

Triple hydrogen bond directed crystal engineering of metal assembled complexes: the effect of a bifunctional ligand on supramolecular structure

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The crystal structures of compounds $[\text{Hmel}]_2[\text{M}(\text{tdpd})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{2+}$, Co^{2+} ; $\text{Hmel}^+ =$ melaminium cation; $\text{H}_2\text{tdpd} = 1,4,5,6$ -tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile) are reported; the metal complex supramolecular structures can be rationally designed *via* hydrogen bonding interactions.

Crystal engineering has become an area of great interest in this decade.¹ So far, however, the rational design and preparation of new materials for specific applications are still at an early evolutionary stage with the current focus mainly on understanding the factors that determine crystal packing. During the last few years, several types of weak interactions, such as versatile hydrogen bonding interactions and electrostatic interactions have been recognized and used in constructing extended networks.² Particularly, the hydrogen bonding interaction has emerged to be a powerful tool for the design of supramolecular systems based on noncovalent synthesis.^{3,4} Although many research groups have focused on the usage of melamine (mel) and its derivatives⁵ to form supramolecular networks by hydrogen bonding to other organic molecules, the concepts have recently been extended into the inorganic domain.^{6,7} Transition metal ions can be incorporated into hydrogen bonding networks by employing bifunctional ligands that contain, in addition to metal binding sites, hydrogen bonding functionalities that are retained on complexation.

Tdpd^{2-} ($\text{H}_2\text{tdpd} = 1,4,5,6$ -tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile) has attracted our interest as a potential bifunctional ligand with necessary hydrogen bonding characteristics. We have previously shown that it can construct metal-assembled complexes with triangular and rectangular lattices by coordination bonds.⁸ Tdpd^{2-} is a planar ligand and has both multi metal binding and hydrogen bonding sites. We now present the synthesis and structural study of the two-dimensional compounds $[\text{Hmel}]_2[\text{M}(\text{tdpd})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{2+}$ (**1**), Co^{2+} (**2**)).

An aqueous solution (1 ml) of nickel(II) chloride hexahydrate (5 mmol l^{-1}) and H_2tdpd (5 mmol l^{-1}) was transferred to a glass tube, then an ethanolic solution of melamine (mel) (5 mmol l^{-1}) poured into the tube without mixing the two solutions. Light green plate crystals (**1**) began to form in two weeks; yield, 70%.[†] One of these crystals was used for X-ray

crystallography. Compound **2** was synthesized from cobalt(II) acetate tetrahydrate by a procedure similar to that employed for **1**. Orange plate crystals began to form in two weeks; yield, 60%.[†]

X-ray crystallography reveals that **1** and **2** are isostructural to each other (Table 1). The structure of **1** consists of mononuclear $[\text{Ni}(\text{tdpd})_2(\text{OH}_2)_2]^{2-}$ dianions, Hmel^+ cations and uncoordinated water molecules. An ORTEP⁹ drawing of the structure around the nickel ion in **1** with the atom numbering scheme is shown in Fig. 1. The structure of **1** shows that the desired coordination and aggregation have been

Table 1 Crystal data for $[\text{Hmel}]_2[\text{M}(\text{tdpd})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{2+}$ (**1**), Co^{2+} (**2**))^a

Properties	Values
Complex	1 ^b 2 ^c
Empirical formula	$\text{C}_{18}\text{H}_{22}\text{NiN}_{20}\text{O}_8$ $\text{C}_{18}\text{H}_{22}\text{CoN}_{20}\text{O}_8$
<i>M</i>	705.20 705.43
Crystal system, space group	Triclinic, \bar{P} (no. 2) Triclinic, \bar{P} (no. 2)
<i>a</i> /Å	9.5650(3) 9.517(3)
<i>b</i> /Å	9.6958(6) 9.654(4)
<i>c</i> /Å	9.9663(3) 9.964(1)
α /°	61.490(4) 61.68(2)
β /°	75.585(3) 75.91(2)
γ /°	62.714(4) 63.62(2)
<i>V</i> /Å ³	721.28(7) 721.3(4)
<i>Z</i> , <i>D</i> _c /g cm ⁻³	1, 1.623 1, 1.624
<i>F</i> (000)	362.00 361.00
<i>R</i> _{collected} [<i>I</i> > 2σ(<i>I</i>)]	3113 3629
<i>T</i> /°C	23.0 23.0
2θ range/°	5.18–148.66 3–55
<i>R</i> , <i>wR</i> 2	0.039, 0.115 0.057, 0.142

^aClick here for full crystallographic data (CCDC no. 1350/38).

