

Two different coordination dimers of pyromellitic acid in terms of molecular geometry and supramolecular architecture

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ABSTRACT

Two mixed-ligand coordination dimers, $[\text{Ni}_2(\text{pm})(\text{ina})_2(\text{H}_2\text{O})_4]$ (**1**) and $[\text{Mn}_2(\text{Hpm})_2(\text{ina})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**2**) (pm = tetraanion of pyromellitic acid, Hpm = trianion of pyromellitic acid and ina = isonicotinamide), were comparatively investigated by focusing on their supramolecular architectures. Their structural properties were characterized by X-ray diffraction technique (XRD) and Fourier transform infrared spectroscopy (FT-IR). In **1**, each pm^{4-} anion adopts μ_2 -bridging mode to connect two Ni(II) ions through carboxylate groups while in **2** Hpm³⁻ anion bridges Mn(II) ions with tridentate coordination mode of carboxylate groups in *cis* positions. In **1**, 1D H-bonded linear chain consists of $R_2^2(8)$ synthons. Linear chains are inter-connected by O–H...O bonds with DA:AD type organization of aqua ligands, resulting in $R_4^4(8)$ synthons to form 2D structure. The increase in the dimensionality of the network is achieved by the involvement of aqua ligands in H-bonds with DD:AA fashion. In **2**, the amide group of ina ligand and the aqua ligand involve in DD:AA type H-bond with COO^- group of Hpm³⁻ in the formation of ribbon structure. The ribbon structures are inter-connected by H-bonds between the aqua ligands and carboxylate groups, forming 2D supramolecular sheet through $R_2^2(4)$ synthons. Unlike the case of **1**, the pyridinium plays an important role to form 3D network of **2** by connecting 2D sheets through $R_2^2(22)$ and $R_4^4(30)$ synthons. The FT-IR investigation of the complexes was performed within the mid-IR region, mainly focusing on the characteristic vibrations of pyromellitic acid and isonicotinamide moieties by considering their free states and ligand behavior in the case of complex formation.

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1. Introduction

The potential applications of supramolecular structures in catalysis, optics, sensors, magnetism and molecular recognition [1–8] draw current attentions to the construction of supramolecular architectures. Non-covalent interactions are indispensably used to arrange molecular building blocks in the crystal engineering of supramolecular architectures [9–11]. Previously, we investigated the role of non-covalent hydrogen bond, C–H... and cation... π interactions in the construction of supramolecular networks [12–14]. Currently, we use polycarboxylic acids in our studies to benefit from their properties which are very useful in the construction of supramolecular networks. These properties are as

follows: Polycarboxylic acids have carboxyl groups (COOH) which can be fully or partially deprotonated. This makes a variety of coordination mode possible for the formation of metal-organic complexes. Moreover, polycarboxylates are both H-bond donors and acceptors with their COOH and/or the COO^- groups. Therefore, the possibility of inter-molecular H-bond interaction to form higher dimensional networks in the metal-organic complexes increases [15–20]. In this study, we have used pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) as a member of aromatic polycarboxylic acids. Using its quadruply and triply deprotonated forms (pm, Hpm), two coordination dimers, $[\text{Ni}_2(\text{pm})(\text{ina})_2(\text{H}_2\text{O})_4]$ (**1**) and $[\text{Mn}_2(\text{Hpm})_2(\text{ina})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**2**), were synthesized by conventional methods. The structural properties of the complexes were characterized by XRD technique and FT-IR spectroscopy. The complexes were investigated comparatively by considering their differences (molecular geometries and supramolecular architectures) arising from different bonding mode, protonation and deprotonation states of the ligands.

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2. Experimental

2.1. Synthesis

The aqueous solution (35 ml) of H_4pm (2 mmol, 0.52 g) was added slowly to the aqueous solution (20 ml) of NaOH (8 mmol, 0.32 g) with stirring. Then, the solution of $NiCl_2 \cdot 6H_2O$ in methanol/water (4 mmol, 0.95 g) was added drop wise. The aqueous solution (30 ml) of *ina* (4 mmol, 0.49 g) was added slowly with stirring. The final solution was heated to $\sim 60^\circ C$ with stirring for 1 h, then filtered and left for crystallization at ambient temperature. Blue single crystals of **1** were obtained in 67% yields within two weeks. A similar procedure to that of **1** was followed to synthesize **2**, but using NaOH (6 mmol, 0.24 g). Yellow colored single crystals of **2** were obtained in 58% within two weeks.

2.2. Materials and instrumentation

All reagents were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded in mid-IR region ($4000\text{--}400\text{ cm}^{-1}$) with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets. XRD data were collected at 296 K with a Stoe IPDS diffractometer using graphite monochromatic MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved by direct methods using the program SHELXS97 [21]. All non-hydrogen atoms were refined anisotropically by full matrix least-squares methods [21]. WinGX [22], ORTEP-3 for Windows [23]

and MERCURY [24] softwares were used for molecular drawings and other materials. Crystal data and structure refinement parameters of the complexes are given in Table 1.

