

# Self-assembly synthesis of precursors to potential open framework alkali earth metal–organic complexes†

Cite this: *New J. Chem.*, 2014, **38**, 2135

Louise B. Hamdy, Paul R. Raithby, Lynne H. Thomas and Chick C. Wilson\*

Received (in Victoria, Australia)  
4th October 2013,  
Accepted 21st March 2014

DOI: 10.1039/c3nj01218b

www.rsc.org/njc

The synthesis and crystal structures of a series of six magnesium pyridinecarboxylic and dicarboxylic acid complexes are reported. These complexes have been prepared to establish the nature of the hydrogen-bonding within this series and to investigate the potential of using these complexes as precursors in the self-assembly of network materials. Two Mg picolinic acid complexes (**Mg1**, **Mg2**) display a 1:2 metal:ligand ratio and are polymorphic. A Mg isonicotinic acid complex (**Mg3**) is a constitutional isomer of **Mg1** and **Mg2**, while a 1:1 Mg picolinic acid complex (**Mg4**) is also reported and compared to the other members of the series. The set of complexes reported is completed by the synthesis and structural characterisation of two complexes containing the 2,4-pyridinedicarboxylic acid (2,4pdca) ligand, both a 1:1 (**Mg5**) and 1:2 (**Mg6**) Mg 2,4pdca acid complex, in which the presence of the additional carboxylate functionality provides clearer potential to form materials with extended network structures.

## Introduction

Magnesium is an attractive choice of metal for the synthesis of inorganic–organic crystalline complexes such as metal–organic frameworks (MOFs), not only because of its high abundance and availability, but also because of the additional benefit of producing low density adsorbent materials because of the maintenance of the low formula weight resulting from its incorporation when compared to purely organic precursors.<sup>1</sup> Owing to their similar atomic radii, magnesium adopts coordination geometries comparable to those of 3d transition metals such as Cu and Zn which are commonly observed elements in MOF structures.<sup>2</sup> Magnesium has been used to a limited extent in the preparation of MOFs, some of which have been shown to display valuable properties such as selective gas adsorption.<sup>3–6</sup> These materials are typically produced using hydrothermal or solvothermal methods. Adsorbent properties are not restricted to MOFs, however, since metal–organic complexes linked into networks not solely by coordination, but also by non-covalent interactions have been shown to take up small molecules reversibly.<sup>7</sup> Beatty *et al.*<sup>8–10</sup> have prepared a range of 2D networks constructed from pyridine dicarboxylic acids coordinated to transition metals (Fig. 1). It was possible for these to be

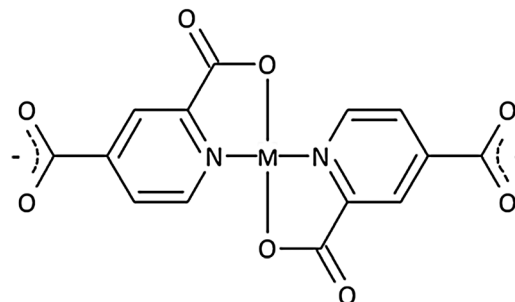


Fig. 1 Metal coordination geometry of 2,4-pyridinedicarboxylic acid as ligand found in a series of transition metal complexes (M = Zn, Co, Ni or Cu).<sup>8–10</sup>

combined with amines and a diamine to form lamellar structures, and in the case of the diamine the layers were effectively pillared by hydrogen (H)-bonds to the carboxyl groups of the metal-containing units.

Previously reported complexes of magnesium have been synthesised with the three pyridine carboxylic acid isomers, picolinic acid,<sup>11–13</sup> nicotinic acid<sup>14,15</sup> and isonicotinic acid<sup>15,16</sup> pyridinedicarboxylic acid isomers,<sup>6,17–21</sup> and 2,4,6-pyridinetri-carboxylic acid,<sup>22</sup> which display a range of hydrogen-bonding motifs primarily involving coordinated and un-coordinated water molecules. The ligands in all but one of these complexes are deprotonated and act both as counter ions and as coordinating ligands (the exception is a chloride salt of Mg picolinic acid, CSD refcode NISJEE<sup>12</sup>). Two open-framework rutile-type magnesium isonicotinate coordination polymers containing

Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.

E-mail: C.C.Wilson@bath.ac.uk

† Electronic supplementary information (ESI) available: Including metal coordination and hydrogen bond geometries for **Mg1**–**Mg6**, PXRD patterns and DSC traces for selected complexes. CCDC 964956–964960 and 992450. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj01218b

Mg(isonicotinate)<sub>2</sub>·H<sub>2</sub>O and Mg(nicotinate)<sub>2</sub> units have been prepared and the structural analyses of these materials show that they have different 3,6-connected frameworks with rutile- and anatase-like topologies, respectively.<sup>15</sup> It is also of interest to compare the structural motifs observed in the magnesium complexes with those observed in the organic precursor systems, which highlights the effect of the presence of the metals. Hamazaki *et al.* reported the crystal structure of picolinic acid where the molecule shows 50:50 disorder between the neutral and zwitterionic forms manifest in the form of positional disorder of a hydrogen atom.<sup>23</sup> Two H-bond motifs featuring this disordered hydrogen atom are observed, an N–H···N between pyridyl nitrogen groups and a single O–H···O between the carboxylic acid groups. The crystal structure of isonicotinic acid has been reported by Takusagawa and Shimada.<sup>24</sup> The structure consists of infinite chains connected by O–H···N bonds with these chains linked into sheets by weaker C–H···O bonds. The crystal structure of anhydrous 2,4-pyridinedicarboxylic acid is unknown. However, the monohydrate reported by Sander *et al.* shows the 2,4-pyridinedicarboxylic acid molecule to be present in its zwitterionic form with hydrogen transfer between adjacent basic N and carboxylic acid groups.<sup>25</sup> A layered 2D H-bonded network is formed featuring the H-bonds, N–H···O from the pyridyl group to the water, O–H···O from the water molecule to the carboxylic acid and to the carboxylate groups and O–H···O carboxylic acid to carboxylate. These organic molecules are ideal ligands due to their coordination and H-bonding potential. However, the intermolecular interactions present in the structures of the precursors are perturbed when a metal complex is formed, and it is important to quantify which ligand–ligand interaction motifs are most robust in such circumstances, to investigate the possibility that they may be harnessed as a design tool in creating desired architectures within metal–organic complexes. Herein, we report the crystal structures of a series of complexes featuring magnesium with the isomers 2- and 4-pyridine carboxylic acid, (picolinic and isonicotinic acid, respectively), and 2,4-pyridinedicarboxylic acid, (2,4pdca). The magnesium pyridine carboxylic–dicarboxylic acid complexes combine the advantages of using a lighter metal centre with the structural flexibility offered by the non-covalent interactions that are fundamental to the connectivity within the structure, among which H-bonds play a significant role. Also highlighted by the formation of these complexes is the role that counterions, in this case nitrate, and deprotonation upon complex formation, play in the potential preservation of the hydrogen bonding capabilities of the ligands. Particular H-bonding patterns are evident in the parent ligand structures, indicating that there is a degree of predictability for these, which could potentially allow for the deliberate and controlled assembly of these supramolecular materials.

