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A 3D chiral supramolecular framework of Cu(II): Synthesis, structure and magneto-structural correlations

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ABSTRACT

A metal–organic coordination chain of Cu(II), *viz* $\{[Cu(Hbtc)(NH_3)_4](H_2O)\}_n$ (**1**) (btc = benzenetricarboxylate) has been synthesized and structurally characterized. The sky blue single crystals of **1** were grown by the dissolution of the as-synthesized insoluble product obtained from the reaction of Cu(II), H_3btc and 4,4′-bipy in aqueous NH_3 solution. Structural determination reveals that **1** crystallizes chiral $P2_12_12_1$ space group and 1D coordination chain of Cu(II) bridged by the Hbtc linker. 1D chains are H-bonded *via* the guest water molecules forming a 2D sheet like structure and 2D sheets through π–π and N–H···O H-bonding interactions produce a 3D supramolecular framework with 1D water filled channels along the *a*-axis. Temperature dependent magnetic measurement exhibits weak antiferromagnetic intrachain interaction between Cu(II) centers through the Hbtc linker with $J = -0.17\ cm^{-1}$ and $g = 2.01$ and at low temperature interchain ferromagnetic interaction is predominates. The dominant antiferromagnetic interaction is supported by the DFT calculations.

1. Introduction

Design and synthesis of metal–organic coordination framework using the self-assembly process is governed by the balance between covalent coordinate bond involving metal ions and organic linkers and close-packing intra or intermolecular non-covalent interactions of the constituent building unit [1–7]. The organization of the molecules in the crystals results different topology and dimensionality which have pronounced influence on the overall functionality, like magnetism, conductivity, NLO, luminescence, porosity, and catalytic activity of the framework [8–14]. Therefore, understanding and controlling the external factors, like pH, temperature, solvent, and reaction time which govern the crystallization process and overall stability of the crystals is very important to get the desired framework and functionality [15,16]. Different di, tri and tetracarboxylate linkers are the most commonly employed for the construction of metal–organic frameworks. Benzene-1,3,5-tricarboxylic acid (H_3btc) has been well exploited as organic linker toward the synthesis of functional hybrid materials due to its rigidity and flexibility, and shows versatile property including permanent porosity, gas storage (H_2, CH_4, etc.), separation, heterogeneous catalysis and luminescent properties [17–25]. The rigidity of btc is conferred by the benzene ring and flexibility is generated by the three equally spaced carboxylate groups having six oxygen donors which can provide versatile binding mode toward the different metal ions [26–28]. Recently, much effort has been given toward the synthesis of chiral frameworks using achiral or chiral organic linkers, due to its application toward the enantioselective separation, asymmetric catalysis and chiral magnets [29–32].

Here, we report the synthesis, unusual crystallization and structural characterization of a 1D coordination framework of Cu(II), $\{[Cu(Hbtc)(NH_3)_4](H_2O)\}_n$ (**1**) using benzenetricarboxylic acid (H_3btc) as an organic linker. The compound was crystallizes in aqueous NH_3 and structure determination reveals a 3D chiral supramolecular framework constructed by the non-covalent interactions of the 1D helical coordination chain of Cu(II) bridged by the Hbtc linker and NH_3 acts as a coligand. Low temperature magnetic measurement shows weak antiferromagnetic interaction ($J = -0.17\ cm^{-1}$ and $g = 2.01$) along the 1D chain and at low temperature inter-chain ferromagnetic interaction was observed.

2. Experimental

2.1. Materials

All the reagents and solvents employed were commercially available and used as supplied without further purification. $Cu(NO_3)_2{\cdot}2.5H_2O$, 4,4′-bipyridine and benzenetricarboxylic acid were obtained from the Aldrich Chemical Co.

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2.2. Synthesis of {[Cu(Hbtc)(NH$_3$)$_4$](H$_2$O)}$_n$ (**1**)

Methanolic solution (10 ml) of 4,4′-bipy (1 mmol, 0.156 g) was slowly added to the aqueous solution (15 ml) of Cu(NO$_3$)$_2$·2.5H$_2$O (1 mmol, 0.232 g) and instantaneous blue precipitate forms and the whole solution was stirred for 30 min. Then aqueous solution (10 ml) of H$_3$btc (1 mmol, 0.210 g) and triethylamine (2 mmol, 0.204 g) was drop wise added to the above reaction mixture and finally resulting solution was stirred for 2 h and sky blue compound separated quantitatively (see Supplementary material). The reaction mixture was filtered and the colorless filtrate was discarded and the sky blue compound treated with aqueous ammonia (14%) until sky blue compound was completely dissolved. The whole solution become deep blue and filtered and the filtrate was kept in an open atmosphere. After slow evaporation of the solution, sky-blue crystals were separated along with the white powder. The sky-blue crystals were manually separated and washed with water and EtOH. Yield 50%. Elemental *Anal.* Calc. for C$_9$H$_{18}$N$_4$CuO$_7$ (**1**): C, 30.18; H, 5.03; N, 15.65. Found: C, 29.98; H, 4.72; N, 16.04%.

