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Synthesis and characterisation of novel layered compounds, $Cs_2MP_3O_{10}$ (M = Al or Ga), containing triphosphate groups†

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The compounds $Cs_2AlP_3O_{10}$ and $Cs_2GaP_3O_{10}$ have been synthesized by solid state reactions and structurally characterised by single crystal X-ray diffraction. They are two dimensional compounds possessing corrugated $[MP_3O_{10}]^{2-}$ anionic layers interleaved with Cs^+ ions. The layers are built from MO_6 octahedra and bent triphosphate groups. Solid state NMR studies corroborate the presence of crystallographically distinct phosphorus atoms of triphosphate groups.

Introduction

Solid compounds possessing framework structures with well defined tunnels and layers are extensively investigated because their unique and complex structural chemistry endows them with interesting chemical and physical properties. Phosphates in the A/M/P/O quaternary system form one such family of compounds showing rich structural chemistry with anionic frameworks built from MO_x polyhedra and PO_4 tetrahedra and A^{n+} ions as counter cations.[1–5] Research on the synthetic and structural chemistry of these open framework materials continues to be pursued with the idea of obtaining them with accessible redox catalytic activity, anisotropic electrical conductivity, high ionic conductivity and ion exchange properties.

We have undertaken a synthetic and structural investigation of the A/M/P/O (A = alkali metal or Tl; M = Al or Ga) system and isolated a number of phosphates possessing novel structural features: $Cs_2AlP_3O_{10}$ and $Cs_2GaP_3O_{10}$ containing triphosphate groups are two such compounds. These compounds were realised in a phase study by Lyutsko *et al.*, who reported XRD powder data without any further crystallographic information.[6] There are two more series of compounds, namely $AMHP_3O_{10}$ and $AM(H_2P_3O_{10})(P_4O_{12})$, reported[7] to contain triphosphate groups and some of them were structurally characterised: $AMHP_3O_{10}$ have been shown to possess both layered and three dimensional structures.[8–10] Here we report the synthesis and characterisation of $Cs_2MP_3O_{10}$ (M = Al **1** or Ga **2**) compounds with novel layered structural frameworks.

Experimental

Synthesis

The compounds $Cs_2AlP_3O_{10}$ **1** and $Cs_2GaP_3O_{10}$ **2** were synthesized in polycrystalline form by solid state reactions from stoichiometric mixtures of $CsNO_3$, $NH_4H_2PO_4$ and $Al(OH)_3$ or Ga_2O_3. These mixtures were heated in open air initially at 400 °C for 12 h to necessitate the decomposition of $NH_4H_2PO_4$ and the temperature was raised in steps of 100 °C to the maximum value of 700 °C, at which the compounds were heated for a duration of 12 h.

Crystal growth

Single crystals of $Cs_2MP_3O_{10}$ were grown by the flux method by using $CsPO_3$ as the flux. Mixtures of Cs_2CO_3, $NH_4H_2PO_4$ and $Al(OH)_3/Ga_2O_3$, taken in the 6:1 mass ratio of $CsPO_3$ flux to aluminum/gallium, were heated at 700 °C for 1 d and then cooled to 550 °C at the rate of 3 °C h^{-1}. Plate-like colorless crystals were separated by washing away the flux with water.

Characterisation

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku desktop X-ray diffractometer using Ni filtered Co-Kα (λ = 1.7902 Å) radiation. Solid state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 78.2 and 121.5 MHz for ^{27}Al and ^{31}P respectively. Chemical shifts were referenced to an external standard of $Al(NO_3)_3$ for ^{27}Al and H_3PO_4 for ^{31}P. The spinning frequency was 7 kHz and recycle delay time 15 µs for both. The pulse length was 5.0 µs for ^{27}Al and 4.0 µs for ^{31}P.

Single crystal X-ray diffraction analysis

Single crystals of compounds **1** and **2** were mounted on glass fibres with epoxy glue and data collected on an Enraf-Nonius CAD4 diffractometer at 298 K by standard procedures. The observed systematic absences indicated that the space group is the centrosymmetric *P*2$_1$/*a* for both **1** and **2**. The programs[11] SHELXS 86 and SHELXL 93 were used for structure solution and refinement respectively. Pertinent crystallographic data for **1** and **2** are given in Table 1. The graphics programs[12] ATOMS and ORTEP were used to draw the structures.

