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# A Self-assembling Trinuclear Molecular Complex of Nickel(II) with Benzene-1,3,5-tricarboxylic Acid

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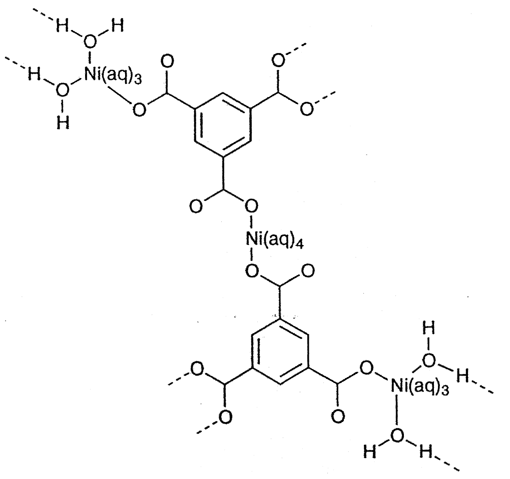
$[Ni_3(trim)_2(H_2O)_{14}]\cdot 4H_2O$ (trim = trimesate trianion), a self-complementary molecule organised in tapes using aqua ligands as hydrogen bond donors and carboxylate groups as hydrogen bond acceptors, is synthesised and the structure confirmed by X-ray crystallography.

The relative positions of the three carboxylic groups in benzene-1,3,5-tricarboxylic acid (trimesic acid) make this molecule an interesting multifunctional ligand capable, in principle, of forming infinite metal–organic structures. Coordination polymers with interesting physical properties, based on this ligand have been recently obtained by Yaghi *et al.*[3] and Wood *et al.*[4] However, here we show that $[Ni_3(trim)_2(H_2O)_{14}]4H_2O$ (trim = trimesate trianion) **1**, is an unusual molecular solid, formed when $Ni^{2+}$ cations interact with trimesic acid.



**1**

Crystals suitable for X-ray analysis were formed by using a double diffusion silica gel method.[5] An aqueous solution of 0.03 M $Ni(NO_3)_2$ was allowed to diffuse in a gel column (pH = 6) in contact with a second gel column containing trimesic acid at pH = 6. The aqueous phase was allowed to evaporate slowly and well formed green prismatic crystals were collected from the top of the first gel after *ca.* five months. The stoichiometric formula of the obtained crystals was based on X-ray crystallography. The molecular structure of **1** is shown in Fig. 1.

*Crystal data for* **1**. $C_{18}H_{42}O_{30}Ni_3$, triclinic, $P\bar{1}$, $a = 6.698(3)$, $b = 10.771(4)$, $c = 12.323(5)$ Å, $\alpha = 73.342(9)°$, $\beta = 77.76(1)°$, $\gamma = 71.76(1)°$, $V = 801.6(6)$ Å$^3$, $Z = 1$ (the asymmetric unit is half of the molecule), $\rho_{calcd} = 1.895$ g cm$^{-3}$, $\lambda(MoK\alpha) = 0.71073$ Å, 3061 independent reflections, 2680 observed $[I > 2\sigma(I)]$, $R_1 = 0.0249$, $wR_2 = 0.0623$. $R_1$ is based on $f$ values and $wR_2$ on $F^2$ values. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-93.

Each trimesate anion acts as a bidentate ligand, leaving one carboxylate group free. The two coordinating carboxylate groups bind the metal atoms in a monodentate mode. The 'central' $Ni^{2+}$ atom is located on a crystallographic inversion centre and therefore the three octahedral metal centres are strictly in a straight line 8.036(1) Å apart. Intramolecular hydrogen bonds are observed between coordinated water ligands and the 'free' oxygen atoms belonging to the coordinating groups, offering an example of simultaneous first and second coordination spheres.[6]

