

Synthesis, characterization and crystal structure of novel supramolecular proton transfer compound from benzene-1,2,4,5-tetracarboxylic acid, diethylenetriamine and copper(ii) chloride

Mehrnoush Ahmadi*, Samaneh Salkhordeh, Majid Esmhosseini
Department of Chemistry, Faculty of Sciences, Urmia University, Urmia, (IRAN)
Department of Chemistry, Urmia University, Urmia, (IRAN)
E-mail: mhr_hmd2@yahoo.com

ABSTRACT

We have recently focused on the proton delivery from acids, which are considered to be suitable proton donors, to amines as proton acceptors. The results were the production of proton transfer ion pairs possessing some remaining donor sites applied for coordination to metal centers in the preparation of metal-organic compounds. A new proton transfer compound, $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$ was synthesized from the reaction of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and $(\text{BTEC})(\text{H}_2\text{dn})_2\cdot 2\text{H}_2\text{O}$, (BTEC) = benzene-1,2,4,5-tetracarboxylate and (H_2dn) = diethylene amine diammonium. The characterization was performed using IR spectroscopy and single crystal X-ray structure determination. The crystal structure of the title compound consists of one copper(II) cation, one diethylene amine diammonium cation, one benzene-1,2,4,5-tetracarboxylate anion, one half of free benzene-1,2,4,5-tetracarboxylate and three water solvent molecule. The Cu(II) atom is four-coordinated in a distorted square-planer configuration by four O atoms from four benzene-1,2,4,5-tetracarboxylate ligand. The Cu-O bond lengths are 1.960(3), 1.963(3), 1.921(3) and 2.020(3) Å. The chemical formula is $[\text{Cu}(\text{C}_4\text{H}_4\text{N}_3)(\text{C}_{10}\text{H}_2\text{O}_8)(\text{C}_{10}\text{H}_6\text{O}_8)_{0.5}\cdot 3\text{H}_2\text{O}]_n$. The title compound crystallizes in the Monoclinic system with unit-cell parameters $a=11.7356(6)$ Å, $b=17.4020(7)$ Å, and $c=11.7253(6)$ Å, and space group P21/c, $Z=4$. Its structure has been determined from single-crystal X-ray diffraction data and refined to a conventional $R=0.053$ ($R_w=0.119$) for 3455 reflections with $I>2\sigma(I)$. The intra and intermolecular N-H...O, O-H...O and C-H...O hydrogen bonds stabilize the crystal structure.

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KEYWORDS

Synthesis;
Copper(II) complexes;
Benzene-1,2,4,5-tetracarboxylic acid;
Hydrogen bonds;
Proton transfer;
Ion pair.

INTRODUCTION

The vast majority of the reported works deal with the use of multidentate ligands containing O- or N-donor, such as polycarboxylic acids to bind to

metal ions to build novel coordination architectures by hydrogen bonding including both strong hydrogen bonding (*e.g.* O-H...O) and weak hydrogen bonding (*e.g.* C-H...O and C-H...N) and aromatic π - π stacking interactions^[1-3]. These two types of

weak interaction usually play an important role in the formation of supramolecular architectures. Organic aromatic polycarboxylate ligands have been extensively employed in the preparation of such metal–organic compounds with multidimensional networks^[4]. Benzene-1,2,4,5-tetracarboxylate appears to be an ideal ligand, since four carboxyl groups, eight O-donor atoms are available for coordination. It is known that the deprotonated forms of H₄Btec can act not only as hydrogen-bond acceptors but also as hydrogen-bond donors, depending on the deprotonated carboxyl groups, to give different supramolecular adducts. H₄Btec is also an excellent bridging ligand, and a number of one-, two- and three-dimensional infinite metal frameworks have already been generated^[5-12]. Furthermore, carboxyl ligand has shown a good capability for bridging^[13]. It forms binuclear or polynuclear complexes with transition metal ions *via* two oxygen atoms coordinating to two metal atoms, separately, forming a three atom bridge, or even *via* a single oxygen atom, coordinating to two metals forming a one-atom bridge. Furthermore, carboxylate ligands exhibit a versatile coordination behavior, including bridging coordination modes that provide exchange-coupling pathways when paramagnetic metals are involved^[14]. Considerable effort has recently been given to understanding a relationship between molecular and crystal structures, especially from the viewpoint of crystal engineering^[15-17]. Therefore, the crystal engineering of supramolecular architectures or metal-organic coordination polymers has attracted much attention in the past decades^[18-21]. The interest in the inorganic–organic solids has been focused upon hydrogen-bonded networks that are sustained by partially deprotonated anionic forms of H₄Btec. Therefore, H₄Btec was of-