For compounds **1** and **2** only some of the atoms could be refined anisotropically and others were refined isotropically to give *R* values of 0.0573 and 0.0971 respectively. The final Fourier map contained 10 peaks for **1** and more than 30 peaks for **2** with electron density of 1 e Å^{-3}, the maximum being 2.99 and 3.31 e Å^{-3} respectively. These peaks were found to be ghosts of the existing atoms indicating a severe absorption problem. Therefore additional absorption corrections using the DIFABS program[13] were applied to the isotropically refined data sets. The final refinement carried out using the corrected data led to improved *R* values of 0.0320 and 0.0471 for **1** and **2** respectively. For **1** all the atoms were refined anisotropically and the final Fourier map contained only two peaks having electron density of 1 e Å^{-3}. For **2** three atoms were refined isotropically

† Supplementary data available: X-ray powder diffraction data available from BLDSC (SUPP. NO. 57700, 3 pp.). See Instructions for Authors, Issue 1 (http://www.rsc.org/dalton).

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Table 1 Crystallographic data for compounds **1** and **2**

Formula	$AlCs_2O_{10}P_3$ **1**	$Cs_2GaO_{10}P_3$ **2**
M	545.64	588.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a/Å	9.420(4)	9.494(6)
b/Å	9.016(3)	9.016(9)
c/Å	12.258(2)	12.290(32)
β/°	94.88(3)	94.97(30)
U/Å^3; Z	1037.3(6); 4	1048.0(3); 4
μ(Mo-Kα)/mm^{-1}	7.190	9.935
Total reflections	1810	1838
Independent reflections (R_{int})	1795 (0.0327)	1838 (0.0552)
R	0.0320	0.0471
R_w	0.0777	0.1282

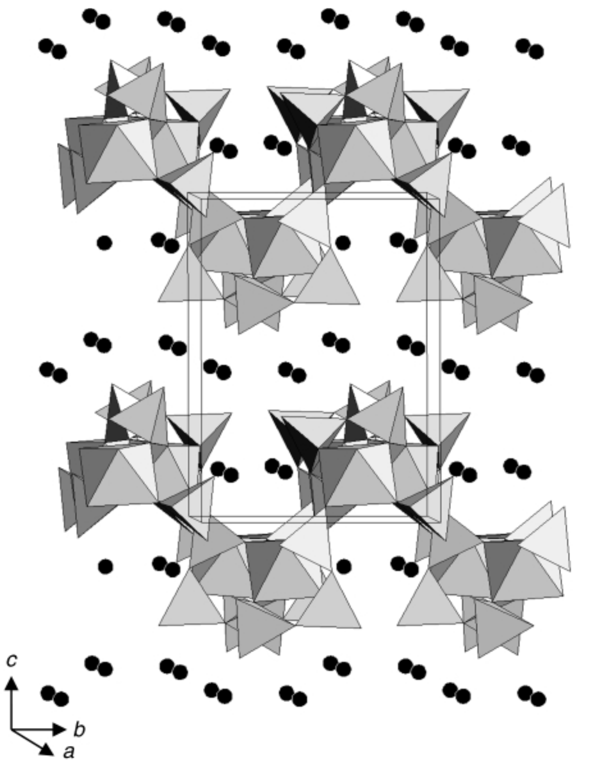

Fig. 1 Polyhedral representation of the unit cell of $Cs_2AlP_3O_{10}$ **1** viewed along the *a* axis; filled circles represent Cs^+ ions.

and the Fourier difference map was significantly better with only 13 peaks having electron density of 1 to 1.5 e Å^{-3}. However, the chemical structures are accurate and not affected by the absorption problem and the correction applied to the data sets.

CCDC reference number 186/1907.

See http://www.rsc.org/suppdata/dt/a9/a909753h/ for crystallographic files in .cif format.

Results and discussion

The two compounds $Cs_2AlP_3O_{10}$ **1** and $Cs_2GaP_3O_{10}$ **2** could be synthesized not only as powders by solid state reactions but also grown as single crystals using $CsPO_3$ as flux. However, the corresponding indium analogue could not be prepared. X-Ray powder diffraction patterns (available as supplementary data) of the polycrystalline samples of these two isostructural compounds are similar and compare well with those simulated by the program[14] LAZY PULVERIX based on the crystallographic data, confirming them to be monophasic.

