Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Magnesium, calcium and strontium salts of phenylacetic acid

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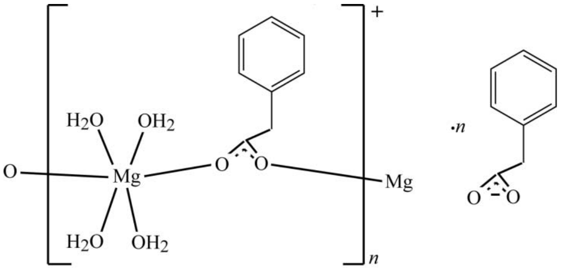
Received 1 December 2011
Accepted 22 December 2011
Online 6 January 2012

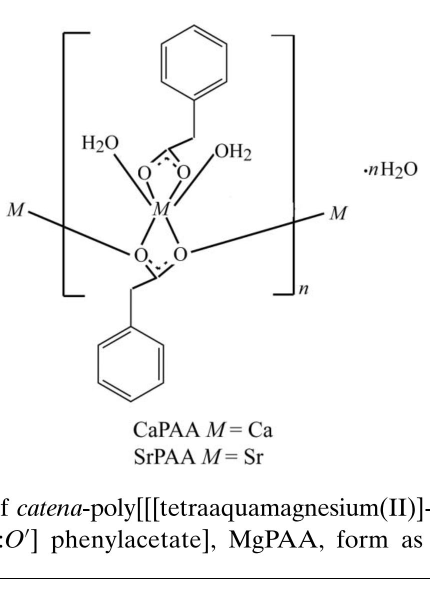
Three alkaline earth metal salts of phenylacetic acid were examined and all were found to have similar structural types to analogous salts of benzoic and halobenzoic acids. Thus, a synchrotron study shows that the cations in *catena*-poly[[[tetraaquamagnesium(II)]-μ-phenylacetato-κ^2O:O'] phenylacetate], $\{[Mg(C_8H_7O_2)(H_2O)_4](C_8H_7O_2)\}_n$, form a one-dimensional coordination polymer that propagates through Mg—O—C—O—Mg interactions involving both crystallographically independent Mg centres (Z' = 2) and through translation along the *a* axis. The polymeric chains pack to give alternate inorganic layers and organic bilayers. The Ca and Sr species *catena*-poly[[[diaqua(phenylacetato-κ^2O,O')calcium(II)]-μ_3-phenylacetato-1$'$:1:1$''\kappa^4O$:O,O':O'] monohydrate], $\{[Ca(C_8H_7O_2)_2(H_2O)_2]\cdot H_2O\}_n$, and *catena*-poly-[[[diaqua(phenylacetato-κ^2O,O')strontium(II)]-μ_3-phenylacetato-1$'$:1:1$''\kappa^4O$:O,O':O'] monohydrate], $\{[Sr(C_8H_7O_2)_2(H_2O)_2]\cdot H_2O\}_n$, are essentially isostructural. Both form one-dimensional coordination polymers through a carboxylate group that forms four M—O bonds. The polymeric chains propagate *via* 2_1 screw axes parallel to the *b* axis and are further linked in the *bc* plane by hydrogen bonding involving the non-metal-bound water molecule. Similarly to the Mg salt, both have inorganic layers that alternate with organic bilayers.