^b $\mu(\text{CuK}\alpha) = 17.05 \text{ cm}^{-1}$ (graphite monochromated). An Enraf Nonius CAD-4 diffractometer was used. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-93).¹¹ ^c $\mu(\text{MoK}\alpha) = 6.77 \text{ cm}^{-1}$ (graphite monochromated). A Mac Science MXC3 diffractometer was used. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-93).

[†]Elemental analysis data for $[\text{Hmel}]_2[\text{Ni}(\text{tdpd})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$: calc. for $\text{C}_{18}\text{H}_{22}\text{NiN}_{20}\text{O}_8$: C 30.66, H 3.14, N 39.73%; found: C 30.32, H 3.17, N 40.19%; elemental analysis data for $[\text{Hmel}]_2[\text{Co}(\text{tdpd})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$: calc. for $\text{C}_{18}\text{H}_{22}\text{CoN}_{20}\text{O}_8$: C 30.65, H 3.14, N 39.71%; found: C 30.16, H 3.10, N 39.90%.

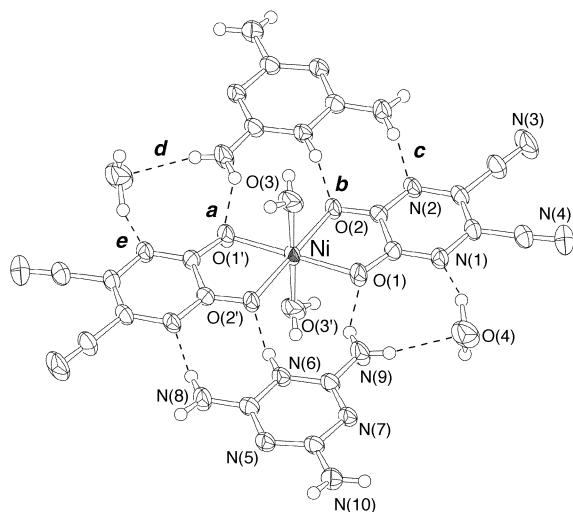


Fig. 1 ORTEP drawing of **1** with labelling scheme and thermal ellipsoids at the 50% probability level for Ni, O, N, and C atoms. Spheres of the hydrogen atoms have been arbitrarily reduced. Hydrogen bonding geometries: N \cdots N/O, H \cdots N/O distances (Å), N/O–H \cdots N/O angles (°): *a* 2.762(4), 1.96, 152; *b* 2.803(3), 1.97, 170; *c* 2.907(3), 2.02, 175; *d*, 2.919(3), 2.14, 162; *e*, 2.988(4), 1.93, 158. Click image or here to access a 3D representation.

achieved with the nickel atom being coordinated to two tdpd^{2-} ligands which are in turn involved in an AAA \equiv DDD (A=hydrogen-bond acceptor, D=hydrogen-bond donor) arrangement with Hmel^+ cations. The coordination geometry around the nickel ion in the monomer is a distorted octahedron involving the four oxygen atoms of two tdpd^{2-} anions and two

