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Self-assembly of a Co(II) dimer through H-bonding of water molecules to a 3D open-framework structure

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Abstract. Reaction of pyridine-2,4,6-tricarboxylic acid (ptcH_3) with $Co(NO_3)_2.6H_2O$ in presence of 4,4′-bipyridine (4,4′-bpy) in water at room temperature results in the formation of {[Co_2(ptcH)$_2$(4,4′-bpy)(H_2O)$_4$].2H_2O}, (**1**). The solid-state structure reveals that the compound is a dimeric Co(II) complex assembled to a 3D architecture via an intricate intra- and inter-molecular hydrogen-bonding interactions involving water molecules and carboxylate oxygens of the ligand ptcH^{2-}. Crystal data: monoclinic, space group $P2_1/c$, a = 11·441(5) Å, b = 20·212(2) Å, c = 7·020(5) Å, b = 103·77(5)°, V = 1576·7(1) Å^3, Z = 2, $R1$ = 0·0363, $wR2$ = 0·0856, S = 1·000.

Keywords. Metal–organic framework; hydrogen-bonding; aromatic polycarboxylate; Co(II) complex; crystal structure.

1. Introduction

Synthesis of metal–organic framework (MOF) structures is an active area of research, as these compounds can be potentially useful[1–10] in several contemporary problems. These structures can be rapidly and conveniently built[11,12] using the modular or tinkertoy approach where topology of multidentate ligands as well as the coordination characteristics of the metal ions direct the self-assembly process. When two or more ligands are used, the design and choice of the components must fulfill criteria for spontaneously generating well-defined architectures. Much of the current effort has been directed[13–17] toward synthesis of open framework structures with aromatic polycarboxylates. We have initiated a research program to synthesize open framework structures with the ultimate goal(s) of having new materials with a range of applications. Herein, we present a structure built from Co(II), pyridine-2,4,6-tricarboxylic acid (ptcH_3) and 4,4′-bipyridine.

2. Experimental

2.1 *Materials*

The compounds, 4,4′-bipyridine and 2,4,6-trimethylpyridine, were acquired from Aldrich and used as received. The metal salts and all solvents were obtained from S.D. Fine Chemicals.

2.2 *Physical measure*ments

Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer model 1320; Microanalyses for the compounds were obtained from CDRI, Lucknow.

2.3 *Synthesis*

2.3a *Pyridine-2,4,6-tricarboxylic acid, L:* This compound was synthesized following a literature method[18] by oxidation of 2,4,6-trimethylpyridine with an aqueous solution of $KMnO_4$ in 50% yield. In a typical experiment, to 12·1 g (0·1 mol) 2,4,6-trimethylpyridine and 200 ml water, solid $KMnO_4$ (125 g; 0·8 mol) was added in 10 g portions in 2 h maintaining the temperature at ~25°C. After the addition was complete, the mixture was allowed to stir for 15 h at room temperature followed by an additional 15 h at 50°C. The MnO_2 formed in the reaction was removed by filtration and the colourless filtrate concentrated in a rotary evaporator to about 50 ml and acidified with conc. HCl to pH 2. The crude product was collected by filtration and washed several times with cold water. It was then taken in 100 ml water, heated to ~95°C and to the hot solution, HCl was

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added slowly till all the solid dissolves. The solution filtered hot and allowed to stand for 3 days at 5°C. The desired product settled as a white solid. It was collected by filtration, washed with cold water and dried in a desiccator over NaOH. Yield ~ 8 g.

2.3b *{[Co_2(ptcH)$_2$(4,4¢-bpy)(H_2O)$_4$].2H_2O}(1):* Reaction of $Co(NO_3)_2.6H_2O$, $ptcH_3$ and 4,4′-bpy in 1 : 1 : 1 molar ratio at room temperature and in aqueous medium afforded crystals of **1** within a week in ~ 45% yield. Analysis Calcd. for $C_{26}H_{26}N_4O_{18}Co_2$: C, 39·01; H, 3·27; N, 7·00%. Found: C, 39·00; H, 3·28; N, 6·98%.

2.4 *X-ray structural studies*

Single crystal X-ray data on **1** were collected at 100 K on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo–K_a radiation (l = 0·71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT[19] software. An empirical absorption correction was applied to the collected reflections with SADABS[20] using XPREP[21]. The structure was solved by the direct method using SHELXTL[22] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[23] program package. All non-hydrogen atoms were refined anisotropically. The H atom positions or thermal parameters were not refined but included in the structure factor calculations. The crystal and refinement data are collected in table 1. The CCDC No for the complex is 253131.