## Results and discussion

### 1:2 polymorphic complexes of Mg with picolinic acid (Mg1 and Mg2)

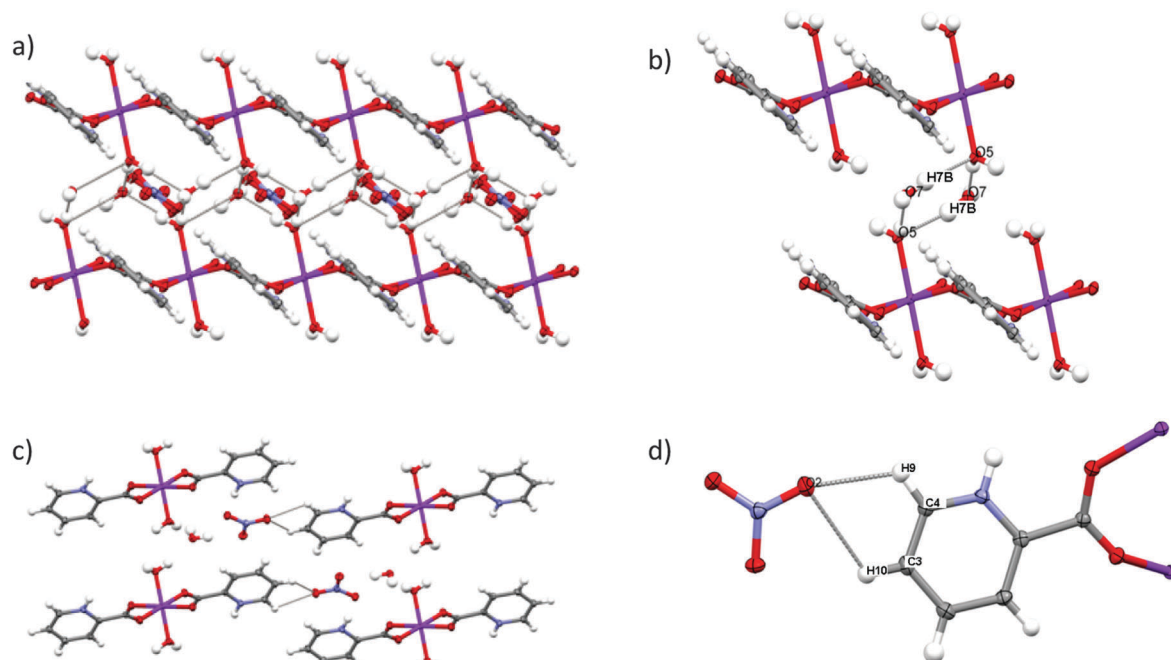
Two crystalline polymorphs of formula [Mg(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, **Mg1** (cuboids) and **Mg2** (platelets) have been prepared from the reaction of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with picolinic acid, in a

1:1 molar ratio, in a dichloromethane–acetone mixture, and recrystallized at room temperature. The crystal structure of **Mg1** (Table 1) can be classed as a coordination polymer, (Fig. 2). Each Mg is located on a crystallographic inversion centre and is coordinated to the oxygen donors of four picolinate ligands and to the oxygen atoms of two water molecules. Nitrate counter ions are included in the framework but these are not coordinated directly to the Mg ions; this enables the picolinic acid ligand to remain in a neutral state existing in its zwitterionic form. Metal–ligand coordination between the zwitterionic picolinic acid ligands and the Mg centre results in 1D chains that run parallel to the *a* axis. The organic ligands coordinate *via* both carboxyl oxygen atoms bridging two separate Mg centres. The protonated pyridyl nitrogen atom is not coordinated to the metal centre and is free to act as a hydrogen bond donor to a free nitrate ion. The Mg centre has a slightly distorted octahedral geometry with the O–Mg–O angles ranging from 84.50(3)° to 95.50(3)° (ESI,† Fig. S1), and are coordinated to the carboxylate group of picolinic acid at their equatorial positions with Mg–O distances of 2.063(1) Å and 2.060(1) Å and axially to two symmetry equivalent water molecules with an Mg–O distance of 2.071(1) Å (bond distances and angles are given in the ESI,† Table S2). Uncoordinated water and nitrate molecules play a role in the connection of the 1D coordination polymers. The coordination chains are stacked along the *b* axis and connected by H-bonds between the coordinated and uncoordinated water molecules, nitrate ions and the picolinic acid ligands (H-bond distances and angles, ESI,† Table S3). The axially coordinated water ligands form H-bonds to the uncoordinated water ligands, linking the coordination polymers (Fig. 2b), with O5 and O7 forming the additional H-bond O7–H4···O5. The uncoordinated water molecule forms a bifurcated H-bond to the nitrate ion. Connecting the structure along the *c* axis is a weaker bifurcated H-bond between two C–H groups of the picolinic acid and the nitrate ion.

