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Magnesium and nickel(II) furan-2,5-dicarboxylate

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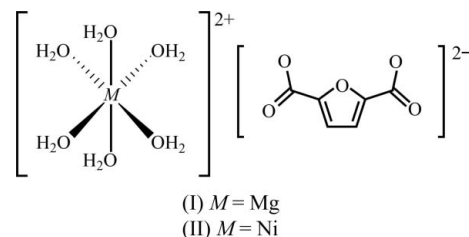
The salts hexaaquamagnesium furan-2,5-dicarboxylate, $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{O}_5)$, (I), and hexaaquanickel furan-2,5-dicarboxylate, $[\text{Ni}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{O}_5)$, (II), provide the first crystallographic characterization of the furan-2,5-dicarboxylate dianion. Both structures exhibit extensive three-dimensional hydrogen-bonding networks between the octahedral coordinated hexaaquametal(II) ions and the dicarboxylate anions. Although the two structures are not isomorphous, they contain essentially identical two-dimensional slabs. The distinction between the structures is that these slabs are related by translation in (II), whereas adjacent slabs in (I) are reflected relative to each other by the action of a glide plane. The reflection occurs so that the local contacts between slabs are not changed, and thus the hydrogen-bond networks are identical except for the orientation of the water molecules at the interface between slabs.

Comment

Furan-2,5-dicarboxylic acid (FDA) has been identified by the US Department of Energy biomass programme as one of the 12 chemicals that in the future can be used as a feedstock from biomass in biorefineries (Werpy & Petersen, 2004; Bozell & Petersen, 2010). Owing to the presence of the two carboxylic acid groups, FDA is considered to be a biorenewable building block in the formation of polymers from biomass and therefore may become an alternative to terephthalic, isophthalic and adipic acids, which are all produced from fossil fuel resources (Bozell & Petersen, 2010; Boisen *et al.*, 2009; Gorbanev *et al.*, 2011). In order to be able to use FDA as a building block for polymers, the compound must be of high purity. Herein we show that it is possible to crystallize furan-2,5-dicarboxylate as magnesium and nickel salts starting from FDA and the metal carbonates in water.

The title compounds, hexaaquamagnesium furan-2,5-dicarboxylate, (I), and hexaaquanickel furan-2,5-dicarboxylate,

(II), have the same molecular structure and the crystals are constitutionally identical. The asymmetric unit comprises one $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ cation and one furan-2,5-dicarboxylate anion. The Mg and Ni structures are illustrated in Figs. 1 and 2, respectively. The metal–water distances in the cations, as well



as the bond lengths in the dianions, are unexceptional. With $\text{Mg1}—\text{O}(\text{water})$ bond lengths of 2.0289 (7)–2.1077 (7) Å and $\text{Ni1}—\text{O}(\text{water})$ bond lengths of 2.0219 (5)–2.0840 (6) Å, all distances are approximately equal to the average bond lengths of previously characterized $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ complexes [$\text{Mg}—\text{O} = 2.06$ (2) Å and $\text{Ni}—\text{O} = 2.05$ (2) Å] in the Cambridge Structural Database (CSD; Version 5.32 of November 2010; Allen,