Both **1** and **2** are two dimensional compounds possessing $[MP_3O_{10}]^{2-}$ anionic layers interleaved with Cs^+ ions as shown in the unit cell diagram (Fig. 1). These layers are highly corrugated and perpendicular to the *c* axis. The $[MP_3O_{10}]^{2-}$ anion, as

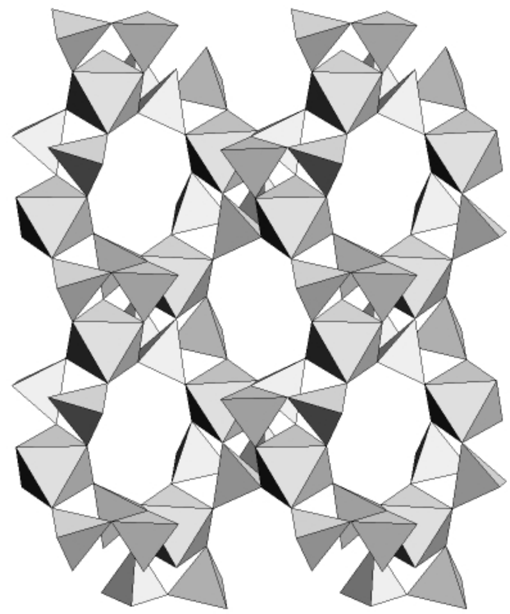

Fig. 2 Polyhedral representation of $[AlP_3O_{10}]^{2-}$ layer viewed perpendicularly.

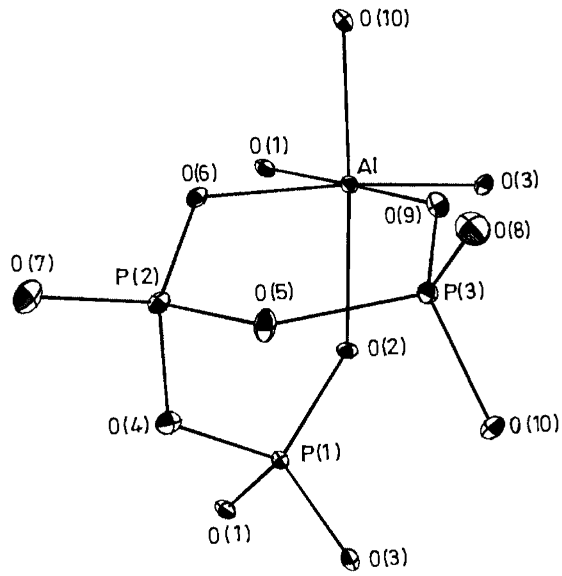

Fig. 3 An ORTEP plot of the corner connection of the AlO_6 octahedron with the P_3O_{10} triphosphate group in $Cs_2AlP_3O_{10}$ **1**, showing the atom labelling scheme (50% thermal ellipsoids).

shown in Fig. 2, is built from corner connections of MO_6 octahedra with $P_3O_{10}{}^{5-}$ triphosphate groups. Each MO_6 octahedron is connected to three triphosphate groups, with one of them capping one triangular face and the other two being connected in bidentate and monodentate fashion. Each P_3O_{10} is thus connected to three MO_6 octahedra. These layers have eight sided windows, formed by edges of alternating four MO_6 octahedra and four PO_4 tetrahedra. It is near these windows that the layers have corrugated folds in which the crystallographically distinct cesium atoms, Cs(2), reside. The other cesium atoms Cs(1) occupy the interlayer region.

Crystallographically distinct three phosphorus and ten oxygen atoms constitute the triphosphate chain. The middle $P(2)O_4$ tetrahedron is connected to the terminal ones, $P(1)O_4$ and $P(3)O_4$, through O(4) and O(5) bridging oxygen atoms respectively. The $P(1)O_4$ tetrahedron shares its other three corners with MO_6 octahedra, whereas $P(2)O_4$ and $P(3)O_4$ tetrahedra share only one and two corners respectively. As shown in Fig. 3, M is octahedrally co-ordinated and the P_3O_{10} group caps one of its triangular faces, through three oxygen atoms, O(2),

Table 2 Bond distances (Å), bond angles (°) and selected O · · · O non-bonding distances (Å) of compounds **1** and **2**

$Cs_2AlP_3O_{10}$ **1**

PO_4 tetrahedra

P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	**1.495(5)**	2.554(7)	2.448(7)	2.464(7)
O(2)	116.3(3)	**1.511(5)**	2.544(7)	2.510(7)
O(3)	108.8(3)	114.4(3)	**1.516(5)**	2.507(7)
O(4)	104.2(3)	106.2(3)	105.8(3)	**1.625(5)**
P(2)	O(7)	O(6)	O(5)	O(4)
O(7)	**1.475(6)**	2.537(7)	2.501(8)	2.488(8)
O(6)	116.9(3)	**1.503(5)**	2.516(7)	2.495(7)
O(5)	110.1(3)	109.6(3)	**1.576(5)**	2.507(8)
O(4)	108.0(3)	107.1(3)	104.3(3)	**1.599(5)**
P(3)	O(8)	O(9)	O(10)	O(5)
O(8)	**1.475(6)**	2.526(7)	2.510(8)	2.475(8)
O(9)	115.2(3)	**1.516(5)**	2.499(7)	2.533(7)
O(10)	113.8(3)	110.7(3)	**1.522(5)**	2.524(7)
O(5)	104.6(3)	106.2(3)	105.4(3)	**1.651(5)**