3. Results and discussion

3.1. Crystal structure of $[Ni_2(pm)(ina)_2(H_2O)_4](1)$

In complex **1**, each pm^{4-} anion adopts a μ_2 -bridging mode to connect two Ni(II) ions through its carboxylate O atoms, forming $[Ni_2(pm)]$ units with the shortest distance of 11.401 Å between the Ni(II) centers (Fig. 1). The bridging carboxylate groups are *trans*-disposed in benzenetetracarboxylate ligand. The geometric values describing the coordination polyhedron of Ni(II) ion correspond to an ideal octahedron (Table 2). Four O atoms of aqua ligands occupy the equatorial positions of the octahedron while there are O and N atoms of pyromellitate ion and *ina* ligand in axial positions, respectively. The geometric parameters related to the coordination geometry of Ni(II) ions are compared with those of $Ni(H_2O)_5(\mu-C_6H_2(COO)_4)Ni(H_2O)_5 \cdot 6H_2O$ [19], $[Ni_2(C_{10}H_2O_8)(C_{10}H_9N_3)_2(H_2O)_6] \cdot 4H_2O$ [25] in Table 2. The intra-ligand bond distances of pm^{4-} and *ina* ligands are in expected range. However, the bridging and uncoordinated carboxylate groups in pm^{4-} are significantly twisted with respect to the phenyl ring plane. This is evident from the dihedral angles of 45.7° and 55.1° between the planes defined by each groups and from relevant torsion angles $[O1-C1-C2-C3 = 45.02(2)^\circ, O2-C1-C2-C3 = -136.45(16)^\circ, O3-C5-C2-C4 = 45.02(2)^\circ, O2-C1-C2-C3 = -136.45(16)^\circ, O3-C5-C2-C4 = 45.02(2)^\circ, O2-C1-C2-C3 = -136.45(16)^\circ, O3-C5-C2-C4 = 45.02(2)^\circ]$.

Table 1
Crystallographic data and structure refinement parameters for **1** and **2**.

	$[Ni_2(pm)(ina)_2(H_2O)_4]$	$[Mn_2(Hpm)_2(ina)_2(H_2O)_2] \cdot H_2O$
Empirical formula	$C_{22}H_{30}N_4O_{18}Ni$	$C_{16}H_{13}N_2O_{12}Mn$
Formula weight	755.92	480.22
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Crystal color	blue	yellow
Crystal size (mm)	$0.57 \times 0.26 \times 0.09$	$0.53 \times 0.413 \times 0.190$
Temperature (K)	293	293
a, b, c (Å)	8.1797(7), 10.1610(9), 10.2477(9)	7.4425(4), 11.7259(6), 12.5700(7)
α, β, γ ($^\circ$)	66.506(6), 72.930(7), 66.088(6)	62.478(4), 75.465(4), 76.919(4)
Volume (Å ³)	705.18(11)	933.89(9)
Z	1	2
μ (Mo K_α) (mm^{-1})	1.43	0.78
D_{calc} ($g \cdot cm^{-3}$)	1.780	1.708
F(000)	390	488
θ Range ($^\circ$)	2.6–27.0	2.9–26.9
Measured reflections	7224	17,394
Independent reflections	3052	3929
R_1, wR_2	0.025, 0.062	0.040, 0.078
Goodness-of-fit on F^2	1.06	1.11
$\Delta\rho_{max}, \Delta\rho_{min}$ ($e \text{ \AA}^{-3}$)	0.46, -0.23	0.74, -0.64

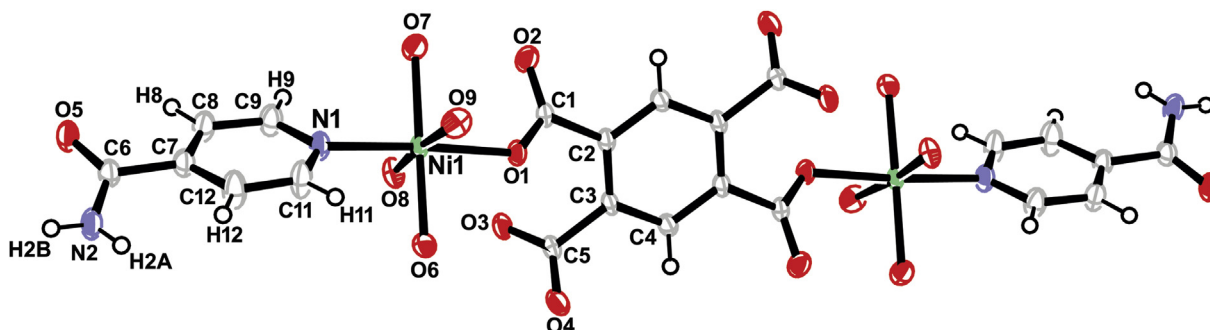


Fig. 1. The structure of $[Ni_2(pm)(ina)_2(H_2O)_4]$ (**1**) with partial atom labeling. H atoms of aqua ligands were omitted for clarity. Displacement ellipsoids were drawn at the 40%.

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