Poly[(μ₄-adamantane-1,3-dicarboxylato-κ⁵O¹:O¹′:O³,O³′:O³′)(μ₃-adamantane-1,3-dicarboxylato-κ⁵O¹,O¹′:O³,O³′:O³′)dimagnesium]: a layered coordination polymer

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The title compound, $[Mg_2(C_{12}H_{14}O_4)_2]_n$, is the first example of an s-block metal adamantanedicarboxylate coordination polymer. The asymmetric unit comprises two crystallographically unique Mg^{II} centers and two adamantane-1,3-dicarboxylate ligands. The compound is constructed from a combination of chains of corner-sharing magnesium-centered polyhedra, parallel to the a axis, connected by organic linkers to form a layered polymer. The two Mg^{II} centers are present in distorted tetrahedral and octahedral coordination environments derived from carboxylate O atoms. Tetrahedrally coordinated Mg^{II} centers have been reported in organometallic compounds, but this is the first time that such coordination has been observed in a magnesium-based coordination polymer. The bond valance sums of the two Mg^{II} centers are 2.05 and 2.11 valence units, matching well with the expected value of 2.

Comment

Coordination polymers (CPs) or metal–organic frameworks (MOFs) (Cheetham et al., 2006) are a new class of material composed of extended arrays of metal centers, connected by organic linkers to form frameworks of various dimensionalities, tailored for specific uses such as gas storage (Murray et al., 2009), separation (Li et al., 2009), catalysis (Ma et al., 2009) and luminescence (Allendorf et al., 2009). A wide range of metal centers is used to construct MOFs or CPs. First-row transition metals are popular choices because of their well known bonding interactions with the functional groups of organic linkers. The application of alkali and alkaline earth metals to form MOFs or CPs is limited, however. The use of s-block metal centers to construct frameworks offers several advantages. Porous frameworks based on early s-block metals

can provide gravimetric advantages for gas-storage applications due to the low atomic weight metal centers (Dinca & Long, 2005; Abrahams et al., 2010). In addition, nontoxic frameworks based on s-block metals (Na, K, Mg and Ca) have potential uses in biological applications (Imaz et al., 2011).

(I)
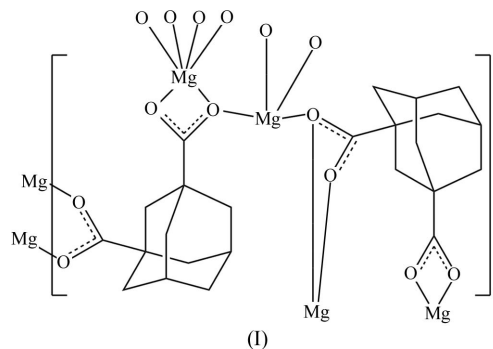
Apart from metal centers, the choice of organic linkers is critical for varying the coordination behavior of metal ions and determining the overall characteristics of the framework. For example, adamantanedicarboxylate linkers are used to form various framework topologies with first-row transition metals, lanthanides and actinides (Nazarenko et al., 2010; Nielsen et al., 2008; Millange et al., 2004; Ok & O'Hare, 2008; Xu et al., 2006).

Our group is currently investigating the structure type and functionalities of different frameworks formed using s-block metal centers (Li, Mg and Ca) for potential use as gas-storage media (Banerjee et al., 2010, 2011). In this work, we report the first example of a magnesium–adamantane-1,3-dicarboxylate [Mg(1,3-ADA)] layered polymer, namely poly[(μ₄-adamantane-1,3-dicarboxylato)magnesium], (I), prepared under solvothermal conditions. Compound (I) crystallizes in the triclinic space group $P\bar{1}$ with an asymmetric unit comprising two Mg^{II} ions and two complete dianionic 1,3-ADA^{2-} ligands (Fig. 1).
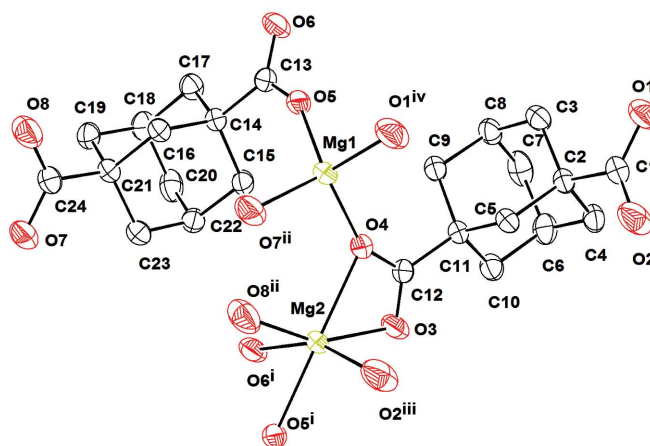