AlO_6 octahedron

Al	O(10)	O(3)	O(9)	O(1)	O(2)	O(6)
O(10)	**1.851(6)**	2.752(8)	2.695(7)	2.599(7)	3.317(7)	2.659(7)
O(3)	95.3(2)	**1.872(6)**	2.678(7)	2.723(7)	2.603(7)	—
O(9)	92.2(2)	90.8(2)	**1.888(5)**	—	2.712(7)	2.680(7)
O(1)	87.8(2)	92.5(2)	176.7(3)	**1.898(5)**	2.694(7)	2.667(7)
O(2)	176.8(2)	86.3(2)	90.5(2)	89.4(2)	**1.932(5)**	2.726(7)
O(6)	89.0(2)	175.7(2)	88.8(2)	87.9(2)	89.4(2)	**1.943(5)**

Cs(1)				Cs(2)			
O(7)	2.990(5)	O(6)	3.284(5)	O(4)	3.080(5)	O(2)	3.226(5)
O(8)	3.031(6)	O(8)	3.373(6)	O(1)	3.085(5)	O(9)	3.366(5)
O(8)	3.035(6)	O(10)	3.585(6)	O(10)	3.157(5)	O(6)	3.455(5)
O(5)	3.127(5)			O(3)	3.162(5)	O(4)	3.548(5)
				O(7)	3.208(6)	O(3)	3.578(5)

$Cs_2GaP_3O_{10}$ **2**

PO_4 tetrahedra

P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	**1.512(8)**	2.549(10)	2.463(10)	2.456(11)
O(2)	114.8(4)	**1.513(6)**	2.534(8)	2.507(10)
O(3)	108.9(4)	113.6(4)	**1.514(7)**	2.507(7)
O(4)	104.2(4)	107.3(4)	107.2(4)	**1.599(8)**
P(2)	O(7)	O(6)	O(5)	O(4)
O(7)	**1.490(8)**	2.576(10)	2.521(10)	2.527(11)
O(6)	118.4(4)	**1.510(6)**	2.543(10)	2.530(9)
O(5)	109.2(4)	109.6(4)	**1.602(8)**	2.567(12)
O(4)	107.5(4)	106.7(4)	104.6(4)	**1.642(8)**
P(3)	O(8)	O(9)	O(10)	O(5)
O(8)	**1.497(9)**	2.479(13)	2.573(11)	2.467(11)
O(9)	111.9(5)	**1.495(8)**	2.512(9)	2.477(10)
O(10)	116.3(4)	112.1(4)	**1.532(6)**	2.559(9)
O(5)	103.6(5)	104.3(4)	107.4(4)	**1.641(8)**

GaO_6 octahedron

Ga	O(9)	O(10)	O(1)	O(3)	O(6)	O(2)
O(9)	**1.903(8)**	2.719(9)	2.682(12)	2.843(11)	2.708(9)	—
O(10)	90.9(3)	**1.913(7)**	—	2.730(11)	2.719(10)	2.788(11)
O(1)	88.8(3)	176.2(3)	**1.929(8)**	2.789(10)	2.686(11)	2.751(9)
O(3)	96.1(3)	90.9(3)	92.9(3)	**1.919(7)**	—	2.647(9)
O(6)	88.8(3)	89.0(3)	87.2(3)	175.0(3)	**1.965(7)**	2.793(11)
O(2)	177.6(3)	91.1(3)	89.1(3)	85.2(3)	89.8(3)	**1.991(7)**

Cs(1)				Cs(2)			
O(7)	2.957(8)	O(6)	3.265(10)	O(4)	3.089(6)	O(2)	3.254(9)
O(8)	3.009(8)	O(8)	3.251(9)	O(1)	3.102(7)	O(10)	3.378(7)
O(8)	3.081(9)	O(9)	3.500(10)	O(9)	3.187(8)	O(6)	3.451(8)
O(5)	3.129(11)			O(3)	3.203(10)	O(4)	3.513(8)
				O(7)	3.250(9)	O(3)	3.521(8)

O(6) and O(9), one from each PO_4 tetrahedron. The P_3O_{10} group is connected also to another octahedron through O(3) and O(10) of terminal phosphate groups in bidentate fashion and yet another octahedron through O(1).