Comment

Often, the simplest way to alter the physicochemical properties of an active pharmaceutical ingredient (API) is to make different salt forms of it. As many of the performance-critical properties of an API (such as solubility, melting point and hygroscopicity) are dependant upon the solid-state structure, a true understanding of structure–property relationships should allow the most appropriate counter-ion to be chosen for any such desired property. However, these structure–property relationships are poorly understood, and thus salt selection of API forms is currently undertaken using time-consuming trial and error methods (Stahl & Wermuth, 2002). One reason for the lack of understanding is a general dearth of large groups of systematically related crystal structures with associated phase-specific physicochemical data. Such studies do exist (for example, Collier *et al.*, 2006; Black *et al.*, 2007; Kennedy *et al.*, 2011) but are relatively uncommon. As a contribution to this field, Arlin *et al.* (2011) showed that the Mg, Ca and Sr (but not Ba) salt forms of a set of simple benzoic acid-derived anions could be systematically structurally classified and that these structural features help rationalize the comparative aqueous solubility data gathered. A major aim of this earlier work was to use the lessons learned from simple model compounds to predict behaviour in larger commercial APIs with similar functionality. Many APIs have aryl carboxylate groups (*e.g.* aspirin and fluoroquinolones), as do the reported model benzoate structures (Arlin *et al.*, 2011). However, several important drug classes (*e.g.* profens and naproxens) have a C*sp*^{3} atom inserted between the aromatic ring and the carboxylate group, and this structural feature was not included in the model data set. To help fill this gap, the Mg, Ca and Sr complexes of phenylacetate (PAA) have been investigated in order to show what effect the extra 'spacer' C*sp*^{3} atom has on the crystal stucture, and thus to determine if the model benzoate data set could be a useful comparative tool for use with salts of ibuprofen and naproxen. Structural studies of both cocrystals and organic salts of PAA have recently been published (Brittain, 2010; Smith & Wermuth, 2010*a*,*b*), but the only *s*-block metal salt of PAA to be structurally characterized is the K salt, which exists as the cocrystal K(PAA)(HPAA) (Bacon *et al.*, 1977).



MgPAA



CaPAA M = Ca
SrPAA M = Sr

Crystals of *catena*-poly[[[tetraaquamagnesium(II)]-μ-phenylacetato-κ^2O:O'] phenylacetate], MgPAA, form as very thin

doi:10.1107/S0108270111055284

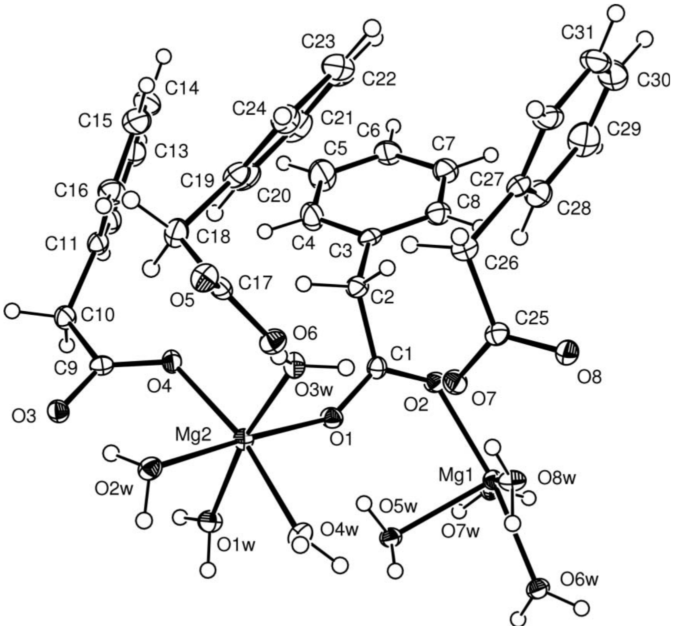


Figure 1
The contents of the asymmetric unit of MgPPA, showing the atom-numbering scheme (for clarity, only essential atom labels are shown). Displacement ellipsoids are drawn at the 40% probability level.