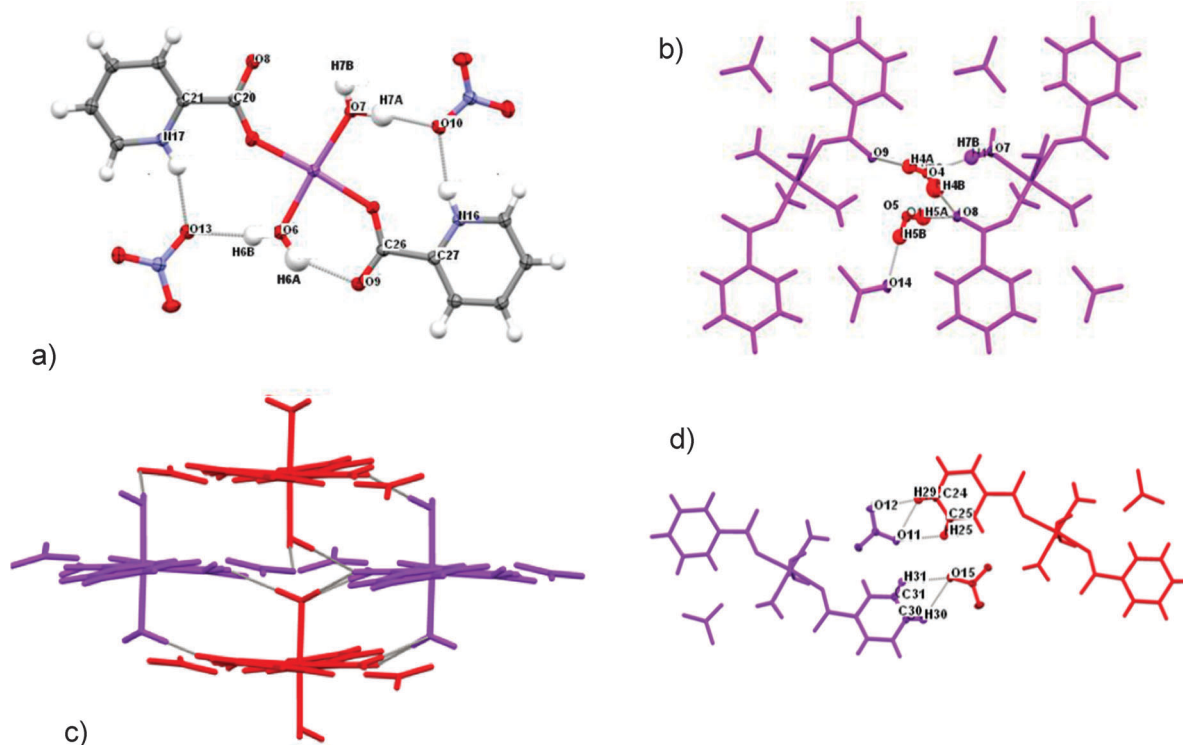
The polymorphic form, **Mg2**, displays a very different structure to that of **Mg1**, with the zwitterionic picolinic acid ligands coordinated to only one Mg *via* a carboxylate oxygen atom and not bridging metal centres (Fig. 3). These isolated molecules are connected through hydrogen bonding interactions. Similarly to **Mg1**, the Mg centre is in a distorted octahedral environment, only here all the water molecules are coordinated to the metal; those with O4 and O5 axial with respect to the picolinate ligands, and those with O6 and O7 equatorially. Picolinic acid is also coordinated to Mg at an equatorial position. There are two H-bonds between the water molecules and nitrate ions, O7–H7A···O10 and O6–H6B···O13, two between the protonated pyridyl nitrogen atoms and the nitrate ions, N16–H16···O10 and N17–H17···O13, and one between the water molecule and one of the uncoordinated carboxyl oxygen atom, O6–H6A···O9. The geometries of the carboxylate groups of the two independent picolinic acid ligands are similar, with bond lengths between the sp<sup>2</sup> hybridised carbon atoms, C20–C21 and C26–C27 of 1.519(2) Å and 1.531(2) Å, respectively. The hydrogen bonds result in a staggering of the Mg units creating 2D structural motifs that run in the {110} direction. Three of these H-bonds

**Table 1** Crystallographic data for Mg pyridinecarboxylic–dicarboxylic acid complexes **Mg1–Mg5**; crystallographic data for **Mg6** was obtained from a three component twinned crystal and refined as a three component twin

	<b>Mg1</b>	<b>Mg2</b>	<b>Mg3</b>	<b>Mg4</b>	<b>Mg5</b>	<b>Mg6</b>
Formula	Mg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Mg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Mg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	Mg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	Mg(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	Mg(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·Mg(H <sub>2</sub> O) <sub>6</sub>
<i>M</i> /g mol <sup>−1</sup>	466.61	466.61	466.61	325.49	540.97	577.06
<i>T</i> (K)	100	100	110	100	100	150
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> <sub>2<sub>1</sub>/n</sub>	<i>P</i> <sub>2<sub>1</sub>/c</sub>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	4.7079(4)	6.9760(12)	6.1279(6)	9.9683(6)	9.5610(8)	7.0638(6)
<i>b</i> (Å)	7.0524(8)	10.184(2)	8.1151(10)	6.8418(3)	8.3362(6)	8.9852(8)
<i>c</i> (Å)	14.1691(17)	13.819(3)	9.4126(12)	18.8376(10)	13.9891(10)	9.6628(12)
$\alpha$ (°)	94.124(4)	80.832(7)	89.443(5)	90	90	83.104(9)
$\beta$ (°)	91.235(3)	83.325(6)	86.609(4)	103.938(2)	102.135(7)	75.593(9)
$\gamma$ (°)	102.963(3)	77.664(5)	88.628(4)	90	90	83.597(7)
<i>V</i> (Å <sup>3</sup> )	456.92(8)	943.4(3)	467.11(9)	103.938(2)	1090.05(15)	587.58(11)
<i>Z</i>	1	2	1	4	4	1
$\rho_{\text{calc}}$ (g cm <sup>−3</sup> )	1.696	1.643	1.659	1.734	1.648	1.631
$\mu$ (mm <sup>−1</sup> )	0.186	0.180	0.181	0.211	0.201	0.198
$\theta$ range (°)	3.20–27.48	3.0–27.6	3.30–27.48	3.18–27.48	3.28–27.48	3.24–28.96
Reflections collected	10 795	22 236	11 191	15 569	13 467	7669
Independent	2072	4289	2125	2829	2498	7669
Observed $>2\sigma(I)$	1805	3075	1808	2318	1414	4917
<i>R</i> <sub>int</sub>	0.021	0.0463	0.0278	0.0387	0.0834	0.0485
Completeness (%)	99.8	99.8	99.9	99.4	99.8	99.9
Parameters	178	352	178	234	194	210
GoF	1.119	1.226	1.090	1.102	1.135	1.078
<i>R</i> <sub>1</sub> (observed)	0.0277	0.0341	0.0332	0.0381	0.0787	0.0627
<i>R</i> <sub>1</sub> (all)	0.0324	0.0583	0.0401	0.0471	0.1317	0.1042
w <i>R</i> <sub>2</sub> (all)	0.0751	0.0994	0.0888	0.0970	0.2809	0.1925
$\rho_{\text{max,min}}$ (e Å <sup>−3</sup> )	0.306, −0.224	0.409, −0.343	0.412, −0.300	0.283, −0.301	0.576, −0.851	0.615, −0.856



**Fig. 2 Mg1:** (a) 1D coordination polymer chains, (b) H-bonds connecting chains along *b* axis. (c) and (d) Bifurcated H-bonds between picolinic acid and nitrate connecting structure along *c* axis. [Distances and angles of hydrogen bonds are given in the ESI,† for this and subsequent complexes, as are the required symmetry equivalencies where appropriate.]



