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catena-Poly[hexaaquamagnesium(II) [bis(μ_3-5-nitro-2-oxidoisophthalato)-dicopper(II)] dihydrate]

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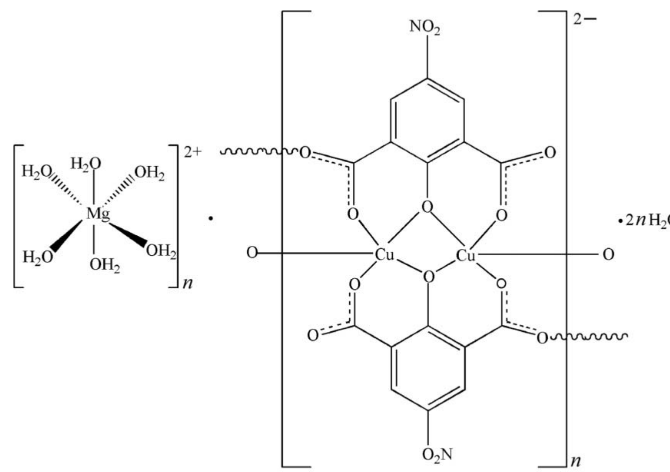
In the centrosymmetric dinuclear anions of the title bimetallic complex, $\{[Mg(H_2O)_6][Cu_2(C_8H_2NO_7)_2]\cdot 2H_2O\}_n$, each Cu^{II} ion is strongly coordinated by four O atoms in a distorted square-planar geometry. Two of these O atoms belong to phenolate groups and the other two to carboxylate groups from 5-nitro-2-oxidoisophthalate (*L*1) trianions, derived from 5-nitrobenzene-1,2,3-tricarboxylic acid (O_2N–H_3L). The phenolate O atoms bridge the two Cu^{II} ions in the anion. In addition, each Cu^{II} cation interacts weakly with a symmetry-related carboxylate O atom of an adjacent *L*1 ligand, giving a square-pyramidal coordination geometry. The copper residue forms a ladder-like linear coordination polymer *via* *L*1 ligands. The $[Mg(H_2O)_6]^{2+}$ cations sit on centres of inversion. The polymeric anions, cations and free water molecules are self-assembled into a three-dimensional supramolecular network *via* O—H···O hydrogen bonds.

Comment

The current great interest in the design and construction of functional metal–organic coordination polymers stems from their potential applications in molecular adsorption, heterogeneous catalysis, ion exchange, and magnetic and photochemical areas, and is also due to the intriguing variety of topologies they display (Zhang *et al.*, 2009; Xamena *et al.*, 2007; An *et al.*, 2009; Pan *et al.*, 2008; Zheng *et al.*, 2007; Ockwig *et al.*, 2005). Choosing the correct multifunctional ligand to link metal cations to generate novel solid-state frameworks is of vital importance (Liu *et al.*, 2002). Multicarboxylate ligands such as benzene-1,3-dicarboxylate, benzene-1,4-dicarboxylate and benzene-1,3,5-tricarboxylate have been widely used to construct metal–organic complexes with fascinating structures and potential applications (Zhou *et al.*, 2004; Wen *et al.*, 2005; Manna *et al.*, 2007; Du *et al.*, 2006; Ma *et al.*, 2009). Benzene-1,2,3-tricarboxylic acid, with its particular orientation and the strong steric hindrance of the three carboxylic acid groups, could lead to novel metal–organic complexes (Zheng *et al.*, 2004; Gutschke *et al.*, 2001) different from those constructed by other symmetric benzenecarboxylates. From a structural point of view, 5-nitrobenzene-1,2,3-tricarboxylic acid (O_2N–H_3L) possesses two interesting characteristics: (i) as a multidentate and rigid ligand with multiproton acceptor–donor sites it might be utilized as a versatile linker to construct interesting coordination polymers with abundant hydrogen bonds and π–π stacking interactions; (ii) the carboxylate groups can display a variety of bonding geometries, such as monodentate, chelating, bidentate bridging, monodentate bridging and chelating bridging. However, to the best of our knowledge, syntheses and characterization of coordination polymers based on the O_2N–H_3L ligand are still very scarce (Tan & Yi, 2010; Ding & Zhao, 2010; Ma *et al.*, 2010). Based on the above, we chose O_2N–H_3L as a multifunctional linker to construct the title novel metal–organic complex, $\{[Mg(H_2O)_6][Cu_2(L1)_2]\cdot 2H_2O\}_n$, (I), which represents the first example of a metal-based supramolecular framework constructed from the 5-nitro-2-oxidoisophthalate trianion (*L*1), where *L*1 is derived from O_2N–H_3L.



