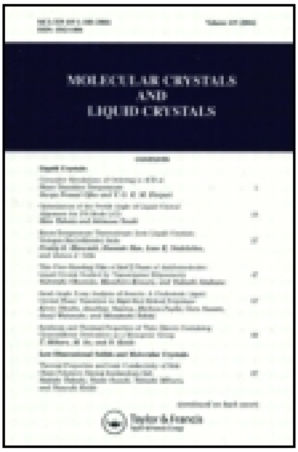

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Triple Hydrogen Bond Directed Crystal Engineering of Metal Assembled Complexes: The Effect of a Novel Organic-Inorganic Module on Supramolecular Structure

Yuichi Sugiyama [a] , Keiichi Adachi [c] , Md. Khayrul Kabir [a] , Susumu Kitagawa [b] , Takayoshi Suzuki [c] , Sumio Kaizaki [c] & Satoshi Kawata [d]

[a] Department of Chemistry, Shizuoka University, 836 Ohya, Shizuoka, 422-8529, Japan

[b] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan

[c] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[d] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan E-mail:

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YUICHI SUGIYAMA[a], KEIICHI ADACHI[c],
MD. KHAYRUL KABIR[a], SUSUMU KITAGAWA[b],
TAKAYOSHI SUZUKI[c], SUMIO KAIZAKI[c]
and SATOSHI KAWATA*[c]

[a]*Department of Chemistry, Shizuoka University, 836 Ohya, Shizuoka, 422-8529, Japan,*
[b]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan and*
[c]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan*
(E-mail: kawata@chem.sci.osaka-u.ac.jp)

The new manganese(II) and zinc(II) triply hydrogen-bonded complexes $[Hmel]_2[M(tdpd)_2(OH_2)_2]\cdot 2H_2O$ (M = Mn^{2+} (**1**), Zn^{2+} (**2**); $Hmel^+$ = melaminium cation; H_2tdpd = 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile) have been synthesized and characterized. These complexes are isostructural as revealed by their single crystal structure analyses. Both the compounds are composed of triply hydrogen-bonded module of the AAA ≡ DDD system.

Keywords: triple hydrogen bonding; manganese; zinc

INTRODUCTION

In the last few years there has been a surge of research activity in the development of new solid-state structure which involve the self-assembly of molecules into well-defined supramolecules *via* noncovalent, multiple intermolecular interactions[1]. Strong, selective, and directional hydrogen bonding has been noted as a most powerful organizing force in molecular assembly, and the vast majority of publications and reviews have been devoted to the self-organization of organic molecules into one-, two- or three-dimensional hydrogen-bonded architectures[2,3]. We have previously shown how the construction of assembled metal complexes based on triple hydrogen bonding resulted in the crystal engineering of aggregates based on bifunctional transition-metal complexes and organic molecules containing complementary arrangements of hydrogen bond donors and acceptors[4]. The extension of this chemistry would afford new materials if the common structures are constructed by other metals. This system is of great interest because the incorporation of transition-metal ions into such systems introduce optical and electric properties characteristic of these ions into materials with potential for nonlinear optical[5] and ferroelectric properties[6].

The $tdpd^{2-}$ (H_2tdpd = 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. $Tdpd^{2-}$ is a planar ligand and has both multi metal binding and hydrogen bonding sites[7,8]. We now present the synthesis and structural study of the two-dimensional compounds $[Hmel]_2[M(tdpd)_2(OH_2)_2]\cdot 2H_2O$ (M = Mn^{2+} (**1**), Zn^{2+} (**2**)).

EXPERIMENTAL

An aqueous solution (1 ml) of manganese(II) acetate tetrahydrate (5 $mmol\cdot l^{-1}$) and H_2tdpd (5 $mmol\cdot l^{-1}$) was transferred to a glass tube, then an ethanolic solution of melamine (mel) (5 $mmol\cdot l^{-1}$) poured into the tube without mixing the two solutions. Yellow plate crystals (**1**) began to form in two weeks. One of these crystals was used for X-ray crystallography. Compound **2** was synthesized from zinc acetate dihydrate by a procedure similar to that employed for **1**. Colorless plate crystals began to form in two weeks. Details of the X-ray experiments and crystal data for the two complexes in Table 1.

TABLE 1. Crystallographic Data for $[Hmel]_2[M(tdpd)_2(OH_2)_2]\cdot 2H_2O$[a]

Complex	**1**	**2**
Empirical formula	$C_{18}H_{22}MnN_{20}O_8$	$C_{18}H_{22}ZnN_{20}O_8$
Crystal system, space group	Triclinic, $P\bar{1}$ (no. 2)	Triclinic, $P\bar{1}$ (no. 2)
a / Å	9.4404(5)	9.661(2)
b / Å	9.6317(5)	10.019(2)
c / Å	9.9861(7)	9.569(2)
α / degree	61.495(2)	104.23(1)
β / degree	80.895(4)	116.89(1)
γ / degree	94.921(2)	61.74(1)
V / Å^3	721.60(8)	726.6(3)
Z	1	1
R, wR_2	0.028, 0.106	0.040, 0.135

[a] A Rigaku R-AXIS RAPID Imaging Plate System and a Rigaku AFC7R four circle diffractometer was used for **1** and **2**, respectively. The structures of **1** and **2** were solved by direct methods (Rigaku Crystal Structure crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-97)[11].