3. Results and discussion

The high yield of the product suggests that the compound is thermodynamically stable under the reaction conditions. The compound is stable in air and insoluble in water as well as common organic solvents. It exhibits strong peaks between 1350 and 1560 cm^{-1} attributable[24] to coordinated carboxylates.

The structure of 1 consists of dimeric units with each Co(II) showing distorted octahedral geometry (figure 1) with equatorial coordination from N and two carboxylate O of the $ptcH^{2-}$ moiety and one N of the 4,4′-bipyridine group. The carboxylic acid group at the 4-position is protonated and remains uncoordinated. The two axial sites are occupied by two water molecules. The asymmetric unit contains a half of this dimeric entity and one molecule of water. The 4,4′-bipyridine is almost coplanar with the two $ptcH^{2-}$ ligands. The Co–O distances are all different: the distances involving the $ptcH^{2-}$ unit are 2·161(6) and 2·192(6) Å, and those involving coordinated water are 2·090(7) and 2·011(5) Å. The two Co–N distances are 2·051(6) and 2·093(5) Å respectively. However,

Table 1. Crystal data and structure refinement data for **1**.

Empirical formula	$C_{26}H_{26}N_4O_{18}Co_2$
Formula weight	800·36
Temperature	100 K
Radiation MoK_a	MoK_a
Wavelength	0·71069 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	11·441(5)
b (Å)	20·212(2)
c (Å)	7·020(5)
b (°)	103·77(5)
V ($Å^3$)	1576·7(1)
Z	2
r_{calc} (Mg/m^3)	1·686
m, (mm^{-1})	1·141
F (000)	816
Refl. collected	10441
Independent refl.	3809
Refinement method	Full-matrix least-squares on F^2
GOOF	1·000
Final *R* indices	*R1* = 0·0363
[$I > 2s$ (I)]	*wR2* = 0·0856
R indices	*R*1 = 0·0421
(all data)	*wR2* = 0·0890

Table 2. Selected bond distances (Å) and bond angles (°) in **1**.

Co1–N1	2·0497(17)	Co1–N2	2·0943(18)
Co1–OW1	2·099(2)	Co1–OW2	2·103(2)
Co1–O4	2·1691(14)	Co1–O6	2·1908(14)
N1–Co1N2	174·06(6)	N1–Co1–OW1	92·67(7)
N2–Co1–OW1	89·21(7)	N1–Co1–OW2	87·99(7)
N2–Co1–OW	290·07(7)	OW1–Co1–OW2	179·06(6)
N1–Co1–O4	75·93(6)	N2–Co1–O4	109·64(6)
OW1–Co1–O4	92·29(6)	OW2–Co1–O4	88·52(6)
N1–Co1–O6	75·31(6)	N2–Co1–O6	99·10(6)
OW1–Co1–O6	89·00(6)	OW2–Co1–O6	90·52(6)
O4–Co1–O6	151·24(5)	C1–O4–Co1	116·14(12)
C8–O6–Co1	115·76(12)	C7–N1–C2	120·97(17)
C7–N1–Co1	119·76(13)	C2–N1–Co1	119·09(13)
C13–N2–C9	116·75(17)	C13–N2–Co1	118·29(13)
C9–N2–Co1	124·94(14)		

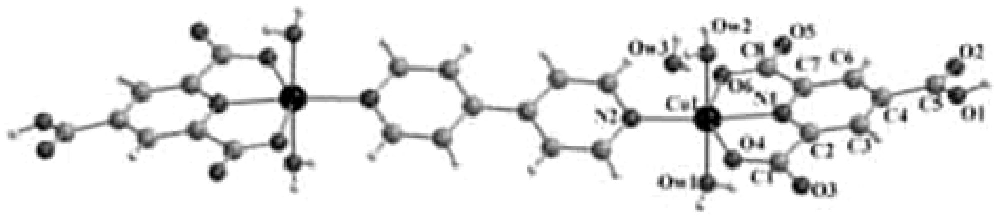

Figure 1. A perspective view of the dimeric unit in **1**.