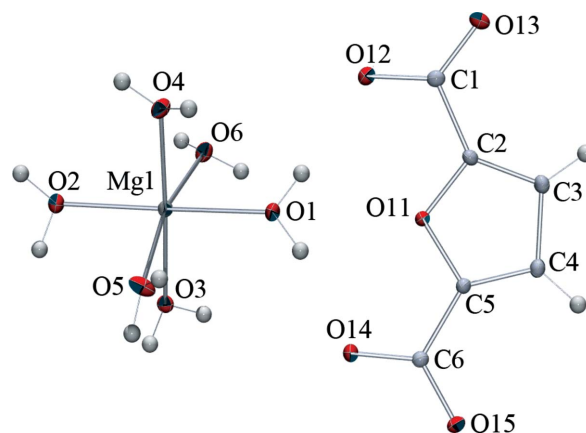


Figure 1

View of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

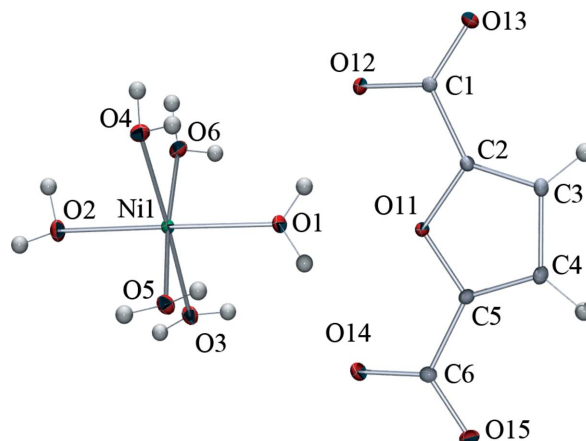


Figure 2

View of the molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

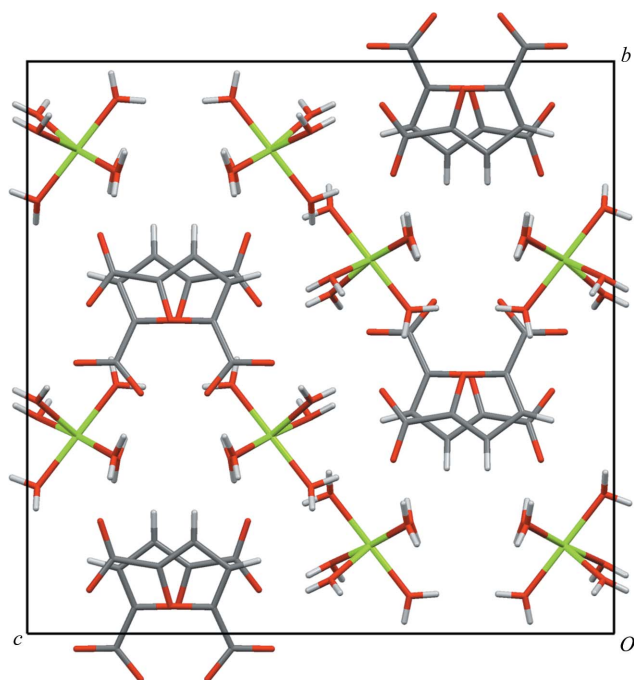


Figure 3
Packing diagram of (I), shown in projection along the *a* axis. For clarity, the extensive hydrogen-bonding network is not shown.

2002). All bond lengths in the dianions are approximately equal to the bond lengths of the parent furan-2,5-dicarboxylic acid (Martuscelli & Pedone, 1968) and also the monoanion in potassium *catena*-(2,5-dicarboxyfuran) (Jaulmes *et al.*, 1982).

The intermolecular interactions are consequently the most interesting features of the structures. The packing in both (I) and (II) is governed by an elaborate three-dimensional hydrogen-bonding scheme. The presence of both an excellent hydrogen-bond donor (aqua ion) and acceptor (dicarboxylate) should lead to strong intermolecular interactions, and in both structures the packing allows short, almost linear, O—H...O hydrogen bonds (Tables 1 and 2), consistent with strong interactions (Jeffrey, 1997). It is also in the packing that the only significant distinction between the two structures becomes apparent. In (II), the planes of all of the furan-2,5-dicarboxylate anions are parallel, whereas in (I) there exists two sets of anions where the molecular planes form an angle of $28.14(2)^\circ$ with each other.

Although the two compounds are not isomorphous, there is a very close relationship between them, which is expressed by the cell parameters: *c* in (I) [$18.579(3) \text{ \AA}$] $\simeq b$ in (II) [$18.4255(9) \text{ \AA}$], *a* in (I) [$6.6577(17) \text{ \AA}$] $\simeq c$ in (II) [$6.5942(8) \text{ \AA}$] and β in (I) = α in (II) = 90° . Consequently, the structures contain almost identical two-dimensional slabs parallel to these specified unit-cell faces. The structures appear essentially identical in projection along the *a* axis for (I) and along the *c* axis for (II) (see Figs. 3 and 4). The crystallographic repeat unit of the two-dimensional slabs corresponds to the unit-cell contents of (II) (Fig. 4). In (II), adjacent slabs are related by direct translation along the *a* axis. This gives rise to a monoclinic structure. In (I), the arrangement is such that the next slab is reflected compared to its neighbour (see Fig. 5), by

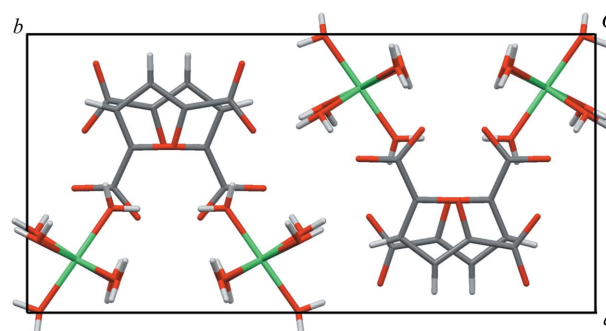


Figure 4
Packing diagram of (II), shown in projection along the *c* axis. For clarity, the extensive hydrogen-bonding network is not shown.