**Fig. 3 Mg2:** (a) formula unit, Mg coordinated to picolinic acid and water, H-bonded to nitrate ions, (axially coordinated water molecules excluded for clarity). (b) Formula units connected by H-bonds, (nearest axially coordinated water molecule of red formula units located above and below purple formula units along the *a* axis shown only for clarity). (c) Packing of formula units creating 2D structural motifs. (d) H-bonds connecting adjacent motifs along the *c* axis.

are between uncoordinated carboxyl oxygen atoms and coordinated water molecules, O4–H4A···O9, O4–H4B···O8 and O5–H5A···O8, one is between one equatorial and one axial water molecule, O7–H7B···O4, and one is between the coordinated water molecule and the uncoordinated nitrate ion, O5–H5B···O14 (Fig. 3). These are reasonably short interactions with D···A distances ranging from 2.696(2) Å to 2.906(2) Å. The 2D structural motifs are connected to adjacent motifs by H-bonds, including bifurcated H-bonds, between the C–H groups of picolinic acid and the nitrate ions.

Hot stage microscopy and DSC investigations show that the melting point of **Mg1** is in the range of 80–87 °C and for **Mg2** is in the range of 85–88 °C. It is interesting that **Mg2** may have a very slightly higher melting relative to **Mg1** despite there being no coordination polymer chains present in the former, which could be testament to the stabilisation afforded by the extensive H-bonding present in this structure.

### 1 : 2 complex of Mg with isonicotinic acid (**Mg3**)

**Mg3** has the formula  $[\text{Mg}(\text{C}_6\text{H}_5\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$  and was obtained from a solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and isonicotinic acid, in a 1 : 1 ratio, in isopropanol, at 50 °C. It is a constitutional isomer of **Mg1** and **Mg2**. Similarly to **Mg2**, the Mg centre, which in this case is located on a crystallographic inversion centre, is in a slightly distorted octahedral environment and coordinates to two isonicotinic acid ligands through one carboxyl oxygen atom, with a distance of 2.040(1) Å, and four water ligands with Mg–O distances of 2.071(1) Å and 2.089(1) Å (ESI,† Fig. S4).

Isonicotinic acid is in its zwitterionic form, with the pyridyl nitrogen atom protonated, and with one uncoordinated carboxyl oxygen atom. Two isonicotinic acid ligands coordinate to the metal centre through one carboxyl oxygen atom resulting in discrete uncoordinated formula units, also containing two uncoordinated nitrate ions (Fig. 4).

Two approximately linear H-bonds are present in the formula unit between the water molecules and the nitrate ions, O6–H8···O2 and O7–H11···O1. Layers are formed along the {011} plane by H-bonding (C3–H3···O4) between units through the uncoordinated carboxyl oxygen atom of isonicotinic acid and a C–H group of isonicotinic acid from the next formula unit. Also connecting the structure into layers are two H-bonds involving nitrate ions; N2–H7···O1 where the donor is a protonated pyridyl nitrogen atom and C4–H4···O3 where the donor is a contiguous carbon atom. There are also linear H-bonds connecting the structure along the *a* axis between a coordinated water molecule of one formula unit to the uncoordinated carboxyl oxygen atom of the adjacent formula unit, O6–H9···O4, and between the other coordinated water molecule of the first formula unit to the H-bonded nitrate ion of the adjacent formula unit, O7–H10···O2.

### 1 : 1 complex of Mg with picolinic acid (**Mg4**)

**Mg4** has the formula unit  $[\text{Mg}(\text{C}_6\text{H}_5\text{NO}_2)(\text{NO}_3)(\text{H}_2\text{O})_3](\text{NO}_3)$  and features picolinic acid and Mg in a 1 : 1 ratio. It was obtained by recrystallization from a methanolic solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and picolinic acid, at 50 °C. The picolinic acid ligands are in

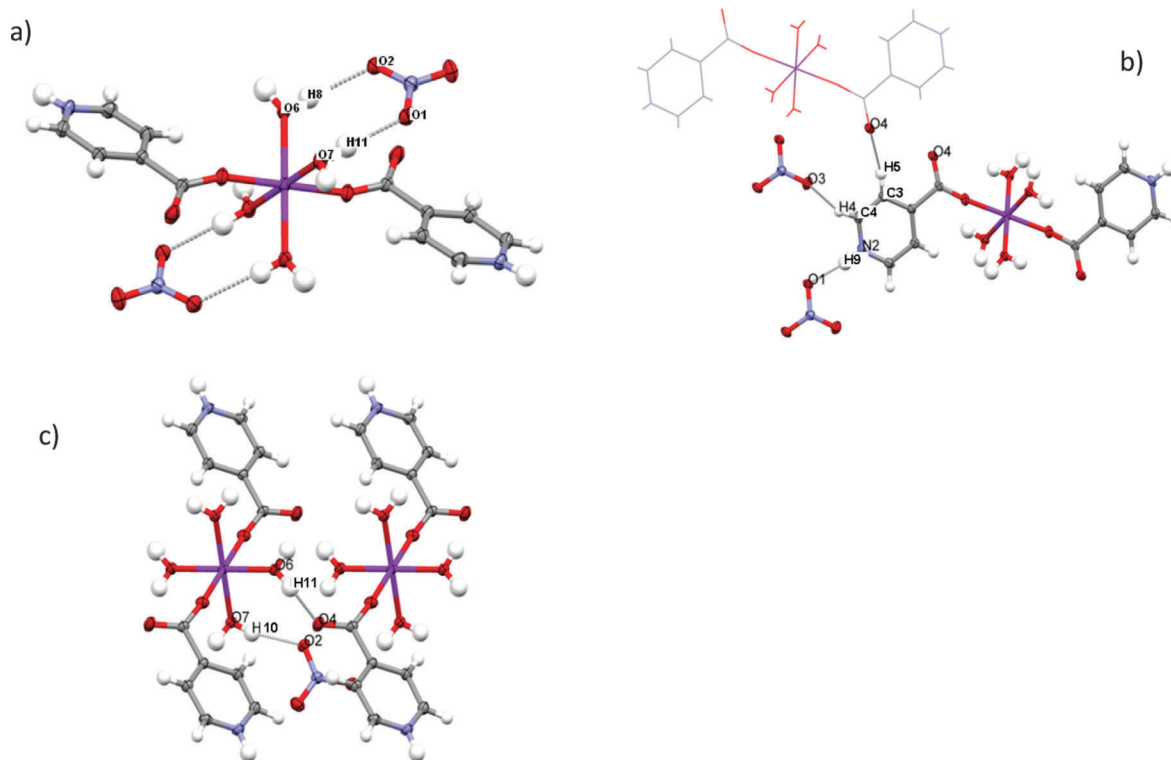


Fig. 4 **Mg3**; (a) formula unit showing H-bonds between the metal–ligand complex and the uncoordinated nitrate ion. (b) H-bonds between formula units connecting the structure along the {011} plane. (c) H-bonds between formula units connecting the structure along the *a* axis.