Figure 1
A view of the local environment of the Mg^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + 1, y, z$.]
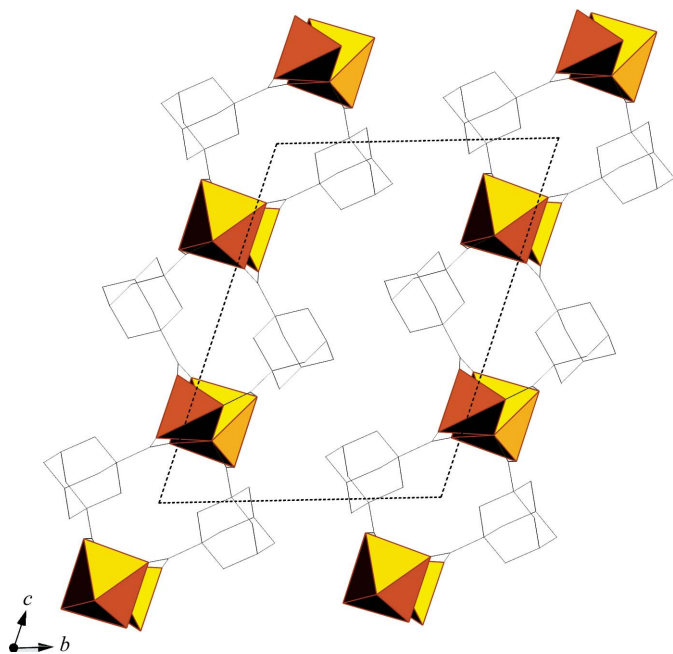
metal-organic compounds

Figure 2
A view of the structure of (I), along the [100] direction, parallel to the layers. H atoms have been omitted for clarity.

There are two types of crystallographically independent Mg site, *viz.* Mg1 with a tetrahedral MgO$_4$ environment and Mg2 with a distorted octahedral MgO$_6$ environment.

Atom Mg1 is coordinated to four bridging bidentate 1,3-ADA^{2-} ligands, with Mg—O bond lengths and internal O—Mg—O angles of 1.919 (2)–1.9470 (18) Å and 104.53 (8)–112.92 (8)°, respectively (Table 1). Tetrahedral coordination of magnesium is well established in magnesium-based organometallic compounds (Cambridge Structural Database, Version 5.32, update of November 2010; Allen 2002), but to the best of our knowledge this is the first time that such coordination has been seen in a magnesium-based polymer. Atom Mg2 is also coordinated by four 1,3-ADA^{2-} ligands, where two of these act as bidentate chelating ligands donating four O atoms [O3, O4, O5^{iv} and O6^{iv}; symmetry code: (iv) $x + 1$, y, z] which occupy two axial and two equatorial sites. The other equatorial O atoms [O8^{ii} and O2^{iii}; symmetry codes: (ii) $-x + 1$, $-y$, $-z$; (iii) $-x + 1$, $-y$, $-z + 1$] are donated by two different bridging bidentate 1,3-ADA^{2-} ligands. The coordination octahedron is highly distorted, with two narrow O—Mg—O angles [O3—Mg2—O4 = 60.72 (7)° and O5^{iv}—Mg2—O6^{iv} = 60.59 (7)°] from chelating carboxylate groups (Table 1). The Mg2—O bond lengths lie in the range 1.969 (2)–2.1739 (17) Å and the distances involving bidentate chelating O atoms are significantly longer than those involving bidentate bridging O atoms, *viz.* 2.1147 (19)–2.1739 (17) (O3, O4, O5^{iv} and O6^{iv}) *versus* 1.969 (2)–1.971 (2) Å (O2^{iii} and O8^{ii}) (see Table 1 for symmetry codes).