plates which required the use of synchrotron radiation to characterize them as [Mg(PAA)$(H_2O)_4$](PAA), with two crystallographically independent formula units per asymmetric unit ($Z' = 2$). Measurements were made at Station 9.8 of Daresbury SRS. Each Mg centre is approximately octahedral and bonds to four terminal water ligands and to single O atoms of two PAA anions. These last are in mutually *cis* positions (see Table 1 for geometric details and Fig. 1 for an illustration). Although the shortest Mg—O bond lengths involve the PAA anions, some of the Mg—OH_2 bonds are shorter than the other Mg—PAA bonds. Thus, bonding to the PAA anion does not appear to be systematically stronger than Mg bonding to water. Two of the PAA anions each bridge across two Mg centres using both O atoms of their carboxylate groups to make single O—Mg contacts. This results in a one-dimensional cationic coordination chain based on Mg—O—C—O—Mg units, which propagates by translation along the crystallographic *a* direction (Fig. 2). The remaining two PAA anions form no Mg—O bonds. Fig. 3 shows that the structure packs to give alternate hydrophobic and hydrophilic layers along the *c* direction. The organic bilayer thus formed means that, although all the water molecules utilize both of their H atoms to form hydrogen bonds, these only connect the structure in two dimensions, *e.g.* there is a hydrogen-bonding network in the *ab* plane. This packing motif, with alternating layers, an organic bilayer and a one-dimensional coordination chain based on bridging carboxylates, is the same as that found previously for Mg salts of benzoic and halobenzoic acids. It is conspicously different from the structures found for other salts involving benzoate ions with hydroxy, amino or nitro substituents (Arlin *et al.*, 2011).

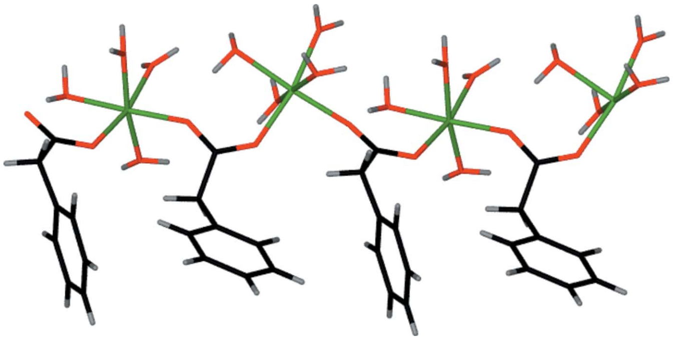


Figure 2
Part of the one-dimensional coordination polymer found in MgPAA. The polymer chain is parallel to the crystallographic *a* direction. The non-coordinating PAA anions are not shown.

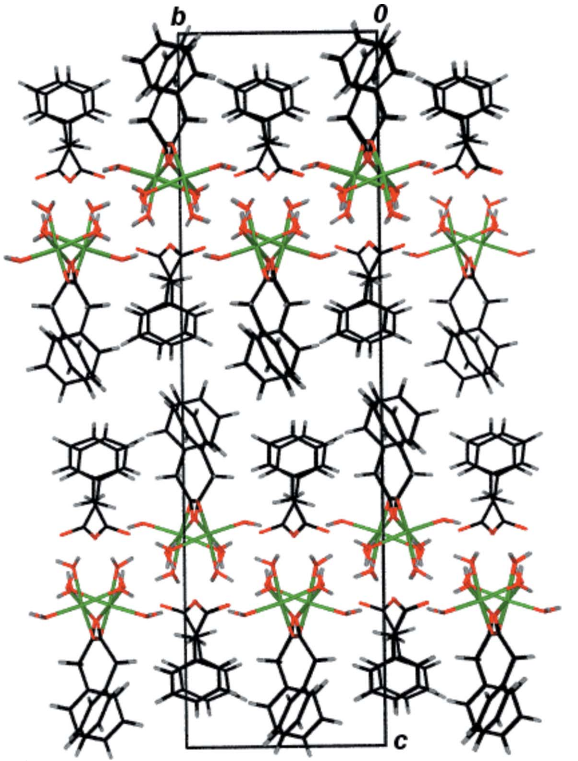


Figure 3
The packing mode of MgPAA, viewed down *a* to show the alternating inorganic layers and organic bilayers along the *c* direction.