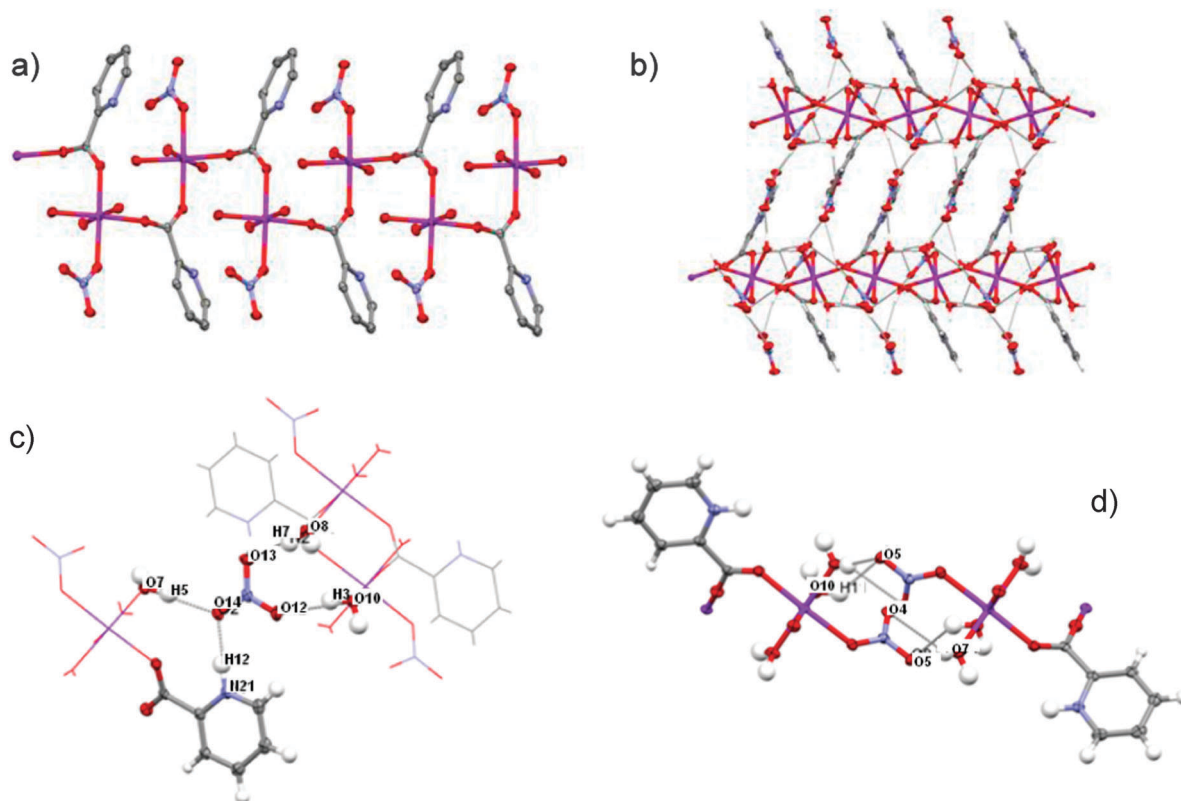
their zwitterionic form and are coordinated to two Mg atoms *via* the carboxyl group oxygen atoms effectively bridging the metal centres forming 1D coordination polymers along the *b* axis.

**Mg4** forms 1D coordination polymer chains, but these contrast to those found in **Mg1** due to the differing stoichiometries. The two Mg centres are only bridged by one common picolinic acid ligand, and the metal coordinates to one ligand axially, and the other equatorially (Fig. 5). The Mg atom is also coordinated to three water molecules in equatorial positions, and to one nitrate ion at an axial position; this is the only complex in this series which shows metal coordination to a nitrate anion and there is also an uncoordinated nitrate ion. The Mg centre has a slightly distorted octahedral geometry, with all O–Mg–O angles within about 4° of 90° (ESI,† Fig. S5). The longest Mg–O coordination interaction is to the nitrate ion at 2.133(1) Å. The distances between the Mg centre and the oxygen atoms of the carboxyl groups of the picolinic acid ligands are different, with the axial oxygen, O2, at 2.076(1) Å and the equatorial oxygen, O9, at 2.030(1) Å. The extended structure is connected along the *a* axis by H-bonding between the coordinated water molecules and the coordinated nitrate ions (ESI,† Fig. S6). The H-bonds linking the two parallel polymer chains are between the coordinated water molecules of one chain and the coordinated nitrate ion of the other chain, (O10–H1···O5, O7–H4···O4 and O7–H4···O5). The uncoordinated nitrate ion is central to connecting the extended structure

along the *c* axis. All oxygen atoms of the nitrate ion act as acceptors in four different H-bonds.

### 1 : 1 complex of Mg and 2,4-pyridinedicarboxylic acid (Mg5)

The complex  $[\text{Mg}(\text{C}_7\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})_4] \cdot 0.5\text{H}_2\text{O}$  was obtained by the treatment of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with 2,4-pyridinedicarboxylic acid (2,4pdca) monohydrate, in methanol, followed by the addition of *m*-xylylenediamine, with recrystallization over the period of a week. The asymmetric unit of **Mg5** features half of a 50 : 50 disordered uncoordinated water molecule (disordered over an inversion centre) in addition to the complex  $[\text{Mg}(\text{C}_7\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})_4]$  (Fig. 6). The composition differs from the previously reported  $[\text{Mg}_2(\text{C}_7\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_6]$  complex which forms isolated units comprised of two Mg atoms bridged by a single carboxylate O atom of the 2,4pdca ligand.<sup>17,18</sup> The Mg centre is coordinated to four water molecules and the N and O donor atoms of the bidentate 2,4pdca ligand in a similar manner to the known complex.<sup>6,17,18</sup> It is in a rather distorted octahedral environment with the angles between coordinated atoms ranging from 76.1(1)° for the O1–Mg1–N1 angle to 97.6(2)° for the O3–Mg1–O5 angle, (ESI,† Fig. S7). The Mg1–N1 distance has the longest coordination distance of 2.203(4) Å, whereas the distance between Mg1 and the coordinated carboxyl oxygen atom (Mg1–O1) is shorter at 2.066(3) Å. The 2,4pdca ligand is doubly deprotonated to the dianion and features three uncoordinated carboxyl oxygen atoms. Each of the formula units are H-bonded to eight neighbouring



**Fig. 5** **Mg4**: (a) 1D coordination polymer running parallel to the *b* axis (hydrogen atoms removed for clarity). (b) 1D coordination polymers stacked along the *c* axis. (c) H-bonding of 1D polymers to uncoordinated nitrate ion connecting chains along the *c* axis. (d) H-bonding of 1D polymers *via* coordinated nitrate ion and coordinated water molecules connecting structure along the *a* axis.

