Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Group 2 metal salts of pyromellitic acid: $[Mg(H_2O)_6](C_{10}H_4O_8)$ and $[Ba(C_{10}H_4O_8)(H_2O)_5]$

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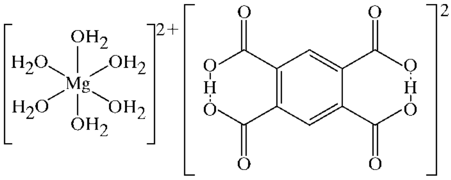
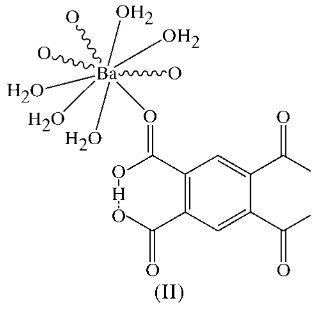
Received 8 September 2003
Accepted 13 October 2003
Online 8 November 2003

Structural determinations of the magnesium(II) and barium(II) salts of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) are presented. Hexaaquamagnesium(II) benzene-1,2,4,5-tetracarboxylate(2−), $[Mg(H_2O)_6](C_{10}H_4O_8)$, (I), and pentaaqua[benzene-1,2,4,5-tetracarboxylato(2−)]barium(II), $[Ba(C_{10}H_4O_8)(H_2O)_5]$, (II), are both centrosymmetric and both possess a 1:1 metal–ligand ratio, but the two structures are found to differ in that the magnesium salt contains a hexaaqua cation and possesses only hydrogen-bonding interactions between cations and anions, while the barium salt exhibits coordination of the carboxylate ligand to the nine-coordinate metal centre. In (I), both ions sit on a $2/m$ site symmetry, and in (II), the cation and anion are located on m and i site symmetries, respectively.

Comment

Pyromellitic acid (H_4PMA, benzene-1,2,4,5-tetracarboxylic acid), a member of the well studied benzenepolycarboxylic acid family, has found applications in the creation of hydrogen-bonding arrays (Mrvoš-Sermek *et al.*, 1996; Biradha & Zaworotko, 1998) and, in particular, in the synthesis of coordination polymers, including, for example, mixed-ligand systems (Poleti *et al.*, 1988; Zhang *et al.*, 2003). Many authors strive to form functional porous supramolecular arrays (Yaghi *et al.*, 1995, 1998; Janiak, 1997) using benzenepolycarboxylic acids amongst a very large number of possible ligands, and it is with this intention that we too have investigated the salts of benzenepolycarboxylic acids, concentrating on their alkali and alkaline earth metal salts.


(I)


(II)

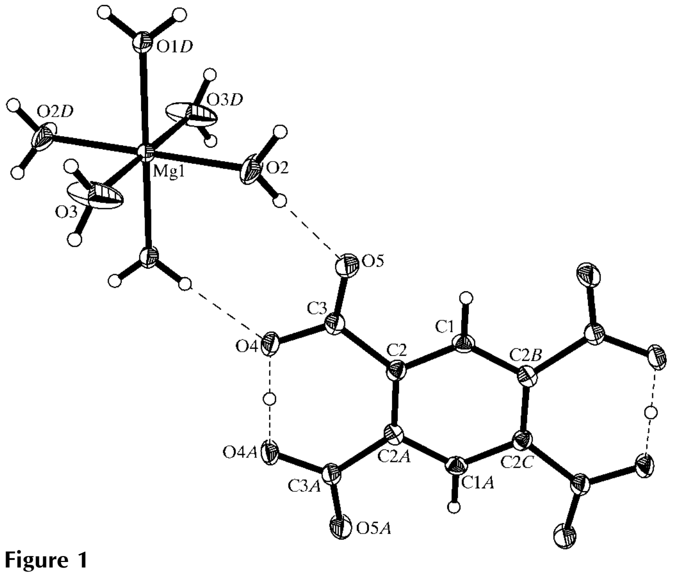


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii and hydrogen bonds are shown as dashed lines. [Symmetry codes: (*A*) $x, 1-y, z$; (*B*) $1-x, y, 2-z$; (*C*) $1-x, 1-y, 2-z$; (*D*) $-x, -y, -z$.]

