

Cs₂Al₂P₂O₉: an exception to Löwenstein's rule. Synthesis and characterization of a novel layered aluminophosphate containing linear Al–O–Al linkages

Qun Huang and Shiou-Jyh Hwu*

Department of Chemistry and Materials Science and Engineering Program, Clemson University, Clemson, SC 29634-0973, USA. E-mail: shwu@clemson.edu

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A caesium aluminophosphate compound synthesized via high-temperature, solid-state methods reveals a new composition for a layered AIPO structure; it exhibits a non-Löwensteinian framework which contains linear Al–O–Al linkages in six-rings of alternating Al₂O₇ and PO₄ groups.

In spite of the large number of aluminophosphates known (*ca.* 250 compounds), the only established compositions adopted by layered structures consisting of AlO₄ and PO₄ tetrahedra are [Al₃P₄O₁₆]³⁻, [AlP₂O₈]³⁻, [Al₂P₃O₁₂H_x]^{(3-x)-} (*x* = 1,2), [Al(HPO₄)₂(H₂O)₂]⁻, and [Al₄P₅O₂₀H]²⁻.¹ Their frameworks are built up from either 4 × 6, 4 × 8, 4 × 6 × 8, or 4 × 6 × 12 rings. The title compound exhibits a new framework formula, [Al₂P₂O₉]²⁻, which contains an equal number of Al and P atoms. The single crystal structure reveals an unusual feature with respect to the direct Al–O–Al linkages and, in turn, a new type of 4 × 6 aluminophosphate (AIPO) network. All the above mentioned AIPOs, except the current compound, show frameworks avoiding direct Al–O–Al linkages between AlO₄ tetrahedral units; for zeolites (aluminosilicates) this is known as Löwenstein's rule.² According to the Löwensteinian structure, each Al is coordinated through oxygen to four Si (or P) and *vice versa* (the 4:0 ordering scheme). Theoretical calculations predict that the formation of Al–O–Al linkages (in the 3:1 ordering scheme, for example) is energetically unfavorable.³ The experimental findings on compounds prepared by hydrothermal routes, such as the organically templated AIPO synthesis, support this claim.¹ However, calculations based on the lattice energy of an ionic model by Bell, Jackson, and Catlow,^{3b} suggest that the energy loss due to the direct linkages could be overcome by thermal energies. This prediction is confirmed by some scattered examples of non-Löwensteinian frameworks prepared by high-temperature methods.⁴ Among these exceptions, there are about 45 out of over 2,450 reported aluminosilicates, but only two aluminophosphates. These include sodalite,^{4a} a common example for aluminosilicates, as well as metal-containing MAIPO₅ (M = Mg, Fe).^{4b,c}

Crystals of Cs₂Al₂P₂O₉, **1**, were grown by high-temperature, solid-state methods using CsCl flux,⁵ and the structure was characterized by single crystal X-ray diffraction methods.⁶ As shown in Fig. 1, **1** adopts a layered structure where the aluminophosphate slabs are held together by electropositive Cs⁺ cations. The extended AIPO slab consists of alternately arranged Al₂O₇ and PO₄ groups sharing corner oxygen atoms. Each slab adopts a mixed four- and six-ring (4 × 6) network [Fig. 2(a)]. The 4-ring (2Al + 2P) structure is made up from alternating 2 × AlO₄ and 2 × PO₄ groups while the 6-ring (4Al + 2P) is built of 2 × Al₂O₇ and 2 × PO₄ groups. The Al–O–Al linkages [highlighted by solid lines in Fig. 2(a)] exist in the form of Al₂O₇ units in between rows of fused 4-ring units. The latter form a corrugated Al₂P₂O₄ chain [Fig. 2(b)], in which the 4-ring units are in a chair configuration.

The aluminium powder may facilitate a chain 'zipping' process *via* oxidation intercalation *en route* to the formation of AIPO slabs.⁵ The 4-ring chain shown in [Fig. 2(b)] resembles the so-called precursor structure for extended lattices.^{1a} In our study, aluminium powder was employed along with an oxidant, potassium superoxide. This approach is unconventional com-

pared to commonly employed methods using aluminium oxide (or hydroxide) as starting material.⁵ For the mechanism, one can imagine the processes of bond breaking *via* dissociation of the Al–O–Al linkages of Al₂O₃, prepared *in situ* in this case,

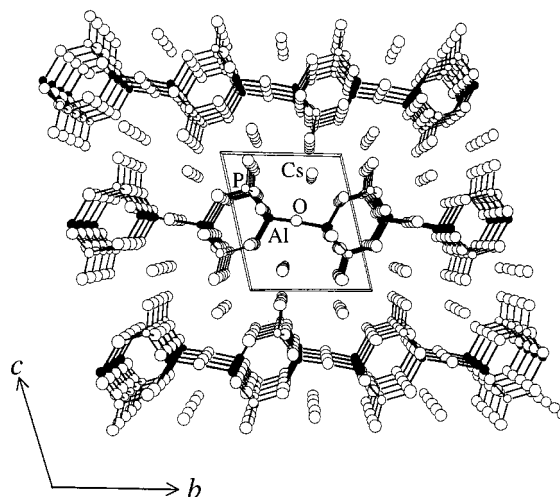


Fig. 1 Projected view showing the layered structure of **1**. The small filled and open circles, as for Fig. 2, represent Al³⁺ and P⁵⁺ cations, respectively, and the large open circles represent O²⁻ (bonded) and Cs⁺ (non-bonded) ions.