The structures of the calcium(II) and strontium(II) compounds *catena*-poly[[[diaqua(phenylacetato-$\kappa^2 O,O'$)calcium(II)]-μ_3-phenylacetato-$1':1:1''\kappa^4 O:O,O':O'$] monohydrate] and *catena*-poly[[[diaqua(phenylacetato-$\kappa^2 O,O'$)strontium(II)]-μ_3-phenylacetato-$1':1:1''\kappa^4 O:O,O':O'$] monohydrate], CaPAA and SrPAA, respectively, were found to be essentially isostructural, with the composition $[M(\mathrm{PAA})_2(H_2O)_2]\cdot H_2O$ (Figs. 4 and 5). This again reflects the structures of the related benzoate derivatives, where the Ca and Sr structures were found to have similar structural types and even, for salicylate, *p*-aminosalicylate and *p*-aminobenzoate, to form isostructural pairs. In each structure herein, the metal centre is formally eight-coordinate, although, as Cotton & Bergman (1964) classically showed, if each chelated group is assigned to one coordination site rather than two, then the structures can be described as distorted octahedral. The water ligands are both *trans* to

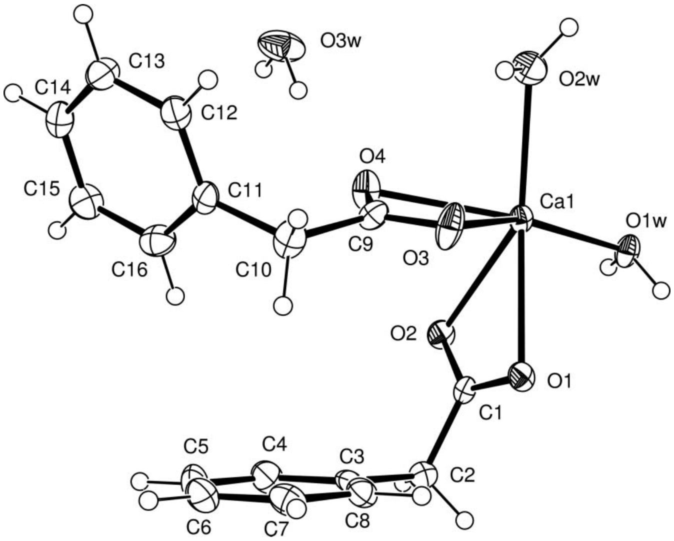


Figure 4
The contents of the asymmetric unit of CaPPA, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

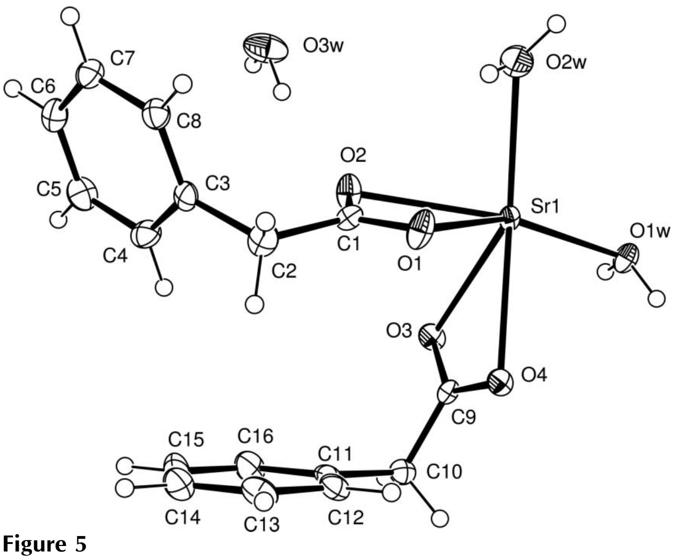


Figure 5
The contents of the asymmetric unit of SrPPA, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