ten chosen as a building unit for the layers being a molecule with predictable and interesting supramolecular properties as a consequence of its molecular symmetry and complementary hydrogen-bonding capabilities. Several pyromellitato complexes with various transition metals have been reported in the literature^[22-25], mainly combined with nitrogen ligands such as 2,2-bipyridine and 4,4-bipyridine^[26-32]. There are also examples of pyromellitato complexes with lanthanide ions^[33].

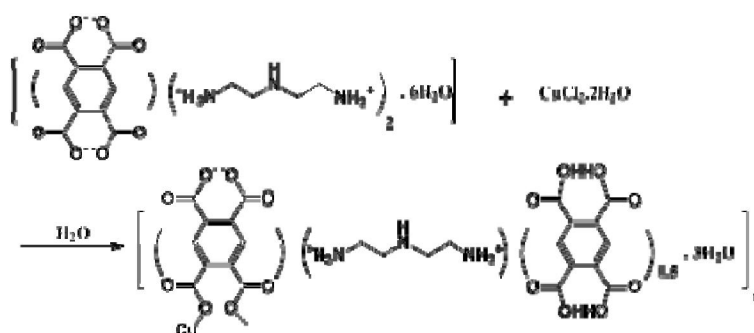
Following this approach, our research group have recently focused on forming ion pairs between benzene-1,2,4,5-tetracarboxylic acid and various inorganic bases such as bis(2-aminoethyl)amine^[34] and N,N-Bis(2-aminoethyl)amine. To this end, we selected a proton acceptor, bis(2-aminoethyl)amine (H₂dn) together with the benzene-1,2,4,5-tetracarboxylic acid (H₄btec) as proton donor.

Here we report the preparation and crystal structures of one novel 3D organic–inorganic hybrid networks self assembled by hydrogen-bonding interactions in which 2D coordination sheets formed by the self-assembly of organic molecules or hydrated metal–ion building blocks are generated first and further extended into 3D networks by hydrogen-bonding interactions. At the same time, its FT-IR modes are also discussed.

EXPERIMENTAL

Materials and methods

All solvents and reagents were commercially available, purchased from Aldrich_ and used without further purification. Infrared spectra were recorded on a FT-IR Nexus 670 spectrometer in the frequency range 4000–400 cm⁻¹ with an average of



Scheme 1 : Preparation of [Cu(BTEC)(H₂dn)(H₄BTEC)_{0.5}.3H₂O]_n

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128 scans and 4 cm⁻¹ of spectral resolution using KBr pellets.

Synthesis of [Cu(BTEC)(H₂dn)(H₄BTEC)_{0.5}·3H₂O]_n

The synthetic procedure for the proton transfer compound is shown in Scheme 1. [(Btec)(H₂dn)₂·2H₂O] ligand can be obtained according to the published method^[34]. An ethanolic solution of H₄Btec (0.21 g, 0.8 mmol) was neutralized by addition of an aqueous solution Na₂CO₃ (0.17 mg, 1.6 mmol) and stirred for 20 min. The pH value was then adjusted to 7.5. Then, an ethanolic solution of H₂dn (13 ml, 1.2 mmol) was added. The milky precipitated was isolated by filtration and washed with cold water (15 mL). Synthesis of [Cu(BTEC)(H₂dn)(H₄BTEC)_{0.5}·3H₂O]_n Compound

was prepared from a mixture of CuCl₂·2H₂O (0.13 g, 0.75 mmol), [(Btec)(H₂dn)₂·2H₂O] (0.37 g, 0.75 mmol) and H₂O (60 mL) in a molar ratio of 1 : 1 : 3330 and the resulting blue solution was stirred for 15 min at room temperature. This solution was left to evaporate slowly at room temperature. After one week, blue prismatic crystals of the title compound were isolated. The crystals obtained were separated and washed with distilled water many times. Finally, the product was dried in air at room temperature and analyzed by vibrational spectroscopy and X-ray diffraction techniques. (Yield 0.17g, 75.6%).