(I)

Compound (I) was obtained under hydrothermal conditions at 433 K. Once formed, the compound is insoluble in most solvents, including water. The structure is composed of $[Mg(H_2O)_6]^{2+}$ cations which sit on centres of inversion, dinuclear centrosymmetric $[Cu_2L1_2]^{2-}$ anions and free water molecules in a 1:1:2 ratio (Fig. 1).

As seen in Fig. 1, the Cu^{II} cation is primarily coordinated to four O atoms in a distorted square-planar geometry [mean Cu—O distance = 1.91 (3) Å]. Two of these O atoms belong to two phenolate groups and the other two to carboxylate groups of two *L*1 ligands. The phenolate O atoms bridge the two Cu^{II} ions in the anion. In addition, the Cu^{II} cation interacts weakly with a symmetry-related carboxylate O atom from a third *L*1 ligand with a substantially longer Cu—O bond distance of 2.379 (6) Å, giving a square-pyramidal coordination geometry

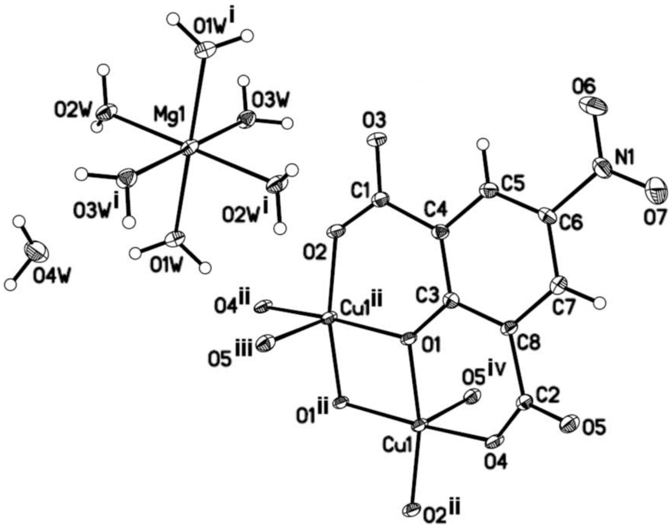


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $x + 1, y, z$.]

(Fig. 1). All Cu—O bond lengths and O—Cu—O angles are within the ranges observed in other Cu^{II} complexes (see, for example, Zheng *et al.*, 2009; Wang & Wang, 2008). The $L1$ ligands all exhibit the same coordination mode, *viz.* μ_3-bridging and chelating, to link three Cu^{II} cations. On the basis of this, atoms Cu1 and $Cu1^{ii}$ [symmetry code: (ii) $-x + 2, -y + 1, -z$] form dinuclear $[Cu_2(L1)_2]^{2-}$ units (Figs. 1 and 2) which are interconnected *via* weak Cu1···O5 interactions, resulting in one-dimensional ladder-like chains along the *a* axis.

The Mg^{II} cation, lying on an inversion centre, is surrounded by six aqua ligands [mean Mg—O distance = 2.07 (2) Å], exhibiting a slightly distorted octahedral environment. It is interesting that the $[Mg(H_2O)_6]^{2+}$ cations and free water molecules act as bridges to connect the chains into a sandwich-like three-dimensional supramolecular structure *via* a wide range of O—H···O hydrogen-bonding interactions through the nitro O atoms, the coordinated and uncoordinated carboxylate O atoms of the $L1$ ligands, and the coordinated and free water molecules (Fig. 2 and Table 1). It is worth noting that an *in situ* reaction occurs in the $CuBr_2{\cdot}2H_2O/H_3L_1/MgCl_2$ system under hydrothermal conditions. In fact, such an *in situ* reaction has previously been observed during the hydrothermal process (Zheng *et al.*, 2009; Wang & Wang, 2008). However, contrary to these earlier reports, Cu^{I} cations and insoluble cuprous oxide or other soluble cuprous compounds are not observed in compound (I). The origin of this *in situ* reaction is not yet clear, and a more in-depth study is required to understand the mechanisms for such a reaction.