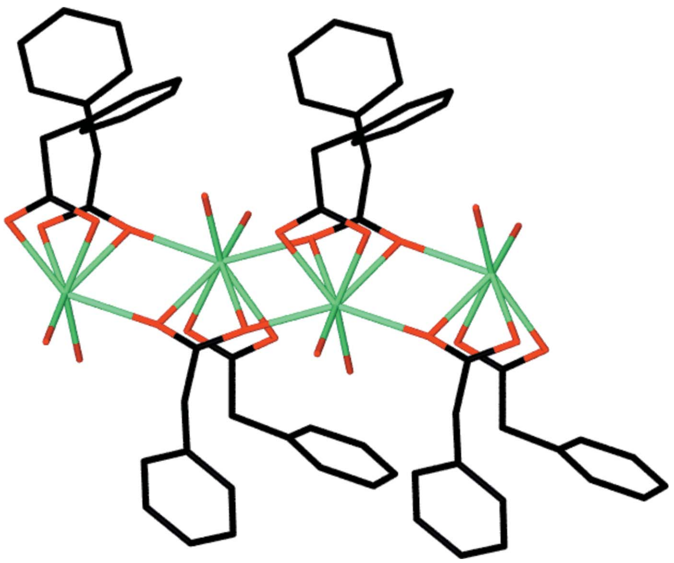


Figure 6
Part of the one-dimensional coordination polymer found in CaPAA. The polymer propagates in the crystallographic *b* direction. Non-metal-bound water molecules and all H atoms have been omitted for clarity.

chelated carboxylate groups. As with MgPAA, the $M-\mathrm{OH}_2$ distances are not systematically longer or shorter than the $M-$O(PAA) distances. One PAA anion is a terminal ligand and uses both its O atoms to bond to a single metal centre, whilst the second PPA anion chelates to one metal centre and bridges to a further two. As both water ligands are terminal, it is this second PAA anion type that leads to the propagation of a one-dimensional coordination chain along the 2_1 screw axis parallel to the *b* direction (Fig. 6). These coordination chains are interlinked by hydrogen bonding through atom O3*W*, the non-metal-bound water molecule. This gives a hydrophilic layer in the *bc* plane with alternating hydrophilic and hydrophobic layers along the crystallographic *a* direction. Again, organic bilayers are formed. This alternating layer motif with organic bilayers is identical to that observed in the Ca salt of benzoate and the Ca and Sr salts of *p*-fluoro- and *p*-chlorobenzoic acid (Senkovska & Thewalt, 2005; Karipides *et al.*, 1988; Arlin *et al.*, 2011). The bonding of the coordination polymer is also somewhat similar to these species, in that the bridging –COO$^-$ group plays an identical role. However, in the benzoic acid derivatives there is no terminal carboxylate ligand. Instead, the third water molecule forms an extra bridge between the metal centres and the benzoate anion plays the role of linker group, hydrogen bonding between the one-dimensional coordination chains. As with MgPAA, both the packing mode and the bonding within the coordination chains are extremely different from those typically observed for salts involving benzoates with hydroxy, amino or nitro substituents (Arlin *et al.*, 2011).

In summary, despite the additional C*sp*^{3} atom between the aryl and –COO$^-$ groups, all three PAA structures presented here have structural types closely related to those found for analogous benzoate and halobenzoate salts. This is shown by similarities in hydration state and in packing and layering behaviour, and by the formation of one-dimensional coordination polymers *via* –COO$^-$ bridges. There is some variation from the benzoate structures in the detail of the metal bonding, but this is on a similar scale to the variation already found within the group of benzoate structures themselves. As the PAA salt structures are markedly different from those found for benzoate ions with active hydrogen-bonding substituents, it is concluded that the addition of CH$_2$ has less overall effect on structure than the addition of hydroxy, amino or nitro groups to the aryl ring.

Experimental

All samples were prepared by slowly adding a slight excess of an aqueous solution of the appropriate metal carbonate to a stirred aqueous slurry of phenylacetic acid. The volumes of the resulting clear solutions were reduced by evaporation until white precipitates were deposited, and these were collected by filtration. Colourless crystals suitable for single-crystal diffraction studies were obtained by recrystallization of the samples from warm water.