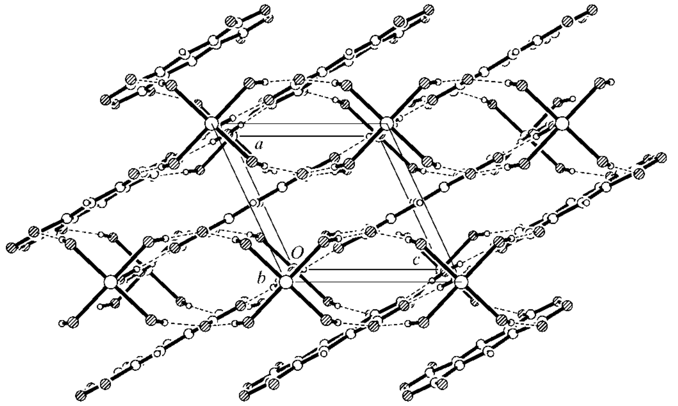


Figure 2
The crystal packing of (I), showing the three-dimensional hydrogen-bonding array, viewed along the crystallographic *b* axis. Hydrogen bonds are shown as dashed lines.

A search of the Cambridge Structural Database (CSD; Version 5.24, July 2003 update; Allen, 2002) highlights numerous determinations of group 1 salts (Li^+, Na^+, K^+ and Cs^+) of H_4PMA (Emsley *et al.*, 1986; Jessen & Küppers, 1990, 1992; Luehrs & Bowman-James, 1994; Hu & Ng, 2002), and yet, of the group 2 metals, only the Ca^{2+} salt $[Ca_2(PMA)(H_2O)_6]_n$ (Robl, 1988) has been determined.

DOI: 10.1107/S0108270103023175

The magnesium salt, $[Mg(H_2O)_6](H_2PMA)$, (I) (Fig. 1), does not possess metal–carboxylate coordination, instead containing a hexaaqua metal cation, as has also been observed in, amongst a total of 86 examples, the structures of magnesium hydrogen phthalate (Kariuki & Jones, 1989) and magnesium hydrogen maleate (Vanhouteghem *et al.*, 1987). Compound (I) is isostructural with the previously determined Co^{2+} (Ward & Luehrs, 1983) and Ni^{2+} (Jessen & Küppers, 1992) salts, and the asymmetric unit comprises a quarter of an $[Mg(H_2O)_6]^{2+}$ cation and a quarter of an H_2PMA^{2-} anion.

Atom Mg1 is positioned on an inversion centre, with a twofold axis through atoms Mg1 and O1, and a mirror plane through atoms Mg1, O2 and O3. The cation is almost perfectly octahedral, having an angle of 89.9 (2)° between the O atoms in the mirror plane (Table 1). The $Mg-OH_2$ bond lengths compare well with the average value [2.06 (2) Å] determined from 50 structures in the CSD containing the $[Mg(H_2O)_6]^{2+}$ cation.

The H_2PMA^{2-} anion is positioned on a twofold axis, crossing through the non-substituted C atoms of the ring, and on a mirror plane bisecting the intramolecular $O4-H4\cdots O4'$ hydrogen bond, resulting in this short intramolecular hydrogen bond being refined as symmetrical (Table 2).

In addition to the intramolecular hydrogen bond, there are three further unique hydrogen bonds, all providing cation–anion interactions (Table 2). These hydrogen bonds create a three-dimensional structure, aided by the angle at which the planar anions lie with respect to the layers of $[Mg(H_2O)_6]^{2+}$ cations (Fig. 2).

In contrast to (I), the barium salt, $[Ba(H_2PMA)(H_2O)_5]$, (II) (Fig. 3), displays metal–carboxylate coordination, and yet (II) still contains the same intramolecularly hydrogen-bonded H_2PMA^{2-} anion as (I). Atom Ba1 has a coordination number of nine, having four metal–carboxylate bonds and five terminal metal–OH_2 bonds (Table 3), and these bond lengths compare well with average values determined from the CSD [2.798 (7) Å for Ba–carboxylate bonds and 2.847 (7) Å for $Ba-OH_2$ bonds]. The asymmetric unit comprises half of a formula unit, with atoms Ba1, O6, O7 and O8 positioned on a mirror plane, and the H_2PMA^{2-} anion on an inversion centre.

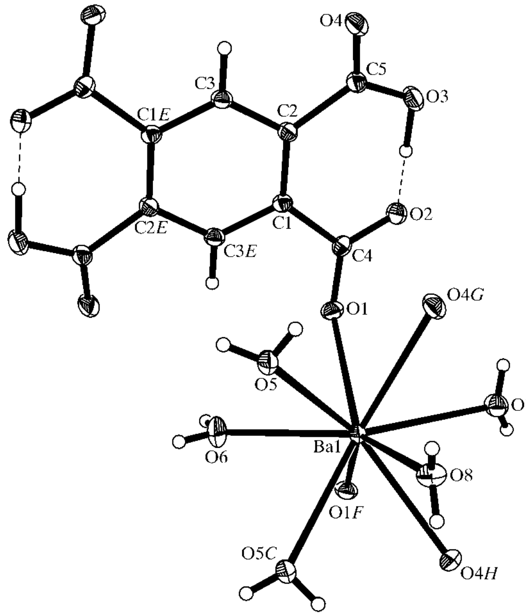


Figure 3
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii and hydrogen bonds are shown as dashed lines. [Symmetry codes: (*E*) $-x, 1-y, 1-z$; (*F*) $x, \frac{1}{2}-y, z$; (*G*) $1-x, 1-y, 1-z$; (*H*) $1-x, y-\frac{1}{2}, 1-z$.]