2.3. Physical measurements

The elemental analysis was carried out on a Perkin Elmer 2400 CHN analyzer. FT-IR spectrum was taken on Bruker IFS-66v spectrometer in the range 4000–400 cm^{-1} using KBr pellet. Thermogravimetric analysis (TGA) experiment was carried out on Metler Toledo TGA-850 TG analyzer in the temperature range between 25 and 500 °C and at a heating rate 3 °C/min under nitrogen atmosphere. The magnetic susceptibility measurement was carried out in SQUID magnetometer in the magnetic field of 500 G at the temperature range 200–1.8 K.

2.4. X-ray crystallography

A suitable sky blue single crystal of **1** was mounted on a glass fiber and coated with epoxy resin, and X-ray data collection was carried out on a Rigaku Mercury diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD 2D detector. The sizes of the unit cell was calculated from the reflections collected on the setting angles of seven frames by changing of 0.5° for each frame. Three different settings were used and were changed by 0.5°/frame, and intensity data were collected with a scan width of 0.5°. Empirical absorption correction was performed for all data [33]. The structure of **1** was solved by direct method and followed by successive Fourier and difference Fourier techniques. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms placed in the ideal positions. The oxygen atom (O1w) of the guest water molecule refined isotropically. All calculations were carried out using SHELXL 97, [34] SHELXS 97, [35] PLATON 99, [36] and WINGX system, Ver 1.70.01 [37]. All crystallographic and structure refinement parameters for **1** was summarized in Table 1. Selected bond lengths and angles and H-bonding parameters were given in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthesis

Reaction of H$_3$btc, and the organic linker *viz.* 4,4′-bipy with Cu(II) in the presence of Et$_3$N produces quantitatively sky blue precipitate, which is insoluble in any common organic solvents. The sky blue compound characterized by elemental analysis, IR spectroscopy and TG analysis and suggesting the composition of Cu(4,4′-bipy)(Hbtc)(H$_2$O)$_2$ (see Supplementary material). Then

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

	1
Empirical formula	C$_9$H$_{15}$CuN$_4$O$_7$
Molecular weight	354.80
Crystal system	0rthorhombic
Space group	$P2_12_12_1$ (no. 19)
a (Å)	6.694(5)
b (Å)	12.540(15)
c (Å)	15.755(11)
V (Å^3)	1323(2)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.781
μ (Mo Kα) mm^{-1}	1.693
F(0 0 0)	728
T (K)	293
λ (Å) Mo Kα	0.71069
θ_{max}	31.0°
Total reflection data	10 962
Unique data	3722
$R_{(int)}$	0.034
Data with [$I > 2\sigma(I)$]	3646
R^a	0.0377
$R_w{}^b$	0.1175
Goodness of fit (GOF) on F^2	1.10
Flack (x)	0.396(16)

[a] $R = \sum||F_o|-|F_c||/\sum|F_o|$.
[b] $R_w = [\sum||w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^2$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Cu1–O1	1.937(3)
Cu1–N1	1.968(4)
Cu1–N2	2.478(4)
Cu1–N3	1.970(3)
Cu1–N4	2.615(4)
Cu1–O6_a	1.937(3)
O1–Cu1–N1	87.67(10)
O1–Cu1–N2	95.08(8)
O1–Cu1–N3	90.14(10)
O1–Cu1–N4	85.68(8)
O1–Cu1–O6_a	178.36(10)
N1–Cu1–N2	92.94(9)
N1–Cu1–N3	176.41(9)
N1–Cu1–N4	91.41(9)
O6_a–Cu1–N1	90.71(10)
N2–Cu1–N3	90.09(9)
N2–Cu1–N4	175.61(9)
O6_a–Cu1–N2	85.25(8)
N3–Cu1–N4	85.58(9)
O6_a–Cu1–N3	91.47(10)
O6_a–Cu1–N4	94.11(8)

Symmetry code: a = 1/2−x,2−y,−1/2 + z.

Table 3
Hydrogen bonds (Å, °) for **1**.

D–H···A	D–H	H···A	D···A	∠D–H···A
N1–H1A···O4^{i}	0.8900	2.0800	2.741(5)	130.00
N1–H1B···O2^{ii}	0.8900	2.0900	2.684(5)	123.00
N2–H2A···O2	0.8900	1.9600	2.657(5)	134.00
N2–H2B···O3^{ii}	0.8900	2.0100	2.852(5)	157.00
N2–H2C···O1W^{v}	0.8900	2.0100	2.842(5)	155.00
N3–H3A···O5^{iii}	0.8900	1.8800	2.693(4)	151.00
N3–H3B···O3^{iv}	0.8900	2.0500	2.755(4)	135.00
N4–H4A···O1W^{v}	0.8900	2.4400	2.753(5)	101.00
N4–H4A···O4^{iv}	0.8900	2.5700	2.891(5)	102.00
N4–H4B···O4^{iv}	0.8900	2.4100	2.891(5)	114.00
N4–H4C···O1W^{v}	0.8900	2.3000	2.753(5)	112.00
N4–H4C···O5^{vi}	0.8900	2.2500	2.640(5)	106.00

Symmetry code: i = 1/2 + x,3/2−y,1−z; ii = 1−x,1/2 + y,1/2−z; iii = −1/2 + x,3/2−y,1−z; iv = −x,1/2 + y,1/2−z; v = 1/2−x,2−y,1/2 + z; vi = 1/2−x,2−y,−1/2 + z.