



Structure and Characterization of 1D Double Chain Copper(II) Complex $[\text{Cu}(\text{BTZX})_2(\text{CH}_3\text{OH})_2]_n$

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A novel copper(II) complex $[\text{Cu}(\text{btzx})_2(\text{CH}_3\text{OH})_2]_n$ (**1**) [btzx = 1,3-bis(tetrazol-1-ylmethyl)benzene] has been synthesized and characterized by elemental analysis, IR and single crystal X-ray diffraction. Results show that in copper(II) complex **1**, the Cu(II) atom is eight-coordinated in a elongated octahedron geometry, with four tetrazol N atoms of the ligand and two O atoms of methanol molecules. Ligands in copper(II) complex **1** adopt a *trans*-conformation acts as a bidentate linker using its two tetrazol groups to coordinate with two Cu atoms extending into an infinite 1D double chain structure. Possible partial π - π stacking interactions involving the tetrazol rings are observed in the crystal structure.

Keywords: 1,3-Bis(tetrazol-1-ylmethyl)benzene, Coordination polymers, Copper complex.

INTRODUCTION

In recent years, the rational design, synthesis and characterization of novel well-defined metal-organic framework have been greatly developed due to their intriguing variety of architectures and topologies, as well as their tremendous potential applications in areas such as electronic, magnetic, optical, absorbent and catalytic materials¹⁻⁴. Organic N-donor rigid building blocks such as 4,4'-bipyridine and 4,4'-azobispyridine are often chosen to modify the structures and properties of these polymers^{5,6}. When the rigid bifunctional ligands are used as spacers to connect metal centers, the topology of the network is usually determined by the coordination geometry of the central metal preference. Contrary to the rigid spacers, the flexible ligand, which can adopt various conformations, may induce coordination polymers with novel topologies. A number of coordination polymers with the flexible triazole or imidazole ligands have been reported^{7,8}. Tetrazolate group has different coordination mode (multi-topic) and could result in different solid-state architectures when reaction to metal ions compared to pyridyl group⁹⁻¹¹. Herein, we select 1,3-bis(tetrazol-1-ylmethyl)benzene (btzx) as the assembly ligand, in which the two tetrazol groups are linked by phenylmethyl group. Meanwhile, the flexible methyl group can induce subtle environmental changes that may change the resulting structures¹²⁻¹⁵. Additionally, to the best of our knowledge, the coordination chemistry of btzx ligand is much less studied and there have been only one published paper on Fe(II) polymer¹⁶.

EXPERIMENTAL

All the chemicals were of reagent-grade quality from commercial sources and used as received without further purification. Ligand btzx was synthesized according to the literature¹⁶. Elemental analyses were determined using a Vario EL III elemental analyzer. The IR spectra were recorded in the 4000-400 cm^{-1} region using KBr pellets and a Nicolet AVATAR-370 spectrometer.

Synthesis of complex 1: Two equivalents of btzx (48.4 mg, 0.2 mmol) were dissolved in methanol (10 mL). A solution of one equivalent of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (24.2 mg, 0.1 mmol) in methanol (10 mL) was added to the ligand solution. The resulting transparent solution was heated for 2 h and filtered. A blue block crystals for X-ray diffraction were obtained upon slow evaporation of the solvent after one week. This solid material was filtered and washed with methanol. Yield = 52 % based on Cu; Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_8\text{O}_8\text{Cu}$ (736.15): C 35.90; H 3.83; N 34.25 %. Found: C 35.62; H 3.57; N 34.63 %. IR (KBr pellet, cm^{-1}): 3451br, 3110m, 1517s, 1383s, 1274s, 1202w, 1135s, 1011s, 987w, 676s, 643m.