Atoms O4 and O5 bridge adjacent Mg1 and Mg2 centers, leading to the formation of ···Mg1···Mg2···Mg1··· chains running parallel to the *a* axis (Fig. 2); the Mg1···Mg2 and Mg2···Mg1^{iv} distances are 3.5419 (11) and 3.5463 (11) Å,
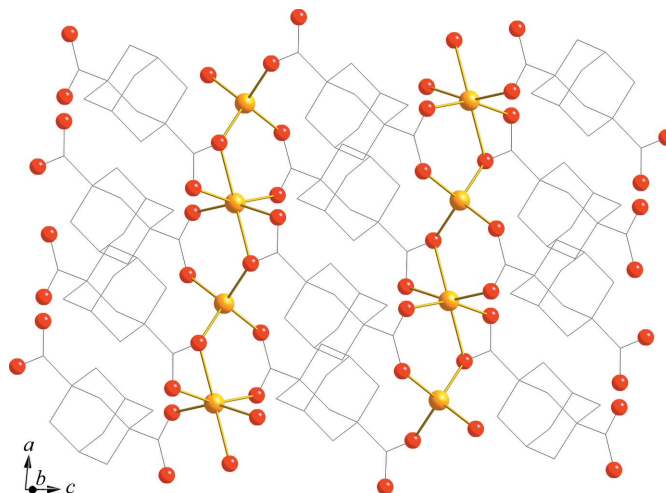

Figure 3
A view of a single layer of the structure of (I), highlighting the chains of alternating MgO$_4$ and MgO$_6$ coordination polyhedra. H atoms have been omitted for clarity.

respectively. The Mg1···Mg2 chains are crosslinked by 1,3-ADA^{2-} ligands. The carboxylate groups of the 1,3-ADA^{2-} linkers display two different coordination behaviors, *viz.* bidentate chelating (O3/O4 and O5/O6) and bidentate bridging (O1/O2 and O7/O8) (Fig. 1), with atoms O4 and O5 shared between atoms Mg1 and Mg2. Hence, each of the organic linkers connects four metal ions to produce two-dimensional layers in the *ac* plane (Fig. 3).

Experimental

Crystal data

[Mg(C$_{12}$H$_{14}$O$_4$)]	$\gamma = 89.141$ (3)°
$M_r = 493.00$	$V = 1124.95$ (7) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.9034$ (2) Å	Mo $K\alpha$ radiation
$b = 11.3549$ (4) Å	$\mu = 0.15$ mm^{-1}
$c = 15.3196$ (6) Å	$T = 293$ K
$\alpha = 70.713$ (4)°	$0.3 \times 0.1 \times 0.05$ mm
$\beta = 83.131$ (3)°	

Data collection

Oxford Xcalibur Atlas Gemini diffractometer	28700 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)	4605 independent reflections
	3157 reflections with $I > 2\sigma(I)$
$T_{min} = 0.979$, $T_{max} = 1.000$	$R_{int} = 0.061$

Table 1
Selected geometric parameters (Å, °).

Mg1—O1[i]	1.922 (2)	Mg2—O3	2.116 (2)
Mg1—O4	1.9443 (18)	Mg2—O4	2.1713 (17)
Mg1—O5[ii]	1.9470 (18)	Mg2—O5[iv]	2.1739 (17)
Mg1—O7[ii]	1.919 (2)	Mg2—O6[iv]	2.1147 (19)
Mg2—O2[iii]	1.971 (2)	Mg2—O8[ii]	1.969 (2)
O1[i]—Mg1—O4	111.03 (9)	O3—Mg2—O4	60.72 (7)
O1[i]—Mg1—O5	104.53 (8)	O3—Mg2—O5[iv]	108.79 (7)
O4—Mg1—O5	112.92 (8)	O5[iv]—Mg2—O6[iv]	60.59 (7)
O7[ii]—Mg1—O1[i]	111.52 (10)	O6[iv]—Mg2—O3	92.72 (8)
O7[ii]—Mg1—O4	104.95 (8)	O6[iv]—Mg2—O4	108.27 (7)
O7[ii]—Mg1—O5	112.07 (9)	O8[ii]—Mg2—O2[iii]	96.80 (11)
O2[iii]—Mg2—O3	89.61 (9)	O8[ii]—Mg2—O4	95.76 (8)
O2[iii]—Mg2—O4	93.73 (8)	O8[ii]—Mg2—O5[iv]	93.49 (8)
O2[iii]—Mg2—O5[iv]	96.04 (8)	O8[ii]—Mg2—O6[iv]	90.71 (9)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	307 parameters
$wR(F^2) = 0.154$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.46$ e Å^{-3}
4605 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}

All C-bound H atoms were placed in calculated positions and treated using a riding model, with C—H = 0.97 (methylene) or 0.98 Å (methine), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Burnett & Johnson, 1996) and *CrystalMaker* (Palmer, 2009); software used to prepare material for publication: *SHELXL97*.

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