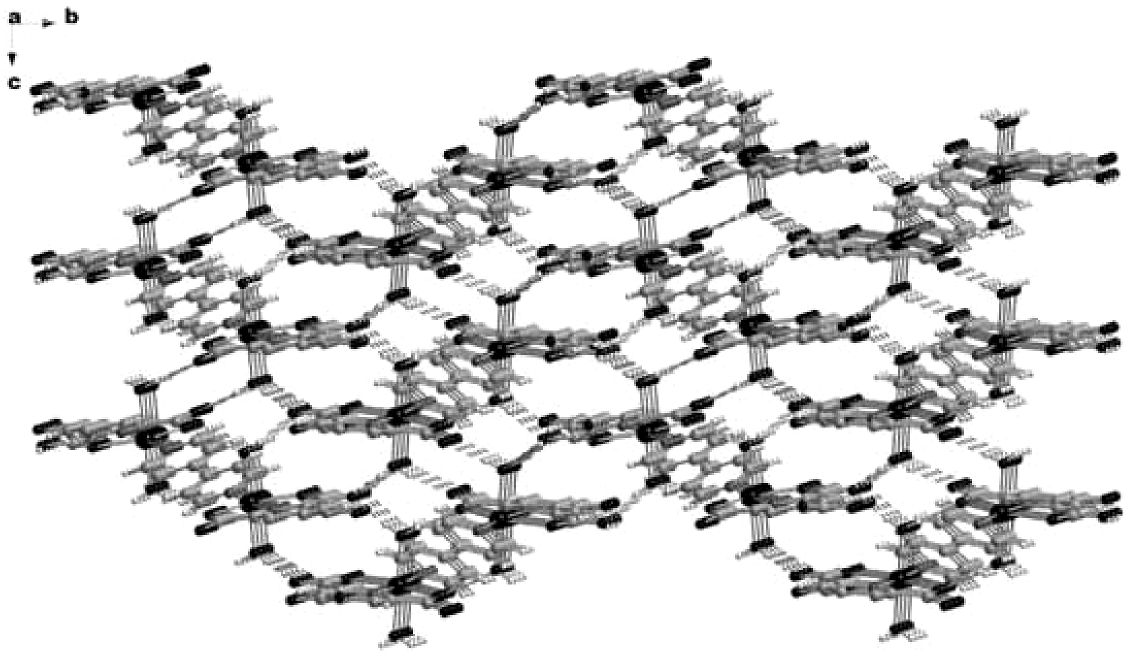

Figure 2. The open framework structure assembled through hydrogen bonding viewed down the crystallographic *a* axis.

Table 3. H-bonding distances (Å) and angles (°) in **1**.

O1…OW3	2·552(2)	O3…OW1	2·641(3)
O4…OW2	2·680(4)	O5…OW1	2·707(2)
O5…OW2	2·699(2)	O5…N1	3·067(2)
O6…OW3	2·740(3)	OW1…OW3	2·976(3)
C5–O1–OW3	111·12(12)	C1–O3–OW1	128·68(10)
C1–O4–OW2	124·58(11)	Co1–O4–OW2	113·78(7)
C8–O5–OW1	130·91(6)	C8–O5–OW2	132·52(13)
C8–O5–N1	108·48(8)	C8–O6–OW3	105·81(8)
Co1–O6–OW3	132·98(5)	Co1–OW1–O3	109·64(9)
Co1–OW1–O5	107·37(7)	Co1–OW1–OW3	131·57(10)
Co1–OW2–O4	112·64(11)	Co1–OW2–O5	114·52(11)

these distances are comparable[25] with reported Co–N and Co–O distances for octahedral complexes (table 2). The uncoordinated carboxylate group and the two axially bound water molecules are involved in intricate hydrogen-bonding interactions forming an overall 3D structure (figure 2). Both the metal bound axial water molecules are strongly hydrogen-bonded (table 3) with the carboxylate O of the nearest neighbour. Besides, two more water molecule per dimeric unit are present in the lattice, both of which are strongly hydrogen-bonded to carboxylate O and the coordinated water molecules. This O–H…O interactions cement the 3D structure. The bridging 4,4'-bipyridyl groups from neighbouring dimeric units are almost parallel to one another although there is no stacking interactions between them as the perpendicular distance is more than 10 Å.

4. Conclusion

It is thus shown here that Co(II) readily forms a dimeric structure with pyridine-2,4,6-tricarboxylic acid

acid and 4,4′-bipyridine that leads to a 3D framework structure through H-bonding interactions. We are presently probing the capability of pyridine-2,4,6-tricarboxylic acid to form MOF structures with different metal ions including lanthanides for possible applications.

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