MgPAA

Crystal data

$[Mg(C_8H_7O_2)(H_2O)_4](C_8H_7O_2)$
M_r = 366.65
Orthorhombic, $P2_12_12_1$
a = 9.7979 (7) Å
b = 10.0424 (8) Å
c = 36.052 (3) Å
V = 3547.3 (5) Å^3
Z = 8
Synchrotron radiation
λ = 0.68840 Å
μ = 0.14 mm^{-1}
T = 120 K
0.12 × 0.08 × 0.001 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.844, T_{max} = 1.000
26335 measured reflections
6253 independent reflections
5231 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.096
S = 1.02
6253 reflections
500 parameters
24 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), with 2701 Friedel pairs
Flack parameter: 0.5 (3)

Table 1
Selected bond lengths (Å) for MgPAA.

Mg1—O3^{i}	2.0278 (19)	Mg2—O1	2.026 (2)
Mg1—O7W	2.0381 (19)	Mg2—O3W	2.032 (2)
Mg1—O2	2.0691 (19)	Mg2—O1W	2.0790 (19)
Mg1—O8W	2.0888 (19)	Mg2—O4	2.079 (2)
Mg1—O6W	2.1291 (19)	Mg2—O4W	2.1252 (19)
Mg1—O5W	2.141 (2)	Mg2—O2W	2.143 (2)

Symmetry code: (i) $x + 1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for MgPAA.

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O5^{ii}	0.87 (1)	1.89 (1)	2.749 (3)	171 (3)
O1W—H2W···O7^{iii}	0.88 (1)	1.98 (1)	2.853 (3)	173 (3)
O2W—H3W···O8^{iii}	0.87 (1)	2.01 (1)	2.875 (2)	172 (3)
O2W—H4W···O3	0.88 (1)	1.75 (1)	2.595 (2)	163 (3)
O3W—H5W···O6	0.87 (1)	1.85 (1)	2.693 (2)	165 (3)
O3W—H6W···O7	0.87 (1)	1.86 (1)	2.729 (3)	171 (3)
O4W—H7W···O6^{iii}	0.88 (1)	1.91 (1)	2.775 (3)	166 (3)
O4W—H8W···O5W^{iv}	0.88 (1)	2.15 (2)	2.939 (3)	149 (2)
O5W—H9W···O1	0.88 (1)	1.76 (1)	2.613 (2)	164 (3)
O5W—H10W···O6^{iii}	0.88 (1)	1.99 (1)	2.864 (2)	175 (2)
O6W—H11W···O8^{v}	0.87 (1)	1.91 (1)	2.770 (3)	169 (3)
O6W—H12W···O2W^{iii}	0.88 (1)	2.12 (1)	2.932 (3)	153 (3)
O7W—H13W···O5^{vi}	0.88 (1)	1.86 (1)	2.730 (3)	172 (3)
O7W—H14W···O8^{ii}	0.87 (1)	1.85 (1)	2.698 (2)	166 (2)
O8W—H15W···O5^{iii}	0.89 (1)	1.95 (1)	2.839 (2)	178 (2)
O8W—H16W···O7	0.87 (1)	1.90 (1)	2.764 (2)	171 (3)

Symmetry codes: (ii) $x, y - 1, z$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x + 1, y - 1, z$.

Table 3
Selected bond lengths (Å) for CaPAA.

Ca1—O2^{i}	2.3527 (16)	Ca1—O1	2.5167 (14)
Ca1—O1^{ii}	2.3632 (16)	Ca1—O3	2.5188 (16)
Ca1—O1W	2.3843 (15)	Ca1—O4	2.5355 (15)
Ca1—O2W	2.4214 (16)	Ca1—O2	2.5695 (15)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for CaPAA.

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O3^{ii}	0.87 (1)	2.00 (1)	2.838 (2)	163 (2)
O1W—H2W···O4^{i}	0.88 (1)	1.98 (1)	2.830 (2)	164 (2)
O2W—H3W···O3W^{iii}	0.87 (1)	1.79 (1)	2.659 (2)	174 (3)
O2W—H4W···O3	0.86 (1)	2.64 (2)	3.177 (2)	121 (2)
O3W—H5W···O3^{iv}	0.88 (1)	1.96 (1)	2.838 (3)	178 (3)
O3W—H6W···O4	0.87 (1)	2.08 (1)	2.939 (3)	167 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $x, y + 1, z$.