virtue of the glide planes lying perpendicular to the *a* axis. The reflection occurs between every slab so that the crystallographic translation encompasses two slabs and is perpendicular to the plane of the slabs. Thus, (I) is orthorhombic. The resulting relationship between the cell parameters in the two structures is: *b* axis in (I) $\simeq [2a \cos(\beta - 90^\circ)]$ in (II).

The reflection of adjacent slabs in (I) occurs so that the local contacts between layers are not changed compared to those in (II), *i.e.* the positions of the atoms in contact between layers remain essentially unchanged. Thus, the hydrogen bonding between slabs is essentially identical in the two structures. The difference is the orientation of the water molecules at the interface between slabs.

This difference in structure for these two compounds with identical composition and comparable size of the metal ion is interesting but difficult to explain. The answer might be a subtle difference in the preferred geometry of the hexa-aquametal(II) ions as a result of the different *d*-orbital configuration. The d^0 -configuration of Mg^{2+} does not impose any energetic penalty on the orientation of the coordinated water ligands compared to nickel (d^8), thus accommodating a packing which leads to a structure with higher symmetry.

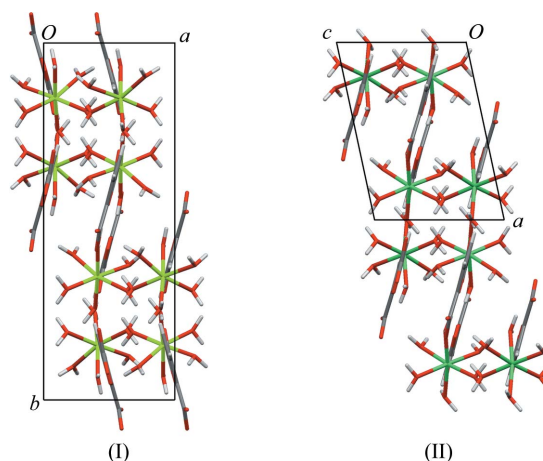


Figure 5
Packing diagrams of (I), in projection along the *c* axis, and (II), in projection along the *b* axis. In (I), the unit-cell repeat along the *b* axis encompasses two slabs, while in (II) the unit-cell repeat along the *a* axis encompasses only one slab.

Experimental

The two title compounds were prepared by an adaptation of the reported synthesis of the related compound pentaqua(furan-2-carboxylato)nickel(II) furan-2-carboxylate (Paluchowska *et al.*, 1994). Furan-2,5-dicarboxylic acid was prepared as described previously (Gorbanev *et al.*, 2009). The compound was recrystallized from warm water and precipitated with hydrochloric acid before use.

To a hot aqueous solution (10 ml) of furan-2,5-dicarboxylic acid (1 mmol, 156 mg) was added the carbonate salt of magnesium or nickel (1 mmol). The solutions were cooled to room temperature. Water was evaporated slowly at room temperature for a few days and colourless crystals of (I) or green crystals of (II) suitable for X-ray analysis were obtained. Elemental analysis found (calculated): for (I), C 24.27 (25.16), H 4.53% (4.93%); for (II), C 22.69 (22.46), H 4.30% (4.40%).

Compound (I)

Crystal data

[Mg(H ₂ O) ₆](C ₆ H ₂ O ₅)	$V = 2241.8$ (6) Å ³
$M_r = 286.48$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 6.6577$ (17) Å	$\mu = 0.21$ mm ⁻¹
$b = 18.1234$ (3) Å	$T = 122$ K
$c = 18.579$ (3) Å	$0.31 \times 0.23 \times 0.07$ mm

Data collection

Nonius KappaCCD diffractometer	107023 measured reflections
Absorption correction: integration (Coppens, 1970)	5972 independent reflections
$T_{\min} = 0.936$, $T_{\max} = 0.986$	4551 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.082$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.092$	$\Delta\rho_{\max} = 0.63$ e Å ⁻³
$S = 1.06$	$\Delta\rho_{\min} = -0.39$ e Å ⁻³
5972 reflections	
199 parameters	
12 restraints	

Compound (II)