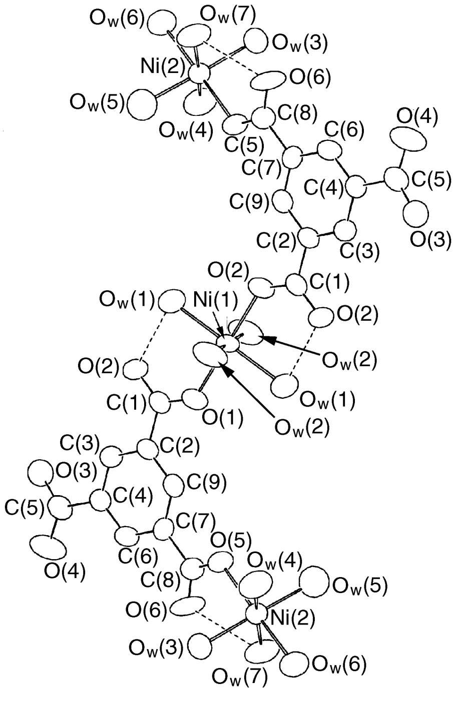
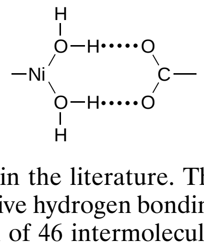


**Fig. 1** Molecular structure of **1**

At first glance, it is surprising that a molecular solid results from the interaction of $Ni^{2+}$ with trimesic acid, but inspection of the crystal packing reveals, in our opinion, the reason for this preference (Fig. 2). Each molecule behaves as a self-complementary building unit, possessing two hydrogen bond donor $[Ni(H_2O)_2]$ and two hydrogen bond acceptor (COO) groups, symmetrically disposed. In these conditions, the formation of infinite tapes, by strict self-assembly, through mutual recognition of the complementary groups, seems inevitable[7] [Scheme 1(*c*), see full text]. In total, eight hydrogen bonds [OW5···O3 = 2.637(3), OW6···O4 = 3.129(3) Å], are used by each molecule for the construction of the tape. To the best of our knowledge, this is the first time that the supramolecular synthon[8]



has been reported in the literature. The structure is further stabilised by extensive hydrogen bonding, each molecule participating in a total of 46 intermolecular bonds. In this way,

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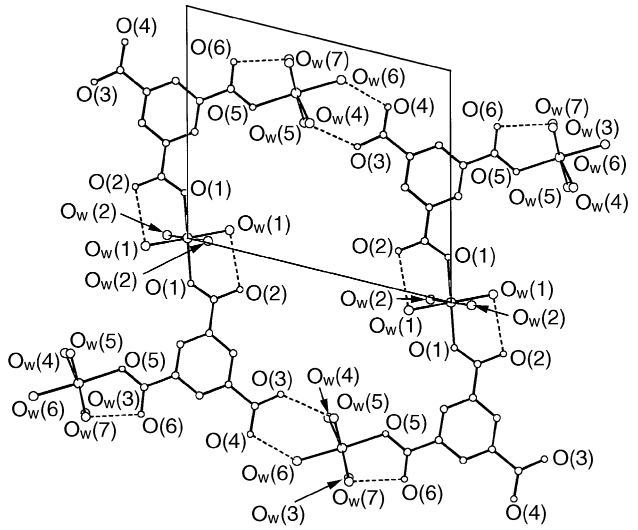

**Fig. 2** View of an infinite tape along the *a* axis. Lattice water molecules are omitted for clarity

each tape is linked to six neighbouring tapes both directly and *via* bridging lattice water molecules [Fig. 3 (full text)].

The existence of numerous hydrogen bond sites accounts for the solubility of this compound in water and solute–solvent interactions,[9] impose a high barrier for nucleation and crystal growth. Crystallisation is certainly due to strong $\pi$–$\pi$ interactions, observed in the direction of the crystallographic *a* axis (Fig. 3). Each aromatic ring lies between two others with plane-to-plane distances of 3.28 and 3.35 Å and lateral offsets of 1.56 and 2.05 Å, respectively. These hydrophobic interactions decrease the nucleation barrier and lead to successful crystal growth.

Techniques used: Crystal growth in gel, X-ray diffraction

References: 9

Tables: 5 [Full crystal data, atomic fractional coordinates and *U*(eq) values, bond distances and angles, geometry of the hydrogen bonds]

Figures: 4 (Molecular structure, views of the structure along the *a* and *c* axes)

Scheme 1: Structures of trimesic acid and **1**. Tape molecular arrangement of **1**

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