CaPAA

Crystal data

$[Ca(C_8H_7O_2)_2(H_2O)_2]\cdot H_2O$
M_r = 364.40
Monoclinic, $C2/c$
a = 29.2249 (10) Å
b = 6.6941 (3) Å
c = 17.8109 (5) Å
β = 92.520 (2)°
V = 3481.1 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 150 K
0.36 × 0.08 × 0.07 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
7271 measured reflections
3814 independent reflections
2429 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.103
S = 1.03
3814 reflections
235 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

SrPAA

Crystal data

$[Sr(C_8H_7O_2)_2(H_2O)_2]\cdot H_2O$
M_r = 411.94
Monoclinic, $C2/c$
a = 29.5111 (15) Å
b = 6.8560 (5) Å
c = 17.7229 (11) Å
β = 93.453 (3)°
V = 3579.3 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.05 mm^{-1}
T = 123 K
0.30 × 0.15 × 0.10 mm

Data collection

Oxford Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.564, T_{max} = 0.767
20190 measured reflections
4034 independent reflections
3175 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Table 5
Selected bond lengths (Å) for SrPAA.

Sr1—O3^{i}	2.4655 (14)	Sr1—O2	2.6386 (14)
Sr1—O4^{ii}	2.4688 (14)	Sr1—O1	2.6453 (15)
Sr1—O1*W*	2.5528 (15)	Sr1—O4	2.6548 (14)
Sr1—O2*W*	2.5772 (18)	Sr1—O3	2.7089 (14)

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Table 6
Hydrogen-bond geometry (Å, °) for SrPAA.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O2^{i}	0.87 (1)	2.01 (1)	2.855 (2)	164 (2)
O1*W*—H2*W*···O1^{ii}	0.85 (1)	2.05 (1)	2.901 (2)	173 (2)
O2*W*—H3*W*···O3*W*^{iii}	0.86 (1)	1.81 (1)	2.654 (3)	169 (3)
O3*W*—H5*W*···O1^{iv}	0.86 (1)	1.97 (1)	2.828 (3)	175 (3)
O3*W*—H6*W*···O2	0.86 (1)	2.19 (1)	3.031 (3)	168 (3)

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iv) $x, y+1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 1.04$
4034 reflections
235 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Water H atoms were positioned as found by difference syntheses and refined with restraints such that the O—H and H···H distances restrained to 0.88 (1) and 1.33 (2) Å, respectively; $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(O). This introduced 24, nine and nine restraints for MgPAA, CaPAA and SrPAA, respectively. C-bound H atoms were positioned geometrically and refined in riding mode, with C—H = 0.95 and 0.99 Å for CH and CH$_2$ groups, respectively, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

Data collection: *APEX2* (Bruker, 2007) for MgPAA; *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998) for CaPAA; *CrysAlis CCD* (Oxford Diffraction, 2009) for SrPAA. Cell refinement: *SAINT* (Bruker, 2007) for MgPAA; *DENZO* and *COLLECT* for CaPAA; *CrysAlis CCD* for SrPAA. Data reduction: *SAINT* for MgPAA; *DENZO* for CaPAA; *CrysAlis RED* (Oxford Diffraction, 2009) for SrPAA. For all compounds, program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *ORTEP-3* (Farrugia, 1997) and *X-SEED* (Barbour, 2001) for MgPAA and CaPAA; *ORTEP-3* for SrPAA. For all compounds, software used to prepare material for publication: *SHELXL97*.

The authors thank the National Crystallography Service staff at the University of Southampton and Newcastle University for the data collection on MgPAA.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3204). Services for accessing these data are described at the back of the journal.

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