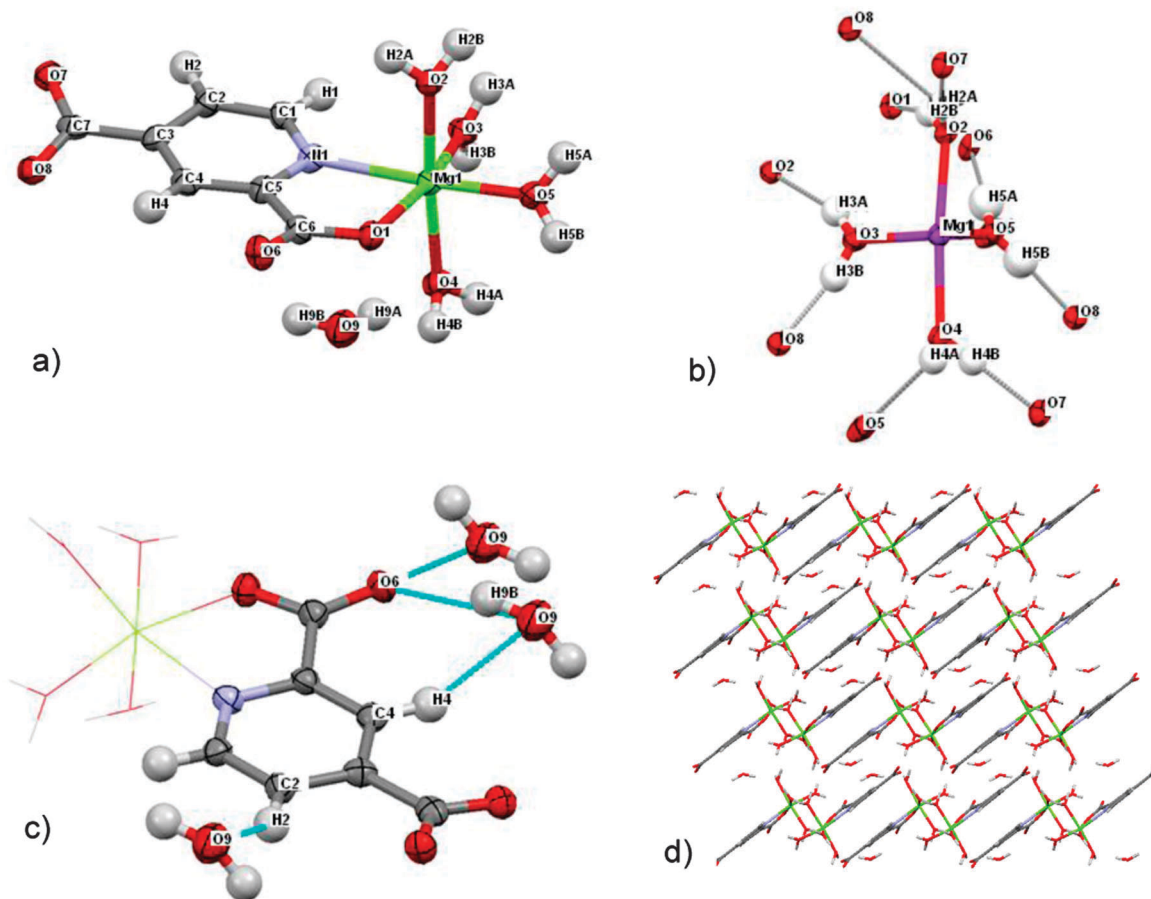


Fig. 6 **Mg5**; (a) formula unit, showing uncoordinated, disordered, water molecule (O9) and N,O-chelation of 2,4pdca to **Mg1**. (b) H-bonds from coordinated water molecules connecting formula unit to 8 neighbouring formula units. (c) H-bonds of uncoordinated disordered water molecule connecting formula units. (d) Global packing of **Mg5**, showing layers of formula units.

formula units, forming layers parallel to the {001} plane. The H-bonds are formed between the coordinated water molecules of one formula unit to the uncoordinated carboxyl oxygen atoms of the next formula units; O2–H2B···O1, O2–H2A···O7, O2–H2A···O8, O3–H3B···O8, O4–H4B···O7, O5–H5B···O8, O5–H5A···O6; and also between coordinated water molecules of neighbouring formula units; O3–H3A···O2, O4–H4A···O5. The layers are connected by nine H-bonds, three of which involve the uncoordinated water molecule (O9); some of these are fairly long interactions. The other interactions connecting the layers are the H-bonds between coordinated water molecules and the doubly uncoordinated carboxyl group oxygen atoms, O7 and O8; O2–H2A···O7, O5–H5B···O8, O4–H4B···O7, O3–H3B···O8, O2–H2A···O8. There is also an H-bond between coordinated water molecules, O4–H4A···O5 which is among the longest of these interactions with a D···A distance of 3.196(5) Å.

**1 : 2 complex of Mg and 2,4-pyridinedicarboxylic acid (Mg6; diaqua-bis(2,4-pyridinedicarboxylato)-magnesium(n) magnesium hexahydrate water solvate)**

**Mg6** is a metal-organic hydrate which has the formula  $\text{Mg}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2 \cdot \text{Mg}(\text{H}_2\text{O})_6 \cdot 1.5(\text{H}_2\text{O})$  and features two different magnesium ions, both located on crystallographic inversion centres.