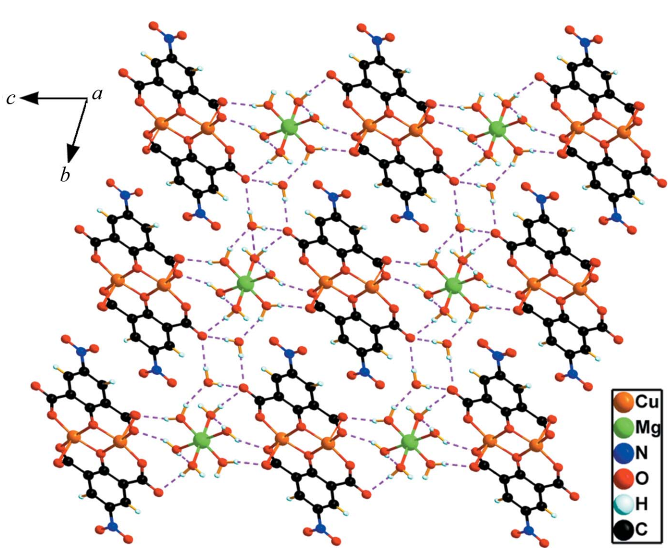


Figure 2
A view of the sandwich-like three-dimensional supramolecular structure of (I), formed *via* a wide range of O—H···O hydrogen-bonding interactions.

Experimental

A mixture of copper bromide (0.112 g, 0.5 mmol), 5-nitrobenzene-1,2,3-tricarboxylic acid (0.12 g, 0.5 mmol), magnesium chloride (0.05 g, 0.5 mmol), NaOH (0.06 g, 1.5 mmol) and H_2O (12 ml) was placed in a 23 ml Teflon reactor, which was heated to 433 K for 3 d and then cooled to room temperature at a rate of 5 K h^{-1}. The crystals obtained were washed with water and dried in air.

Crystal data

$[Mg(H_2O)_6][Cu_2(C_8H_2NO_7)_2]{\cdot}2H_2O$
M_r = 743.73
Triclinic, $P\overline{1}$
a = 5.0936 (8) Å
b = 9.8320 (13) Å
c = 12.8114 (14) Å
α = 73.952 (1)°
β = 78.679 (1)°
γ = 83.706 (2)°
V = 603.55 (14) $Å^3$
Z = 1
Mo $K\alpha$ radiation
μ = 1.90 mm^{-1}
T = 298 K
0.41 × 0.14 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.746, T_{max} = 0.839
3113 measured reflections
2082 independent reflections
1799 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.03
2082 reflections
196 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.67 e $Å^{-3}$

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O4W	0.85	1.97	2.774 (9)	158
O1W—H2W···O5^{i}	0.85	1.96	2.802 (8)	170
O2W—H3W···O3W^{ii}	0.85	2.04	2.857 (8)	162
O2W—H4W···O4^{iii}	0.85	1.99	2.787 (8)	155
O3W—H5W···O3	0.85	1.88	2.728 (8)	174
O3W—H6W···O6^{iv}	0.85	2.24	3.058 (10)	163
O4W—H7W···O3^{v}	0.85	2.17	3.002 (10)	165
O4W—H8W···O3^{vi}	0.85	1.99	2.829 (9)	171

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

Carbon-bound H atoms were placed at calculated positions and treated as riding on their parent C atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the aqua ligands and the water molecule were located in a difference Fourier map and refined as riding on their parent atoms with their O—H distances optimized to 0.85 Å and with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GT3029). Services for accessing these data are described at the back of the journal.

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