IR spectrum (ν, cm⁻¹): νsOH (lattice water)3458, νsNH (dn)3245(s), νs(C-H)aromatic3035, νs(C-H)diethyltriamine2822, νs(C-H)2511, δ(OH)1610, (C-C)skeletal1489, δ(OH), δs(C=O)1434, δ(CHaromatic)in-plane1282, ν(C-N)1016,

TABLE 1 : Details of [Cu(BTEC)(H₂dn)(H₄BTEC)_{0.5}·3H₂O]_n single-crystal X-ray data collection and structure refinement

Complex	[Cu(BTEC)(H ₂ dn)(H ₄ BTEC) _{0.5} ·3H ₂ O] _n
Molecular formula	C ₁₉ H ₂₆ CuN ₃ O ₁₅
Molecular weight	599.98
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.7356 (6) Å
	<i>b</i> = 17.4020 (7) Å
	<i>c</i> = 11.7253 (6) Å
	α = 90.00° β = 105.147 (4)° γ = 90.00°
Volume, Å ³	2311.38(19)
<i>Z</i>	4
Crystal Dimensions (mm)	0.15 × 0.21 × 0.40
θ limit (°)	2.3–26.0°
Limiting indices	-14 ≤ <i>h</i> ≤ 12
	-21 ≤ <i>k</i> ≤ 21
	-14 ≤ <i>l</i> ≤ 14
<i>T</i> _{min} / <i>T</i> _{max}	0.770/ 0.883
Reflections measured	13125
Data/restraints/parameters	4526/5/439
<i>R</i> _{int}	0.072
<i>R</i> 1 ^a , <i>wR</i> 2 ^b [<i>I</i> = 2σ(<i>I</i>)]	0.060, 0.120
Radiation λ (Å)	0.71073
Temperature (K)	298 (2)
Calculated density (mg/m ³)	1.724
μ/mm- 1	1.03

a *R*1 = Σ(|*F*0| - |*F*c|)/Σ|*F*0|, **b** *wR*2 = {Σw(|*F*0|² - |*F*c|²)/Σw(|*F*0|²)²}^{1/2}.

TABLE 2 : Selected bond distances and angles in $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})\cdot(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$

Bond	Distance (Å)	Bond	Distance (Å)
C1 O2	1.245(5)	C11 O9	1.321(5)
C1 O1	1.272(5)	C11 C12	1.494(6)
C1 C2	1.492(5)	C12 C14	1.392(6)
C2 C10	1.398(5)	C12 C13	1.395(6)
C2 C3	1.400(5)	C13 C14	1.396(6)
C3 C5	1.395(5)	C13 H13	0.85(5)
C3 C4	1.502(5)	C14 C13	1.396(6)
C4 O4	1.235(5)	C14 C15	1.528(6)
C4 O3	1.273(5)	C15 O12	1.234(5)
C5 C6	1.389(6)	C15 O11	1.252(5)
C5 H5	0.90(5)	C16 N1	1.461(7)
C6 C8	1.401(5)	C16 C17	1.490(7)
C6 C7	1.506(5)	C17 N2	1.488(6)
C7 O5	1.226(5)	C18 N2	1.475(6)
C7 O6	1.270(5)	C18 C19	1.509(7)
C8 C10	1.383(5)	C19 N3	1.486(6)
C8 C9	1.497(5)	O1 Cu1	1.960(3)
C9 O8	1.232(5)	O3 Cu1	1.921(3)
C9 O7	1.294(5)	O6 Cu1	1.963(3)
C10 H10	0.95(4)	O7 Cu1	2.020(3)
C11 O10	1.207(5)	O9 H9	0.81(6)
Angle	Amplitude (deg)	Angle	Amplitude (deg)
O2 C1 O1	123.7(4)	O10 C11 C12	122.8(4)
O2 C1 C2	119.2(4)	O9 C11 C12	114.4(4)
O1 C1 C2	116.9(4)	C14 C12 C13	120.0(4)
C10 C2 C3	119.5(3)	C14 C12 C11	120.5(4)
C10 C2 C1	117.1(3)	C13 C12 C11	119.5(4)
C3 C2 C1	123.0(3)	C12 C13 C14	121.4(4)
C5 C3 C2	118.9(3)	C12 C13 H13	118(3)
C5 C3 C4	119.1(3)	C14 C13 H13	120(3)
C2 C3 C4	121.9(3)	C12 C14 C13	118.6(4)
O4 C4 O3	125.6(4)	C12 C14 C15	124.4(4)
O4 C4 C3	118.9(4)	C13 C14 C15	117.0(4)
O3 C4 C3	115.5(4)	O12 C15 O11	124.6(4)
C6 C5 C3	121.4(4)	O12 C15 C14	117.1(4)
C6 C5 H5	117(3)	O11 C15 C14	118.3(4)
C3 C5 H5	122(3)	N1 C16 C17	112.8(5)
C5 C6 C8	119.5(4)	N2 C17 C16	112.7(4)
C5 C6 C7	120.1(3)	N2 C18 C19	109.4(4)
C8 C6 C7	120.3(3)	N3 C19 C18	109.9(4)
O5 C7 O6	124.2(4)	C18 N2 C17	112.5(4)
O5 C7 C6	120.1(4)	C1 O1 Cu1	107.3(3)