Mg(1) is N–O chelated by two bidentate 2,4pdca ligands at the equatorial positions, and two water molecules at the axial positions, *trans* to one another. The 2,4pdca ligands are doubly deprotonated, and feature peripheral uncoordinated carboxylate groups. This dianionic monomer component, shown in Fig. 1, corresponds to the magnesium analogue of the component employed extensively by Beatty *et al.*, as precursors in further syntheses, where  $\text{M} = \text{Zn}^{2+}$ ,<sup>10</sup>  $\text{Co}^{2+}/\text{Ni}^{2+}$ ,<sup>8</sup> or  $\text{Cu}^{2+}$ .<sup>9</sup> Therefore, this complex constitutes a potentially versatile building block for the further synthesis of group 2 metal-organic complexes. The carboxylate groups which are not involved in metal coordination present functional groups capable of engaging in intermolecular interactions, such as charge-assisted H-bonds. The magnesium centre Mg(1) is surrounded by two nitrogen atoms and four oxygen atoms, two of which belong to the coordinated water molecules. The octahedral geometry is distorted due to the chelation of the two  $\text{K}^2$  ligands reducing the O2–Mg1–N1 angle, formed by the same ligand, to 77.8(1)° (ESI,† Fig. S8), similar to the geometry found in the complex SUYLEE01<sup>6</sup> (CSD 2013, v1.15), which contains two magnesium centres, each chelated by one bidentate 2,4pdca ligand and bridged by the coordinating carboxyl atom. In **Mg6** the metal-oxygen distances to the oxygen atoms are 2.063(3) Å and

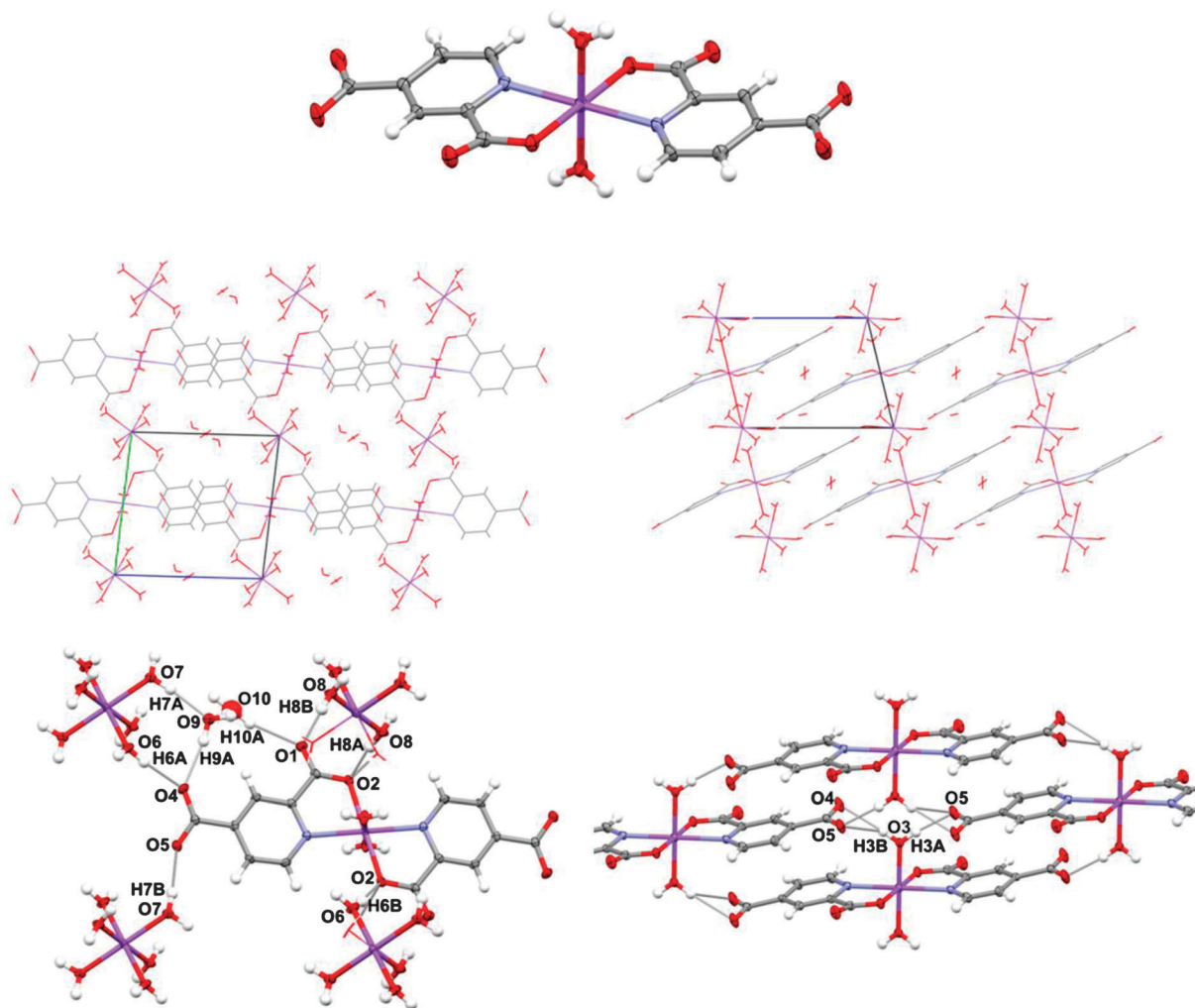


Fig. 7 **Mg6**; dianionic monomer unit,  $\text{Mg}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2$  (top). Global packing viewed down the  $a$  axis (middle left) and  $b$  axis (middle right). H-bonds connecting structure along  $b$  axis (bottom left), and connecting  $\text{Mg}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2$  units (bottom right).

2.037(3) Å for the carboxylate oxygen and oxygen atom of the axial water molecule respectively. The equivalent distances in SUYLEE01 are 2.100(1) Å and 2.036 (1) Å respectively,<sup>6</sup> demonstrating that the magnesium coordination is similar despite the different number of metal centres.

Besides presenting a new group 2 metal–organic complex, and possible precursor for lightweight metal–organic materials, **Mg6** has a rather interesting crystal structure as a whole. **Mg6** is a metal hydrate and features a second magnesium centre, where Mg(2) is coordinated to six water molecules, as found extensively in the CSD. There are two uncoordinated water molecules present in the crystal structure, one of which is located on a centre of inversion and shows evidence of disorder. Mg(2) has a near perfect octahedral geometry with O–Mg–O angles ranging from 89.3(1)° for O6–Mg2–O7 to 90.7(1)° for O6–Mg2–O7<sup>8</sup> (ESI,† Fig. S9) and the coordination distances are also more uniform in Mg(2), with Mg2–O6 and Mg2–O8 distances of 2.068(3) Å and 2.065(3) Å respectively, while Mg2–O7 is marginally shorter at 2.044(3) Å.