RESULTS AND DISCUSSION

X-ray crystallography reveals that **1** and **2** are isostructural to that of $[Hmel]_2[M(tdpd)_2(OH_2)_2]\cdot 2H_2O$ (M = Ni, Co)[4]. The structure of **1** consists of mononuclear $[Mn(tdpd)_2(OH_2)_2]^{2-}$ dianions, $Hmel^+$ cations and uncoordinated water molecules. An ORTEP[12] drawing of the structure around the manganese ion in **1** with the atom numbering scheme is shown in Figure 1. The structure of **1** shows that the desired coordination and aggregation have been achieved with the manganese atom being coordinated to two $tdpd^{2-}$ anions which are in turn involved in AAA ≡ DDD (A = hydrogen bond acceptor, D = hydrogen-bond donor) type of hydrogen bonding arrangement with $Hmel^+$ cations. The coordination geometry around the manganese ion in the monomer is a distorted octahedron involving the four oxygen atoms of two $tdpd^{2-}$ anions and two water molecules in *trans* position

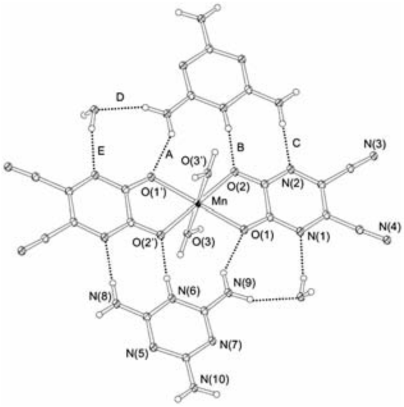

FIGURE 1 ORTEP drawing of **1** with labeling scheme and thermal ellipsoids at the 50% probability level for Ni, O, N, and C atoms. Spheres of the hydrogen atoms have been arbitrarily reduced. Hydrogen bonding geometries: N···N/O, H···N/O distances (Å), N/O-H···N/O angles (°): A 2.809(1), 2.01, 144; B 2.775(1), 1.89, 175; C 2.922(2), 2.02, 179; D, 2.873(1), 2.01, 160; E, 2.988(2), 2.17, 169.

relative to one another (Mn-O distances: 2.1308(8) Å (Mn-O(1) and Mn-O(1')), 2.1675(8) Å (Mn-O(2) and Mn-O(2')) and 2.213(1) Å (Mn-O(3) and Mn-O(3'))). The triple hydrogen bonding distances between the $tdpd^{2-}$ and $Hmel^{+}$ units are O(1)···N(9), 2.809(1) Å; O(2')···N(6), 2.775(1) Å; N(2')···N(8), 2.922(2) Å (A, B and C, respectively, in Figure 1). 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 Figure 1). Triply hydrogen-bonded network of anionic complex with $Hmel^{+}$ cations and water molecules form the building module. This module, is linked to adjacent modules *via* additional N(H)···N and N(H)···O hydrogen bonds (F, G and H in Figure 2) to form planar sheets[13]. Adjacent sheets are mutually offset and linked *via* O(H)···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 K in Figure 2. These complexes

$[Hmel]_2[M(tdpd)_2(OH_2)_2]\cdot 2H_2O$ (M = Ni, Co, Mn, Zn), to the best of

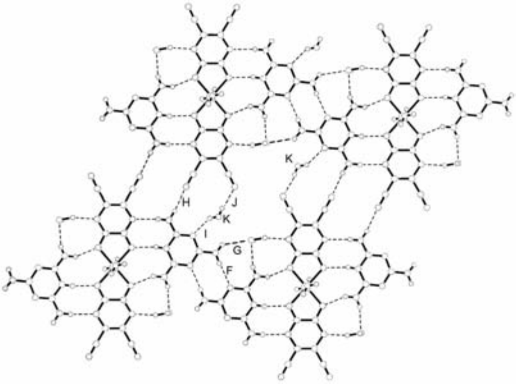

FIGURE 2 Part of the hydrogen-bonded planar sheets formed by **1** showing the intermolecular interactions between adjacent module. Hydrogen bonding geometries: N···N/O, H···N/O distances (Å), N/O-H···N/O angles (°): F 3.029(1), 2.10, 173; G 3.010(1), 2.35, 129; H 3.030(1), 2.17, 172; I 2.803(1), 1.96, 159; J 2.907(2), 2.05, 171. K represents the region where the coordinated water oxygen atom O(3) from adjacent sheets inserts from above and below.

our knowledge, are the first example of AAA ≡ DDD system in the self assembled complexes, while theoretical calculations[9] and experimental data[10] indicated that the hydrogen bonding interactions between two molecules where all of the acceptor sites (A) are localized on one component and donor sites (D) on the second (*i.e.* AAA ≡ DDD) are stronger than those where the acceptor donor sites are distributed between the two molecules (*i.e.* ADA ≡ DAD, AAD ≡ DDA).

CONCLUSION

This research has demonstrated that complementary triple hydrogen bonds (AAA ≡ DDD) can form the basis of a design concept leading to the formation of metal containing hydrogen-bonded module. Furthermore, although the metal ions are changed in the four compounds, the common hydrogen-bonded modules are constructed throughout the crystal structure. The ligand H_2tdpd fulfils its bifunctional role by generating a transition-metal complex as part of a multidimensional co-crystallized network, self-assembled by a combination of coordination and hydrogen bond formation. We are now extending this result by the preparation of supramolecular systems based on noncovalent synthesis through variation of substituted melamine derivatives.

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