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Angle	Amplitude (deg)	Angle	Amplitude (deg)
O6 C7 C6	115.7(4)	C4 O3 Cu1	124.6(3)
C10 C8 C6	119.3(3)	C7 O6 Cu1	113.1(3)
C10 C8 C9	118.1(3)	C9 O7 Cu1	102.8(2)
C6 C8 C9	121.8(3)	C11 O9 H9	106(4)
O8 C9 O7	122.7(4)	O3 Cu1 O1	175.77(14)
O8 C9 C8	119.2(4)	O3 Cu1 O6	91.26(13)
O7 C9 C8	118.0(3)	O1 Cu1 O6	90.24(12)
C8 C10 C2	121.3(4)	O3 Cu1 O7	91.51(12)
C8 C10 H10	120(2)	O1 Cu1 O7	86.97(12)
C2 C10 H10	119(3)	O6 Cu1 O7	177.20(12)
O10 C11 O9	122.8(4)		

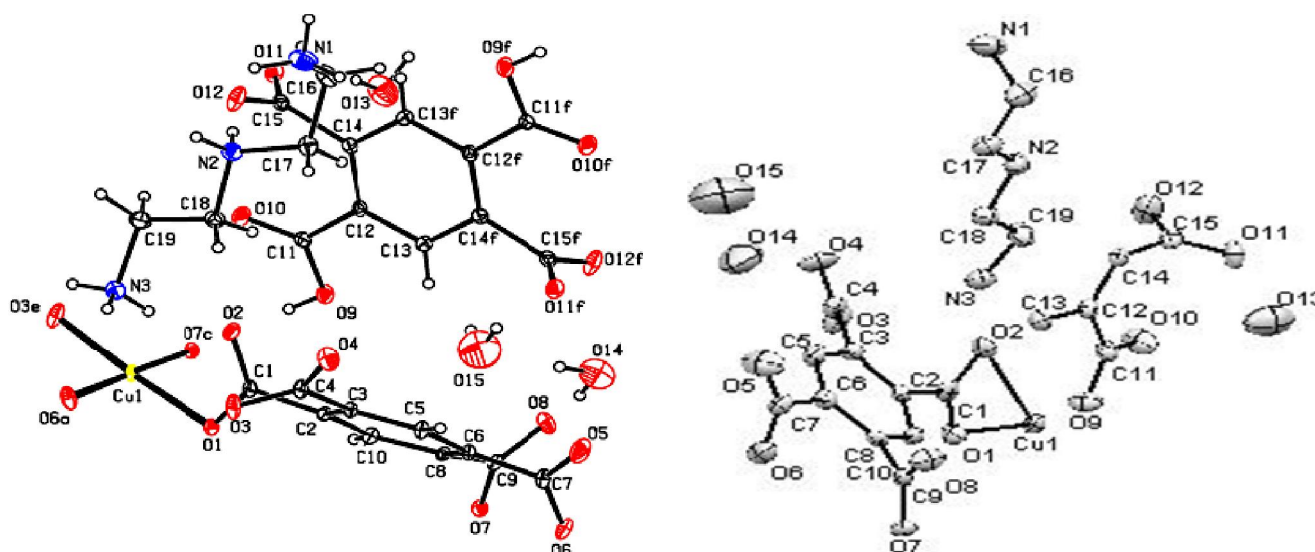


Figure 1 : (a) ORTEP view of structural fragment of compound $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5} \cdot 3\text{H}_2\text{O}]_n$ (b) Molecular structure of asymmetric unit of $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5} \cdot 3\text{H}_2\text{O}]_n$. Thermal ellipsoids are given at 50% probability. The hydrogen atoms have been omitted for clarity; [symmetry codes: (i) “ $x+2$, “ $y+2$, “ $z+1$; (ii) x , “ $y+3/2$, “ $z+1/2$; (iii) “ $x+1$, $y+1/2$, “ $z+1/2$; (iv) “ $x+1$, “ $y+2$, “ $z+1$; (v) x , “ $y+3/2$, $z+1/2$; (vi) “ $x+1$, “ $y+1/2$, “ $z+1/2$]

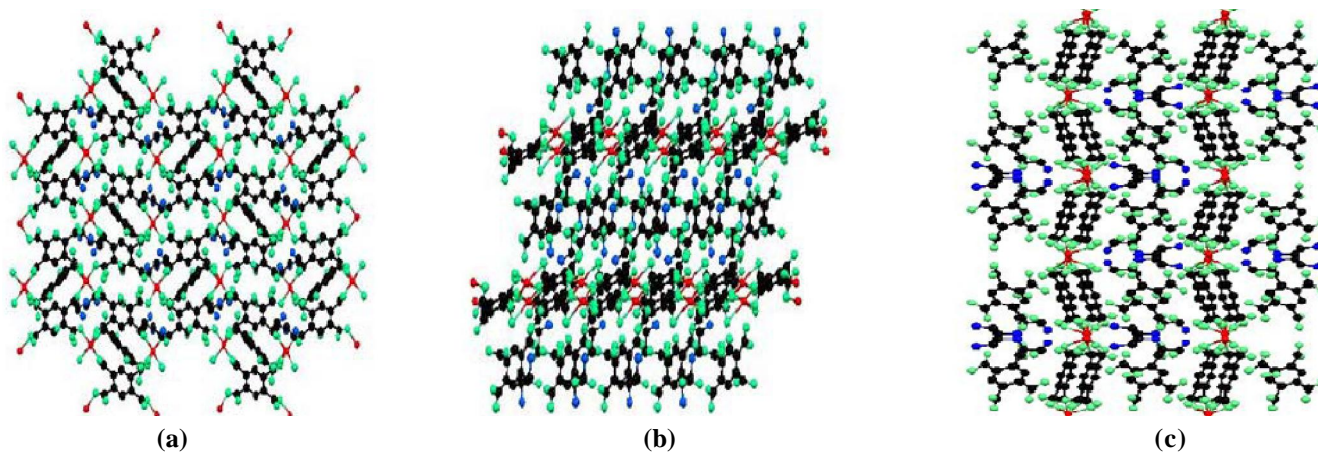


Figure 2 : Ball-and-stick view of $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5} \cdot 3\text{H}_2\text{O}]_n$ as well as the extended structure of as viewed down (a) the a -axis (b) the b -axis (c) the c -axis. All H atoms have been omitted for clarity. (Cu: red, N: blue, O: green, C: black).