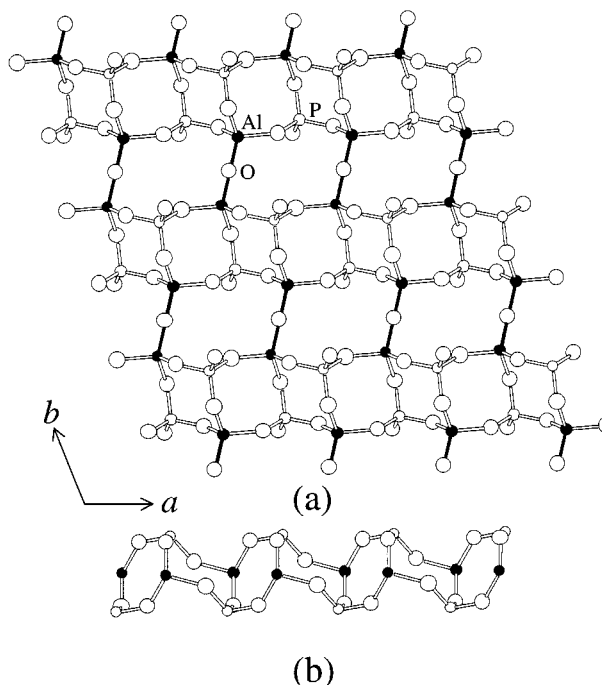


Fig. 2 (a) A partial structure of the [Al₂P₂O₉]²⁻ slab. The linear Al–O–Al linkages are highlighted with thick lines. (b) A side view of fused 4-ring units, see text. The terminal oxygen atoms are omitted for clarity.

followed by bond formation with phosphorus cations through bridging oxygens. While the idea of this reaction pathway is intuitively sound, the framework formation could bypass the formation of Al_2O_3 to undergo simultaneous layer formation *via* oxidative 'zipping' of partially oxidized AlPO chains. Direct heating of a mixture of Al_2O_3 or $\text{Al}(\text{OH})_3$, P_2O_5 and CsOH at 800°C in an open system does not, in fact, yield **1**. Addition of CsCl as a flux results in an as yet unidentified phase, whose PXRD patterns show a close resemblance to those of **1**. Further investigation into the role of aluminium powder is underway.

The title compound reveals a new type of 4×6 network and a fascinating framework of interconnected 4-ring chains. Prior to this research, four 4×6 network structures were known that adopt the above mentioned $[\text{Al}_3\text{P}_4\text{O}_{16}]^{3-}$ and $[\text{HAl}_2\text{P}_3\text{O}_{12}]^{2-}$ compositions.^{1c,7} Fig. 3 presents all the 4×6 networks, including the current example, in which only Al^{3+} and P^{5+} cations are shown. The network structures are adopted by, for example, $(\text{NH}_3\text{CHMeCH}_2\text{NH}_3)_3[\text{Al}_6\text{P}_8\text{O}_{32}] \cdot \text{H}_2\text{O}$ for network type (a), $\text{Co}(\text{en})_3[\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 3\text{H}_2\text{O}$ and *trans*- $\text{Co}(\text{dien})_2[\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 3\text{H}_2\text{O}$ for type (b), $(2\text{-BuNH}_3)_2[\text{HAl}_2\text{P}_3\text{O}_{12}]$ for type (c), $(\text{C}_5\text{N}_2\text{H}_9)_2(\text{NH}_4)[\text{Al}_3\text{P}_4\text{O}_{16}]$ for type (d), and **1** for type (e). It should be noted that the major difference among the frameworks consisting of these networks concerns the tetrahedral units. The framework of **1** is comprised of Al_2O_7 units while the others consist of AlO_4 interlinked with PO_4 units only. The networks (a)–(d), therefore, possess the 4:0 ordering scheme while network (e) has the 3:1 scheme. In addition, the networks