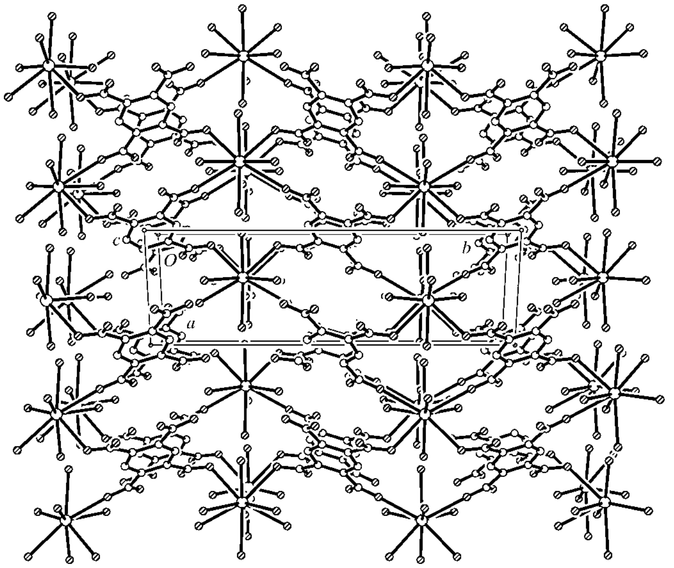


Figure 4
The crystal packing of (II), viewed along the crystallographic *c* axis. The coordinated sheets lie in the *ab* plane, with hydrogen bonds linking neighbouring sheets. H atoms and hydrogen bonds have been omitted for clarity.

The anions in (I) and (II) show expected geometrical similarities (Table 3); however, while the intramolecular hydrogen bond in (I) is constrained as symmetrical as a result of the symmetry of the system, the same bond in (II) is freely refined (Table 4). While the unique carboxyl group in (I) is approximately coplanar with the aromatic ring [with a dihedral angle of 2.35 (7)°], the carboxyl groups in (II) show greater deviation from the plane of the aromatic ring [with dihedral angles of 15.2 (4) and 20.6 (4)°].

Each anion in (II) bridges four Ba^{2+} centres, thus creating a two-dimensional coordination polymer, which extends as sheets in the *ab* plane, with extensive $H_2O\cdots H_2O$ and carboxylate $O\cdots H_2O$ $O-H\cdots O$ hydrogen bonding supporting the network and extending it into the third dimension (Fig. 4 and Table 4).

Experimental

For the preparation of (I), H_4PMA (5 equivalents) and $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$ (1 equivalent) were refluxed in H_2O for 18 h. Slow cooling of the resulting solution produced large X-ray-quality colourless crystals of (I) in quantitative yield, which were observed to desolvate at 343–348 K. IR (KBr, cm^{-1}): ν_{max} 3418 (*br*, OH), 3134 and 2923 (aromatic C—H), 1681 (C═O, acid), 1587 (asymmetric

CO_2^-), 1556, 1538 and 1505 (aromatic C═C), 1349 (symmetric CO_2^-), 1284, 1156 and 1097 (C—O), 745 and 702 (aromatic C—H), 669, 594. Analysis calculated for $C_{10}H_{16}MgO_{14}$: C 31.24, H 4.19%; found: C 31.38, H 3.93%. For the preparation of (II), pale-yellow X-ray-quality crystals of (II) were produced by slowly diffusing together aqueous solutions of H_4PMA (1 equivalent) and $BaBr_2\cdot 2H_2O$ (1 equivalent) at room temperature. The crystals were observed to desolvate at 290 K. IR (KBr, cm^{-1}): ν_{max} 3410 (*br*, OH), 1686 (C═O, acid), 1592 (asymmetric CO_2^-), 1350 (symmetric CO_2^-), 1285, 1142 and 1096 (C—O), 756 (aromatic C—H), 621. Analysis calculated for $C_{10}H_{14}BaO_{13}$: C 25.05, H 2.94%; found: C 24.39, H 3.00%.