TABLE 3 : Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$

Atom	x	y	Z	$U_{\text{iso}}/U_{\text{eq}}$
C1	0.5990(4)	0.8632(2)	0.3658(3)	0.0203(8)
C2	0.5865(3)	0.9332(2)	0.2900(3)	0.0183(8)
C3	0.6288(3)	0.9374(2)	0.1891(3)	0.0182(8)
C4	0.6737(4)	0.8677(2)	0.1388(4)	0.0242(9)
C5	0.6216(4)	1.0072(2)	0.1292(4)	0.0215(8)
C6	0.5759(4)	1.0725(2)	0.1690(3)	0.0202(8)
C7	0.5607(4)	1.1453(2)	0.0973(4)	0.0245(9)
C8	0.5381(3)	1.0688(2)	0.2728(3)	0.0175(8)
C9	0.5137(4)	1.1398(2)	0.3346(3)	0.0190(8)
C10	0.5417(4)	0.9992(2)	0.3306(3)	0.0202(8)
C11	0.8329(4)	0.9224(2)	0.6026(4)	0.0241(9)
C12	0.9201(4)	0.9616(2)	0.5495(3)	0.0223(8)
C13	0.8851(4)	1.0257(2)	0.4773(4)	0.0238(9)
C14	1.0359(4)	0.9352(2)	0.5726(3)	0.0202(8)
C15	1.0833(4)	0.8651(2)	0.6487(4)	0.0243(9)
C16	1.2359(5)	0.8358(3)	0.3305(5)	0.0393(12)
C17	1.1047(5)	0.8322(3)	0.3021(5)	0.0326(11)
C18	0.9318(4)	0.7653(3)	0.3371(4)	0.0291(9)
C19	0.8955(4)	0.7009(3)	0.4064(4)	0.0368(11)
N1	1.2845(5)	0.7886(3)	0.2516(5)	0.0491(13)
N2	1.0616(3)	0.7665(3)	0.3607(4)	0.0295(8)
N3	0.7664(3)	0.6876(2)	0.3636(4)	0.0296(8)
O1	0.5081(3)	0.84190(16)	0.3973(2)	0.0242(6)
O2	0.6980(3)	0.83313(16)	0.4027(3)	0.0260(6)
O3	0.6228(3)	0.80471(16)	0.1505(3)	0.0337(8)
O4	0.7532(3)	0.87570(18)	0.0885(3)	0.0395(8)
O5	0.6362(3)	1.1648(2)	0.0480(4)	0.0527(11)
O6	0.4669(3)	1.18299(16)	0.0926(3)	0.0313(7)
O7	0.4140(2)	1.14419(15)	0.3621(2)	0.0216(6)
O8	0.5914(3)	1.18893(17)	0.3641(3)	0.0336(7)
O9	0.7341(3)	0.96120(18)	0.5930(3)	0.0312(7)
O10	0.8518(3)	0.86091(19)	0.6515(3)	0.0410(9)
O11	1.1083(3)	0.87227(17)	0.7587(3)	0.0335(8)
O12	1.0970(3)	0.80557(18)	0.5966(3)	0.0403(9)
O13	1.0687(5)	1.0134(3)	0.8487(5)	0.0734(14)
O14	0.8142(5)	1.1380(4)	-0.0422(5)	0.0784(15)
O15	0.8567(7)	0.9917(4)	-0.1040(7)	0.130(3)
Cu1	0.56021(5)	0.76634(3)	0.52423(4)	0.01834(14)

$\delta(\text{C}_{\text{aromatic}})$ out-of-plane 886 and 814.

X-ray measurements

X-ray diffraction data of title compound was collected on a Bruker APEX II CCD area detector

diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with SHELXS-97^[35] and refined by full matrix least squares on F 2 with SHELXL-97^[36]. All non-

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TABLE 4 : Hydrogen bond geometries for $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$

Donor---Hydrogen...Acceptor	Don--Hyd [Å]	Hyd--Acc [Å]	Don-- Acc [Å]	D--H----A
N2---H2A...O12	0.70	2.10	2.772	163.7°
N3---H3A...O7 ^v	0.90	2.29	3.021	137.9°
N3---H3B...O4 ⁱⁱⁱ	0.93	2.04	2.900	151.9°
N3---H3C...O2	0.89	1.87	2.731	163.5°
O9---H9...O7 ^{vi}	0.81	1.88	2.672	166.0°
O13---H13B...O11	0.87	1.92	2.760	163.0°
O14---H14A...O15	0.84	1.88	2.727	178.6°
O14---H14B...O5	0.83	1.83	2.618	157.4°

Symmetry codes: (i) "x+2, "y+2, "z+1; (ii) x, "y+3/2, z"1/2; (iii) "x+1, y+1/2, "z+1/2; (iv) "x+1, "y+2, "z+1; (v) x, "y+3/2, z+1/2; (vi) "x+1, y"1/2, "z+1/2

hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters.