Crystal data

[Ni(H ₂ O) ₆](C ₆ H ₂ O ₅)	$V = 1095.99$ (15) Å ³
$M_r = 320.88$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2242$ (5) Å	$\mu = 1.83$ mm ⁻¹
$b = 18.4255$ (9) Å	$T = 122$ K
$c = 6.5942$ (8) Å	$0.46 \times 0.24 \times 0.03$ mm
$\beta = 102.066$ (6)°	

Data collection

Nonius KappaCCD diffractometer	68883 measured reflections
Absorption correction: integration (Gaussian integration; Coppens, 1970)	9072 independent reflections
$T_{\min} = 0.505$, $T_{\max} = 0.950$	7619 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.060$	$\Delta\rho_{\max} = 0.73$ e Å ⁻³
$S = 1.10$	$\Delta\rho_{\min} = -0.87$ e Å ⁻³
9072 reflections	
199 parameters	
12 restraints	

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O11	0.836 (11)	2.280 (13)	2.7201 (8)	113.2 (11)
O1—H1B \cdots O12	0.849 (12)	2.051 (12)	2.8978 (9)	175.0 (12)
O1—H1A \cdots O14	0.836 (11)	1.961 (12)	2.7869 (8)	169.6 (13)
O2—H2A \cdots O15 ⁱ	0.855 (11)	1.908 (11)	2.7624 (9)	176.9 (13)
O2—H2B \cdots O3 ⁱⁱ	0.860 (11)	2.128 (12)	2.9658 (9)	164.5 (12)
O3—H3A \cdots O13 ⁱⁱⁱ	0.832 (11)	1.872 (11)	2.7011 (9)	173.8 (13)
O3—H3B \cdots O14 ⁱ	0.852 (11)	1.838 (11)	2.6756 (9)	167.3 (13)
O4—H4A \cdots O15 ^{iv}	0.839 (11)	1.884 (11)	2.7200 (9)	174.4 (13)
O4—H4B \cdots O12 ^v	0.831 (11)	2.001 (12)	2.8267 (9)	172.4 (13)
O5—H5A \cdots O14 ⁱ	0.806 (11)	2.205 (12)	2.8839 (9)	142.2 (13)
O5—H5B \cdots O13 ^v	0.845 (12)	1.906 (12)	2.7437 (10)	170.9 (14)
O6—H6A \cdots O12 ⁱⁱⁱ	0.819 (11)	2.014 (11)	2.8318 (9)	175.7 (13)
O6—H6B \cdots O15 ^{vi}	0.826 (11)	2.005 (11)	2.8096 (9)	164.5 (12)

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

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B \cdots O11	0.836 (11)	2.277 (13)	2.7107 (7)	112.7 (11)
O1—H1A \cdots O12	0.815 (11)	1.982 (11)	2.7929 (8)	173.4 (13)
O1—H1B \cdots O14	0.836 (11)	2.066 (12)	2.8929 (8)	170.2 (13)
O2—H2A \cdots O4 ⁱ	0.847 (12)	2.131 (12)	2.9510 (8)	162.9 (13)
O2—H2B \cdots O13 ⁱⁱ	0.836 (11)	1.991 (12)	2.8048 (8)	164.2 (13)
O3—H3A \cdots O13 ⁱⁱⁱ	0.816 (11)	2.032 (11)	2.8290 (8)	165.2 (13)
O3—H3B \cdots O14 ^{iv}	0.820 (11)	2.024 (11)	2.8409 (8)	174.9 (13)
O4—H4A \cdots O15 ^v	0.842 (11)	1.835 (11)	2.6766 (8)	177.1 (13)
O4—H4B \cdots O12 ⁱⁱ	0.835 (11)	1.872 (11)	2.6885 (8)	165.8 (13)
O5—H5B \cdots O13 ^{vi}	0.824 (11)	1.911 (11)	2.7325 (8)	175.1 (13)
O5—H5A \cdots O14 ^v	0.831 (11)	1.974 (11)	2.7997 (8)	172.7 (13)
O6—H6A \cdots O12 ⁱⁱ	0.831 (11)	2.065 (12)	2.8105 (8)	149.1 (12)
O6—H6B \cdots O15 ^{iv}	0.841 (11)	1.909 (11)	2.7435 (8)	172.0 (13)

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

The H atoms of the FDA anions were included in idealized positions and refined as riding, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecules were located in a Fourier map and their positions were refined with O—H distances restrained to 0.85 (2) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *OLEX2* (Dolomanov *et al.*, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3023). Services for accessing these data are described at the back of the journal.

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