were not placed and included in the refinement. The maximum and minimum peaks on the final difference Fourier map corresponds to 1.533 and −1.088 e Å^{-3}. Full-matrix least-squares structure refinement against $|F^2|$ was carried out with the SHELXTL-PLUS package of programs.[8] CCDC reference number 151890. See http://www.rsc.org/suppdata/nj/b0/b008498k/ for crystallographic files in .cif format.

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