X-Ray crystallography: Single crystal diffraction data for complex **1** were collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Empirical absorption corrections were applied using SADABS program. The structures were determined by direct method with SHELXS-

97 program¹⁷ and refined by full-matrix least squares on F^2 with SHELXL-97 program¹⁸. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.93–0.97 Å and with $U_{iso}(H)$ set at 1.2 $U_{eq}(C, N)$ and 1.5 $U_{eq}(\text{methyl } C)$. Molecular graphics were drawn with using XP and Diamond software. The crystal data and refinement results are given in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1
CRYSTALLOGRAPHIC AND EXPERIMENTAL
DATA FOR THE COMPLEX

Empirical formula	$C_{22}H_{28}N_{18}O_8Cu$
Formula weight	736.15
Temperature (K)	296
Crystal shape/colour	Block/blue
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$
Crystal system	Triclinic
Space group	P-1
a (Å)	8.758(5)
b (Å)	10.087(6)
c (Å)	10.248(6)
α (°)	80.939(7)
β (°)	71.753(6)
γ (°)	65.238(6)
Volume (Å ³)	780.4(8)
Z	1
D_c (g cm ⁻³)	1.562
μ [mm ⁻¹ (Mo-K α)]	0.777
F(000)	377
R_{int}	0.0131
Reflections collected/unique	4088/2722
Data/restraints/parameters	2722/0/224
Max. and min. transmission	0.8601 and 0.8295
Goodness-of-fit on F^2	1.059
R_1, wR_2 [$I \geq 2\sigma(I)$] ^a	0.0331, 0.0845
R_1, wR_2 (all data) ^a	0.0375, 0.0874
Largest diff. peak and hole/(e.Å ⁻³)	0.498 and -0.341

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

TABLE-2
SELECTED BOND LENGTHS (Å) AND
ANGLES (°) FOR THE COMPLEX

Cu(1)-N(1)	2.042(2)	Cu(1)-N(8)#2	2.108(2)
Cu(1)-O(1)	2.203(2)	N(1)-Cu(1)-N(1)#1	180.0
N(1)-Cu(1)-N(8)#2	91.16(9)	N(1)#1-Cu(1)-N(8)#2	88.84(9)
N(1)-Cu(1)-O(1)#1	86.94(7)	N(1)-Cu(1)-O(1)	93.06(7)
N(8)#3-Cu(1)-O(1)	92.71(8)	N(8)#2-Cu(1)-O(1)	87.29(8)

Symmetry codes: #1 -x,-y+1,-z ; #2 -x+1,-y,-z

RESULTS AND DISCUSSION

Synthesis and general characterization: The reaction of cupric(II) nitrate with btzx is carried out in 1:2 molar ratio in the methanol system by slow volatilization of the solvent so that complex **1** can be isolated. The results of elemental analysis for complex **1** are highly consistent with the theoretical requirements of their compositions (X-ray analysis results). In the IR spectra of complex **1**, compared with the strong absorption band of the tetrazole ring at 1477 and 968 cm⁻¹ in free

btzx, these bands are shifted to slightly higher amplitudes 1517, 1011 cm⁻¹. The strong sharp bands at 3110 and 676 cm⁻¹ further confirm the assignments of C–H stretching and bending frequencies of the tetrazole ring. Compared with vibrational bands of free methanol at 3336 and 1030 cm⁻¹, these vibrations are shifted to lower wavenumber in the complex. The absorption band at 1383 cm⁻¹ corresponds to the uncoordinated NO₃⁻ anion, which is in good agreement with the observed crystal structures.

Description of the crystal structure: The coordination environment surrounding the copper atom in complex (**1**) is shown in Fig. 1. Copper(II) lying on an inversion center is six coordinated by four N atoms from two pairs of different ligands L with a N–Cu–N bond angle from 86.94(7)° to 180.0° and with Cu–N bond distances of 2.042(2) and 2.108(2) Å, respectively (Table-1). Two additional positions are occupied by two O atoms from two symmetry-related methanol molecules with Cu–O bond distance of 2.203(2) Å, close to those of reported Cu(II) complexes¹⁹. Obviously, the axial Cu–O (methanol) distance is much longer than those of Cu–N (btzx). The local coordination geometry around Cu(II) in **1** can be regarded as elongated octahedron geometry with an N₄O₂ donor set, which can be interpreted by Irving-William series and John-Teller effect of Cu(II) ion.