RESULTS AND DISCUSSION

It should be noted here that the synthesis of compounds is sensitive to the reaction temperature and pH: above 40 or below 20 C, no product is obtained; if pH value was higher than 7 or lower than 6, then no crystal was obtained. The reported pH value in Section 2 is the best choice, based on the yield.

Crystal structure determination and refinement

A suitable single crystal with dimensions of 0.40 × 0.21 × 0.15 mm for $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$ was carefully selected under an optical microscope. $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$ crystallized in the space group $P2_1/c$, as determined by systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structure. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters, and refinement statistics for $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$ is listed in TABLE 1. Selected bond distances and bond angles are given in TABLE 2. The atomic coordinates and thermal parameters are listed in TABLE 3. Hydrogen bond geometry in structure of

$[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$ is shown in TABLE 4.

Single-crystal X-ray analysis reveals that the title complex exhibits a 3D framework built from mononuclear units. The asymmetric unit contains 38 non-hydrogen atoms Figure 1b. The central copper ion is depicted as shown in Figure 1a. Figure 1a also shows that each copper atom has a four-coordinated distorted square-planar environment, which is defined by four O atoms from four Btec^{4-} ligand (thereinto, four carboxylate groups are deprotonated; only one (C(1)O(2)O(1)) binds to the copper ions in a monodentate manner). The Cu-O bond lengths are 1.960(3), 1.921(3), 1.963(3) and 2.020(3) Å. The endocyclic angles in the benzene ring of Btec^{4-} are 121.386(°) and 121.285(°) for the unsubstituted C atoms and 118.91(°), 119.514(°), 119.296(°) and 119.516(°) for the substituted C atoms. The exocyclic angles C(1)C(2)C(10), C(1)C(2)C(3), C(4)C(3)C(2), C(4)C(3)C(5), C(7)C(6)C(5), C(7)C(6)C(8), C(9)C(8)C(6), and C(9)C(8)C(10) are 117.1(3)°, 123.0(3)°, 121.9(3)°,

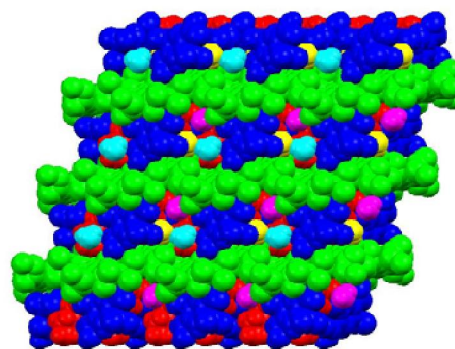


Figure 3 : Space-filling illustration of $[\text{Cu}(\text{BTEC})(\text{H}_2\text{dn})(\text{H}_4\text{BTEC})_{0.5}\cdot 3\text{H}_2\text{O}]_n$

119.1(3)°, 120.1(3)°, 120.3(3)°, 121.8(3)°, and 118.1(3)°, respectively.

CONCLUSIONS

The crystal and molecular structure of poly{[diethylene amine diammonium[μ_4 -benzene-1,2,4,5-tetracarboxylato- $\kappa^4 O, O', O'', O'''$)]copper(II)(semi benzene-1,2,4,5-tetracarboxylate) three hydrate} is reported. Our study of the 1:1 complexes of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with $[(\text{Btec})(\text{H}_2\text{dn})_2 \cdot 2\text{H}_2\text{O}]$ has clearly brought out a molecular recognition process facilitated by proton-transfer interactions. Our complex crystallize in layered structures exhibiting a variety of N–H...O and O–H...O hydrogen bonding interactions, involving several cyclic patterns. Finally, it has been shown that ligand, which has eight oxygen atoms available for coordination toward metal centers or that can act as potential acceptors of hydrogen bonds, is a good candidate to construct supramolecular arrays. As a result of H_4Btec ligand presence in all compounds, three-dimensional supramolecular arrangements, driven by hydrogen bondings that clearly control the system crystal packing, were achieved.

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