Compound (I)

Crystal data

$[Mg(H_2O)_6](C_{10}H_4O_8)$
$M_r = 384.54$
Monoclinic, $P2/m$
$a = 6.447$ (3) Å
$b = 9.942$ (4) Å
$c = 6.455$ (3) Å
$\beta = 115.148$ (7)°
$V = 374.5$ (3) Å^3
$Z = 1$
$D_x = 1.705$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1696 reflections
$\theta = 3.5$–28.7°
$\mu = 0.20$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.25 × 0.21 × 0.10 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω rotation with narrow-frame scans
2794 measured reflections
771 independent reflections
683 reflections with $I > 2\sigma(I)$

$R_{int} = 0.022$
$\theta_{max} = 26.0°$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.171$
$S = 1.17$
771 reflections
74 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1034P)^2 + 0.4203P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.17$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Mg1—O2	2.031 (3)	Mg1—O1	2.067 (3)
Mg1—O3	2.040 (4)		
O2—Mg1—O3	89.9 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4	0.84 (3)	1.99 (3)	2.822 (3)	179 (4)
O2—H2···O5	0.83 (4)	1.95 (4)	2.778 (3)	176 (5)
O3—H3···O5^{i}	0.82 (5)	1.99 (5)	2.799 (5)	169 (6)
O4—H4···O4^{ii}	1.19 (2)	1.19 (2)	2.387 (4)	178 (5)

Symmetry codes: (i) $x, y, z-1$; (ii) $x, 1-y, z$.

Compound (II)

Crystal data

$[Ba(C_{10}H_4O_8)(H_2O)_5]$
$M_r = 479.55$
Monoclinic, $P2_1/m$
$a = 6.6497$ (4) Å
$b = 19.1205$ (10) Å
$c = 6.6971$ (4) Å
$\beta = 116.865$ (2)°
$V = 759.61$ (8) Å^3
$Z = 2$
$D_x = 2.097$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5633 reflections
$\theta = 3.4$–29.1°
$\mu = 2.69$ mm^{-1}
$T = 150$ (2) K
Block, pale yellow
0.29 × 0.20 × 0.17 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω rotation with narrow-frame scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.520$, $T_{max} = 0.632$
6770 measured reflections
1890 independent reflections

1805 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 29.1°$
$h = -8 \rightarrow 9$
$k = -24 \rightarrow 26$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.033$
$S = 1.10$
1890 reflections
134 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0099P)^2 + 0.699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

Ba1—O6	2.6742 (19)	C1—C4	1.523 (2)
Ba1—O1	2.8076 (12)	C2—C3	1.395 (2)
Ba1—O8	2.8131 (18)	C2—C5	1.523 (2)
Ba1—O4^{iii}	2.8183 (12)	C4—O1	1.241 (2)
Ba1—O7	2.8227 (18)	C4—O2	1.281 (2)
Ba1—O5	2.8690 (13)	C5—O4	1.224 (2)
C1—C3^{iv}	1.395 (2)	C5—O3	1.300 (2)
C1—C2	1.413 (2)		

Symmetry codes: (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2	1.10 (2)	1.30 (2)	2.397 (2)	174 (2)
O5—H5A···O2^{v}	0.81 (2)	2.01 (2)	2.803 (2)	165 (2)
O5—H5B···O3^{iii}	0.80 (2)	2.02 (2)	2.803 (2)	166 (2)
O6—H6A···O7^{vi}	0.79 (3)	1.99 (3)	2.778 (3)	172 (3)
O6—H6B···O8^{vi}	0.80 (3)	2.03 (4)	2.818 (3)	169 (4)
O7—H7A···O5^{i}	0.80 (2)	2.01 (2)	2.800 (2)	167 (2)
O8—H8A···O1^{vii}	0.81 (2)	1.98 (2)	2.772 (2)	166 (2)

Symmetry codes: (i) $x, y, z-1$; (iii) $1-x, 1-y, 1-z$; (v) $x, y, 1+z$; (vi) $x-1, y, z$; (vii) $1+x, y, 1+z$.

Aromatic H atoms were placed geometrically (C—H = 0.95 Å) and treated using a riding model, while the coordinates of hydroxy and water H atoms were refined using geometric restraints. U_{iso}(H) values were set at $1.2U_{eq}$(C) for aryl H atoms and $1.5U_{eq}$(O) for hydroxy H atoms. The largest residual electron-density peak in (I) is 1.0 Å from atom Mg1 and is probably caused by marginal crystal quality or lack of absorption correction. The data set resolution for (I) was truncated (to $\theta = 26^\circ$) prior to the final refinement.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

The authors acknowledge the EPSRC for the provision of a studentship (SHD).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1069). Services for accessing these data are described at the back of the journal.

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