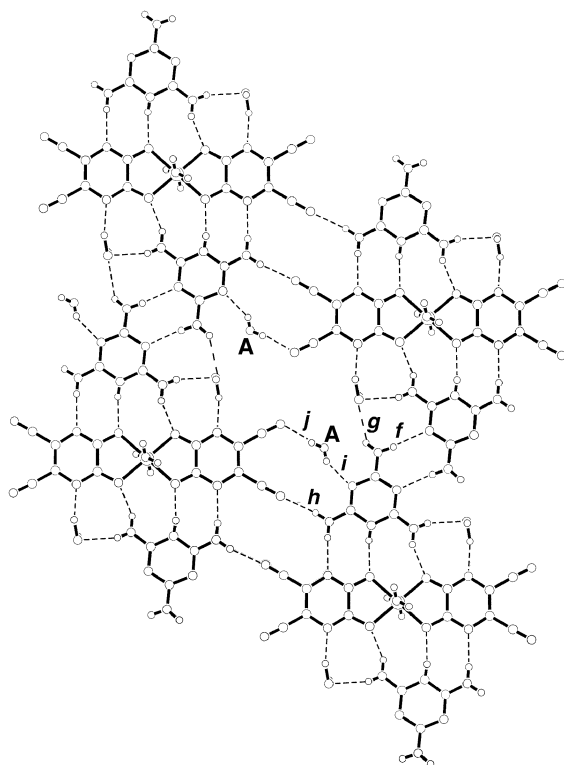


Fig. 2 Part of the hydrogen-bonded planar sheets formed by **1** showing the intermolecular interactions between adjacent module. Hydrogen bonding geometries: N \cdots N/O, H \cdots N/O distances (Å), N/O–H \cdots N/O angles (°): *f* 3.022(2), 2.13, 171; *g* 3.053(4), 2.38, 132; *h* 3.032(4), 2.18, 161; *i* 2.855(3), 2.18, 147; *j* 2.947(3), 2.16, 176. **A** represents the region where the coordinated water oxygen atom O(3) from adjacent sheets inserts from above and below. Click image or here to access a 3D representation.

water molecules in *trans* position relative to one another (Ni–O distances: 2.008(1) Å (Ni–O(1) and Ni–O(1')), 2.046(2) Å (Ni–O(2) and Ni–O(2')) and 2.110(2) Å (Ni–O(3) and Ni–O(3'))). The triple hydrogen bonding distances between the tdpd^{2-} and Hmel^+ units are O(1') \cdots N(9'), 2.762(4) Å; O(2) \cdots N(6'), 2.803(3) Å; N(2) \cdots N(8'), 2.907(3) Å (*a*, *b* and *c*, respectively, in Fig. 1). These complexes, to the best of our knowledge, are the first example of an AAA \equiv DDD system in the self assembled complexes, while theoretical calculations suggested the system AAA \equiv DDD is the most stable relative to ADA \equiv DAD and AAD \equiv DDA systems.^{6,10} One mononuclear complex, two Hmel^+ cations, and two uncoordinated waters form a building module. In the module, uncoordinated water molecules make two types of hydrogen bonds with ring nitrogen atoms of tdpd^{2-} and amino hydrogen atoms in Hmel^+ cation (*d* and *e* in Fig. 1). The triply hydrogen-bonded module, $[\text{Hmel}]_2[\text{Ni}(\text{tdpd})_2(\text{OH}_2)_2]\cdot 2\text{H}_2\text{O}$ is linked to adjacent modules *via* additional N(H) \cdots N and N(H) \cdots O hydrogen bonds (*f*, *g* and *h* in Fig. 2) to form planar sheets. Adjacent sheets are mutually offset and linked *via* O(H) \cdots N hydrogen bonds between terminal nitrogen atoms of tdpd^{2-} , N(4), and coordinated water oxygen atoms, O(3), which are inserted from above and below into the 'vacant' region indicated by **A** in Fig. 2.

We conclude that hydrogen bonding interaction may play an important role in determining the structure of assembled complexes. Complexes $[\text{M}(\text{tdpd})_2(\text{OH}_2)_2]^{2-}$ with AAA hydrogen bonding recognition sites have been synthesized and shown to form co-crystals with Hmel^+ cations involved DDD motif. The ligand H_2tdpd fulfils its bifunctional role by generating a transition-metal complex as part of a multidimensional co-crystallised network, self-assembled by a combination of coordination and hydrogen bond formation. We are now extending this result by the preparation of the design of supramolecular systems based on noncovalent synthesis through variation of substituted melamine derivatives.

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