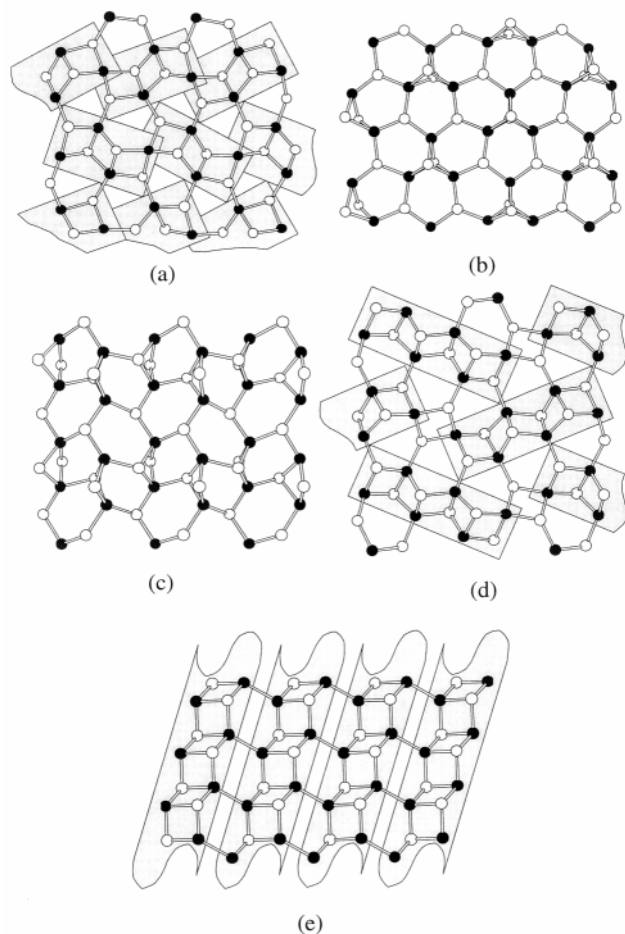


Fig. 3 Five types, (a)–(e), of 4×6 Al–P–O frameworks. Aluminum atoms (●) and phosphorus atoms (○) are linked by oxygen bridges (not shown). In (a)–(d), strict alternation of Al and P is observed, whereas in (e), the 3:1 ordering scheme is shown. The fused 4-ring units in (a), (d), and (e) are highlighted, see text.

(a) and (d) consist of short, (3- and 5-, respectively) edge-shared, four-ring units while (e) contains parallel chains of fused four-rings.

The Al–O–Al linkage in **1** reveals two unusual features; namely, a linear bond angle and a fairly short Al–O^b (O^b: bridging oxygen in the Al_2O_7 unit) bond. The Al–O^b–Al angles are usually nonlinear and are much smaller than 180° . In the frameworks of two previously mentioned non-Löwensteinian compounds, MgAlPO_5 and FeAlPO_5 , for instance, the Al–O^b–Al angles are $129.8(2)^\circ$ and $131.8(2)^\circ$, respectively.^{4b,c} Also, the Al–O^b bond in **1**, (1.69 Å) is shorter than the three Al–O^t (O^t: terminal oxygen in the Al_2O_7 unit) bonds, (1.75–1.76 Å). Based on chemical intuition, the linear bond angle and short bridging oxygen to aluminium bond distance suggest possible π character. It would be interesting to look at the thermal behavior of the framework in relation to the Al–O^b–Al linkage.

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- 0.0540 g of Al (2.0 mmol), 0.1422 g of KO_2 (2.0 mmol), 0.0795 g of CuO (1.0 mmol) and 0.1419 g of P_2O_5 (1.0 mmol) were ground and mixed with the flux CsCl . The charge to flux ratio was 1:2 by weight. The reaction was carried out in a carbon-coated quartz ampoule. The mixture was heated up to 500°C over 24 h, and isothermed for 6 h, followed by heating to 800°C , and isothermal treatment for an additional 4 d. The reaction was cooled slowly to 500°C over 72 h, followed by furnace cooling to room temperature. Colorless columnar crystals of **1** (ca. 60%), as well as some other unidentified black and white polycrystalline phases (ca. 40%), were retrieved from the flux by washing the products with deionized water using suction filtration. EDAX shows no contamination from potassium, chlorine, and copper in this crystalline phase, as the presence of the latter is attributed to CuO used for the synthesis of Cu-containing AlPO. An alternative reaction of $2\text{Al}/2\text{KO}_2/\text{P}_2\text{O}_5/4\text{CsCl}$ without adding CuO resulted in a slightly lower yield of **1**, ca. 50%.
- Crystal data for **1**: $\text{Cs}_2\text{Al}_2\text{P}_2\text{O}_9$, $M = 525.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 4.925(2)$, $b = 7.121(2)$, $c = 8.066(2)$ Å, $\alpha = 96.51(2)^\circ$, $\beta = 107.12(2)^\circ$, $\gamma = 108.68(2)^\circ$, $V = 249.3(1)$ Å³, $Z = 1$, $D_c = 3.502$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 7.835$ mm⁻¹, $\lambda = 0.71073$ Å, $3.50^\circ < 2\theta < 55.00^\circ$. Final $R = 0.024$, $R_w = 0.035$, GOF = 1.36 were obtained for all the data and 71 parameters. The final Fourier map had a minimum and maximum of -1.04 and 1.60 eÅ⁻³, respectively. CCDC 182/1446. See <http://www.rsc.org/suppdata/cc/1999/2343/> for crystallographic files in .cif format.
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