In compound **1**, the AlO_6 octahedron is distorted with two long (>1.9 Å) *cis* bonds, Al–O(2) and Al–O(6), and four short (<1.9 Å) (Table 2) bonds and thus aluminium is displaced from its best centre[15] by 0.006 Å away from O(2) and O(6) atoms that form an edge of the capped triangular face. The O–Al–O bond angles deviate from the ideal value of 90° by as much as 5.3°.

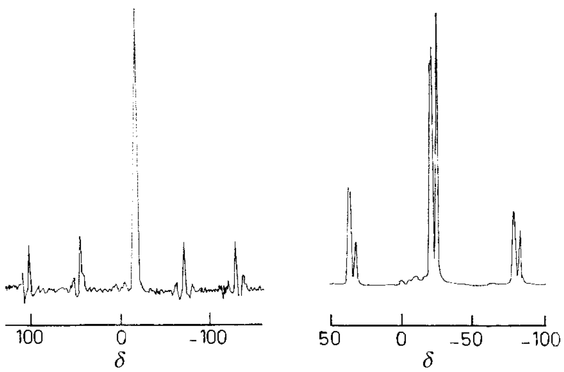

Fig. 4 ^{27}Al (left) and ^{31}P NMR (right) spectra of $Cs_2AlP_3O_{10}$ **1**.

The P–O bond lengths of PO_4 tetrahedra vary from 1.475 to 1.651 Å. Atoms P(2) and P(3) form short (<1.503 Å) bonds with unshared oxygen atoms, O(7) and O(8) respectively; P(1), P(2) and P(3) form long (≥1.576 Å) bonds with the bridging oxygen atoms, O(4) and O(5), and bonds of intermediate lengths (1.503–1.522 Å) with other oxygen atoms connected to aluminium. The bond angles vary from 104.2 to 116.9°. Similar features are seen in compound **2**. Atoms Cs(1) and Cs(2) are seven- and ten-co-ordinated respectively, with Cs–O bond lengths varying from 2.990(5) to 3.585(6) Å for **1** and 2.957(8) to 3.521(8) Å for **2**. Structural elucidation for **1** and **2** confirms the isostructural nature of hitherto reported $Cs_2MP_3O_{10}$ (M = Al, Ga, Cr or Fe) compounds.

Layered $AMHP_3O_{10}$ compounds containing MO_6 octahedra and P_3O_{10} triphosphate groups are known to be of two types,[8,9] namely, $CsGaHP_3O_{10}$ and $NH_4AlHP_3O_{10}$. In these compounds the triphosphate group forms bidentate connectivity through the oxygen atoms of the adjacent PO_4 tetrahedra. In the case of compounds **1** and **2** the triphosphate group is bent with oxygen atoms of the terminal PO_4 tetrahedra forming the bidentate connectivity. The bent nature, however, need not and, in fact, does not affect the P–O–P angle. The P–O–P angles of these triphosphate groups are 130 and 126° in **1** and **2** and 115° in other compounds. We have found that other new $A_2MP_3O_{10}$ (A = K, Rb or Tl; M = Al or Ga) compounds possess, as determined from their XRD powder patterns, different structures and our efforts to grow their crystals have not been successful so far. Our efforts to synthesize these analogues by ion exchange reactions of **1** and **2** have led to the disintegration of the parent compounds.

Solid state NMR spectroscopy

Compound **1** was characterised by ^{27}Al and ^{31}P solid state NMR spectroscopy. The ^{27}Al NMR spectrum (Fig. 4) has a single peak at δ −16.7, indicating the octahedral co-ordination of aluminium.[16] The ^{31}P NMR spectrum (Fig. 4) showed clear distinction between the terminal and middle phosphorus atoms.[17,18] The peak at δ −25.6 is due to the middle P(2) atom and the peak at δ −21 is resolved into two, at δ −21.8 and −20.85, assigned to P(3) and P(1) respectively.

Conclusion

Novel two dimensional compounds **1** and **2** have been characterised by single crystal XRD and solid state NMR spectroscopy. They have corrugated $[MP_3O_{10}]^{2-}$ anionic layers built from MO_6 and bent P_3O_{10} triphosphate groups and Cs^+ ions as counter ions. Other $A_2MP_3O_{10}$ compounds have probably diverse open framework structures and it is worthwhile to characterise them structurally.

Acknowledgements

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