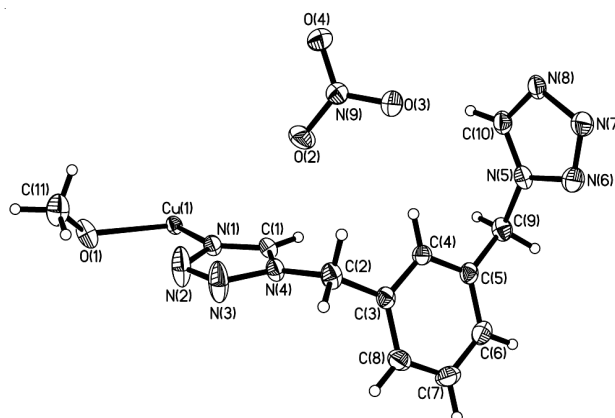


Fig. 1. Coordination environment of Cu(II) ion in **1** drawn at 30 % probability thermal ellipsoids. [Symmetry codes: #1 -x,-y+1,-z #2 -x+1,-y,-z #3 x-1,y+1,z #4 x+1,y-1,z]

On the other hand, The btzx ligands exhibit *trans* conformation and work as shorter spacers (N...N 8.093 Å) between the two donor atoms. The dihedral angles between each tetrazole group and the central benzene ring plane are 69.08° and 81.05°, respectively. Two bent conformation of the ligands link two metal atoms using its two flexible arms to generate an infinite 1D hinged cation chain containing 24-membered M₂L₂ macrocycle (Fig. 2). The Cu...Cu distance within the M₂L₂ ring is 10.22 Å, which is significantly shorter than the Fe...Fe distances of reported [Fe(btzx)₃]X₂ (X = PF₆⁻, CF₃SO₃⁻, ClO₄⁻) complexes¹⁶. The weak π - π stacking interactions are also observed between the parallel tetrazole rings of adjacent chains (Fig. 3). The interplanar perpendicular distance and ring-centroid separation distance are 3.43(2) Å and 4.13(2) Å, respectively. The 1-D chain structure is expanded into two-dimensional network in the ac plane by π - π stacking interactions which are favourable to stabilize the coordination complex.

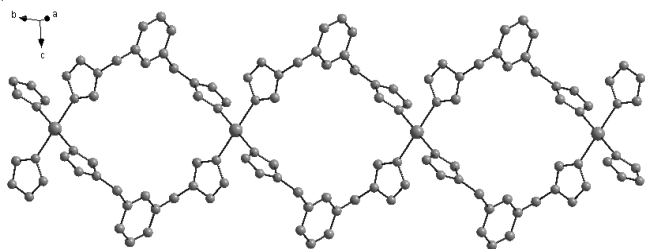


Fig. 2. 1D hinged cationic double chain of the complex with 28-membered macrometallacyclic repeating units

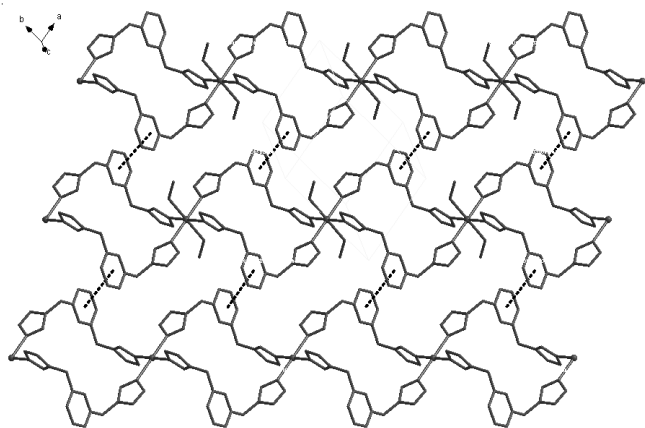


Fig. 3. 2-D crystal packing for **1**, showing π - π stacking interactions as dashed lines (H atoms are omitted for clarity)

Conclusion

The flexible ligand 1,3-bis(tetrazol-1-ylmethyl)benzene adopt a *trans*-conformation coordinates to two Cu atoms to extend into an infinite 1D double chain structure. The adjacent 1-D chains is expanded into two-dimensional network in the *ac* plane by π - π stacking interactions to stabilize the coordination complex. The nitrate anions are not favourable to coordinate to the metal atoms, but can be easily located at the lattice of the crystal.

Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 915839. Copies of these information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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