The components of **Mg6** are arranged in columns running down the  $a$  axis, as shown in Fig. 7. Similarly to the previous

magnesium–organic complexes, hydrogen bonds play a major role in the connectivity of the crystal structure of **Mg6**. The  $\text{Mg}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2$  dianionic monomer units are interlinked by three H-bond interactions creating 2D tapes parallel to the  $ac$  plane. These H-bonds exist between the axially coordinated water molecules of one unit to the carboxyl oxygen atoms of the non-coordinating carboxylate group of another unit. The  $\text{Mg}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2$  units are connected by H-bonds to  $\text{Mg}(\text{H}_2\text{O})_6$  and the uncoordinated water molecules, effectively connecting the structure along the  $b$  axis. There are also H-bonds between the uncoordinated water molecules to the carboxyl oxygen atoms of 2,4pdca, along with other H-bonds involving the water molecules.

## Conclusions

It has been shown that Mg salts and pyridine carboxylic and dicarboxylic acid ligands will readily form crystalline metal–organic complexes. In the case of the Mg complexes involving pyridinecarboxylic acid isomers prepared using  $\text{Mg}(\text{NO}_3)_2$  salts,



the ligands tend to exist in their zwitterionic forms utilising the nitrate units as the charge-balancing anions. This allows the ligands to have the potential to act as hydrogen bond donors as well as acceptors increasing the propensity for hydrogen bonding. In all but one of the complexes, the nitrate anions act as bridging units which are not directly coordinated to the metal centres. The complexes tend to exist in 1:2 Mg:ligand stoichiometries regardless of the stoichiometry of the preparation. The exception to this is **Mg3** which forms in a 1:1 stoichiometry. The pyridine-dicarboxylic acid complex, **Mg5**, does not include nitrate counterions, instead the charge balance is obtained through double deprotonation of the ligand to form the dianion and a 1:1 stoichiometry of the Mg:ligand. The ligands primarily coordinate to the Mg centres through carboxylate oxygen atoms reflected in the preference for the zwitterionic forms of the pyridinecarboxylic acid ligands; in the case of **Mg5** and **Mg6**, featuring 2,4-pyridine-dicarboxylic acid, the ligand additionally coordinates to Mg through the pyridyl nitrogen atom acting as a bidentate ligand with the N atom located adjacent to the coordinating carboxylate group. Uncoordinated carboxyl oxygen atoms are H-bond acceptors in all cases. Water incorporated in the crystal is crucial in connecting the extended structures for all of the reported Mg complexes and is found in both a metal coordination role and as free molecules; the counterion,  $\text{NO}_3^-$  also acts as a linking unit.

This work confirms that the strong and consistent H-bonding motifs (synthons) in the starting materials do not translate into the metal-organic complexes due to deprotonation and metal coordination of carboxylic acid groups, along with the inclusion of counter ions and water, and also that **Mg6** represents the magnesium analogue of a useful building block that can potentially be employed to introduce a group 2 metal into metal-organic complexes, by analogy with previous work on transition metal complexes.

## Acknowledgements

LBH is funded by an EPSRC studentship. We thank Dr Dyanne Cruickshank and Prof. Carlos Pinheiro for discussions.

## References

- 1 M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376–9377.
- 2 Z. Hulvey and A. K. Cheetham, *Solid State Sci.*, 2007, **9**, 137–143.
- 3 Q. Zhai, Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, *Dalton Trans.*, 2012, **41**, 2866–2868.
- 4 D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 20637–20640.
- 5 P. D. C. Dietzel, V. Besikiotis and R. Blom, *J. Mater. Chem.*, 2009, **19**, 7362.
- 6 A. Mallick, S. Saha, P. Pachfule, S. Roy and R. Banerjee, *J. Mater. Chem.*, 2010, **20**, 9073–9080.
- 7 M. N. Xanthopoulou, S. K. Hadjikakou, N. Hadjiliadis, A. Michaelides, S. Skoulika, N. Kourkouvelis and T. Bakas, *Inorg. Chim. Acta*, 2006, **359**, 215–220.
- 8 A. M. Beatty, B. A. Helfrich, G. A. Hogan and B. A. Reed, *Cryst. Growth Des.*, 2006, **6**, 122–126.
- 9 C. L. Chen and A. M. Beatty, *J. Am. Chem. Soc.*, 2008, **130**, 17222–17223.
- 10 G. A. Hogan, N. P. Rath and A. Beatty, *Cryst. Growth Des.*, 2011, **11**, 3740–3743.
- 11 J.-P. Deloume, H. Loiseleur and G. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1973, **29**, 668–673.
- 12 Z. Karimov and G. M. Ismailova, *Uzb. Khim. Zh.*, 1997, 2–4 (CSD refcode NISJEE).
- 13 M. A. Sharif, H. Aghabozorg, E. Motyeian, M. Ghadermazi and J. Attar Gharamaleki, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m2235–m2236.
- 14 M. B. Cingi, A. C. Villa, C. Guastini and D. Viterbo, *Gazz. Chim. Ital.*, 1974, **104**, 1087.
- 15 T. Liu, D. Luo, D. Xu, H. Zeng and Z. Lin, *Dalton Trans.*, 2013, **42**, 368.
- 16 L. B. Cole and E. M. Holt, *Inorg. Chim. Acta*, 1985, **108**, 159–164.
- 17 X.-S. Tai, J. Yin and M.-Y. Hao, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1850.
- 18 D. Saha, R. Sen, T. Maity and S. Koner, *Dalton Trans.*, 2012, **41**, 7399.
- 19 L. B. Cole and E. M. Holt, *Inorg. Chim. Acta*, 1989, **160**, 195.
- 20 H. Aghabozorg, P. Ghasemikhah, M. Ghadermazi, J. Soleimannejad and H. Adams, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1487.
- 21 H. Pasdar, S. Heidari, H. Aghabozorg and B. Notash, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, m1581.
- 22 M. C. Das, S. K. Ghosh, E. C. Sanudo and P. K. Bharadwaj, *Dalton Trans.*, 2009, 1644–1658.
- 23 H. Hamazaki, H. Hosomi, S. Takeda, H. Kataoka and S. Ohba, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 9800049.
- 24 F. Takusagawa and A. Shimada, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1976, **32**, 1925–1927.
- 25 J. R. Sander, D. K. Bučar, R. F. Henry, J. Baltrusaitis, G. G. Zhang and L. R. MacGillivray, *J. Pharm. Sci.*, 2010, **99**, 3676–3683.