

A Cyclic Trinuclear 1,2,4-Triazole-containing Copper(II) Complex Involving a Pyramidal $\text{Cu}_3(\text{OH})$ Core: Synthesis, Structure and Fluorescence

Xiu-Cheng Zhang* and Bing Liu*

College of Science, Northeast Forestry University, Harbin, Heilongjiang, 150040, P. R. China

*E-mail: xiuchengzhang@163.com and bliu_1203@yahoo.com.cn

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Various trinuclear copper(II) compounds have been extensively explored, which have generated considerable interest in structures and magnetism as well as the role in homogeneous catalysis and active sites of multicopper oxidases.¹ The fact the oxidized ascorbate oxidase contains an angled triangular array of copper atoms with short $\text{Cu}\cdots\text{Cu}$ separations suggests the importance of trinuclear copper(II) compounds to model of those active sites.² 1,2,4-Triazole and its derivatives can form polynuclear triazole aggregates and multiframewords with its three N atoms severing as donor sites, which adopts its three bridging modes ($\mu_2\text{-}\kappa\text{N}^1\text{:}\kappa\text{N}^2$, $\mu_2\text{-}\kappa\text{N}^2\text{:}\kappa\text{N}^4$, and $\mu_3\text{-}\kappa\text{N}^1\text{:}\kappa\text{N}^2\text{:}\kappa\text{N}^4$).³ The $\mu_2\text{-}\kappa\text{N}^1\text{:}\kappa\text{N}^2$ mode can support the very strong ligand field binding paramagnetic centers to effectively transmit magnetic interaction, thus to afford polynuclear compounds with unique magnetic properties.⁴ With this short bridge, the attempts often led to 1D chains⁵ and linear trinuclear entities $[\text{M}_3(\text{trz})_6(\text{H}_2\text{O})_6]$ ($\text{trz} = 1,2,4\text{-triazoles}$).⁶ The examples of cyclic trinuclear compounds with 1,2,4-triazole derivatives are, however, few.^{3c,7} The cyclic trinuclear triangular copper(II) core Cu_3X ($\text{X} = \mu_3\text{-O}$, $\mu_3\text{-OH}$, and halide) can be regarded as geometrically frustrated and offer an opportunity to study the magnetic exchange models.⁸ The cyclic trinuclear clusters can also act as secondary building blocks to fabricate multi-dimensional frameworks. However, few examples have been reported.⁹

Aiming at the exploration into the $[\text{Cu}_3(\mu_3\text{-OH})]$ core combining with 1,2,4-triazole, we employed Htrr as building block in this work. A cyclic trinuclear copper(II) compound, $[\text{Cu}_3(\text{Htrr})_2(\text{trr})(\text{OH})(\text{DMF})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 5\text{H}_2\text{O}$ (**1**), was produced by hydrothermal reaction, and we report its crystal structure and fluorescence. To our knowledge, it is the first cyclic trinuclear compound containing Htrr ligand.

Experimental Section

Materials and Physical Measurements. The reagents and solvents were used directly as supplied commercially without further purification except Htrr and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Htrr was synthesized as standard literature procedure and recrystallized from ethanol (yield: 92%, m. p. = 158 - 159 °C).¹⁰ Blue crystals of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystallized on freezing a solution of HClO_4 and superfluous $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (Caution: great care should be taken in handling $\text{Cu}(\text{ClO}_4)_2$ in solution or in the dry state, as explosions may occur if it is brought into contact with organic or other readily oxidizable substances).

The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range 4000 ~ 400 cm^{-1} . Elemental analysis of C, H and N was carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a Fluoro-Max-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of $[\text{Cu}_3(\text{Htrr})_2(\text{trr})(\text{OH})(\text{DMF})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 5\text{H}_2\text{O}$ (1**).** $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 37.0 mg) and Htrr (0.2 mmol, 17.0 mg) were mixed with 10 mL $\text{H}_2\text{O}/\text{DMF}$ (v:v = 1:1) in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 120 °C for 5 days in a furnace and then naturally cooled to obtain blue prismatic crystals. Yield based on Cu: 10.4 mg, 26.2%. Elemental analysis found (calcd) for $\text{C}_{12}\text{H}_{41}\text{Cl}_4\text{Cu}_3\text{N}_{14}\text{O}_{27}$: C, 12.29 (12.78); H, 3.85 (3.48); N, 17.32 (17.38). IR data (in KBr, cm^{-1}): 3431(s), 2975(w), 1627(s), 1593(s), 1522(m), 1397(m), 1330(m), 1225(m), 1087(s), 1066(m), 935(m), 774(w), 753(w), 687(w), 648(w), 489(w).

X-ray Crystallography. Data collection for the title compound was performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 293(2) K and corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique and reduced using CrystalClear program.¹¹ The structure was resolved by direct method using SHELXTLTM package and refined by full-matrix least-squares technique on F^2 .¹² All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions and refined with isotropic thermal parameters included in the final stage of the refinement on calculated positions bonded to their carrier atoms. The amino group bearing on the half occupancy 1,2,4-triazole ring shows a positional disorder, which appears in the 3- and 5-positions of triazole moiety. Crystallographic data, and the selected bond distances and angles for compound **1** are respectively listed in Table 1 and 2.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-267575). The data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic and Refinement Data.

Empirical formula	C ₁₂ H ₃₉ Cl ₄ Cu ₃ N ₁₄ O ₂₆
Color and Habit	Blue Prism
Crystal Size (mm)	0.2 × 0.2 × 0.15
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> (Å)	7.571(4)
<i>b</i> (Å)	25.198(11)
<i>c</i> (Å)	10.826(4)
β (°)	90.5780(10)
<i>V</i> (Å ³)	2065.2(17)
<i>Z</i>	2
<i>F</i> _w	1112.87
<i>D</i> _{calcd} (Mg m ⁻³)	1.790
μ (mm ⁻¹)	1.891
<i>F</i> (000)	1114
Final ^a <i>R</i> ₁ , ^b <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0749, 0.1537
<i>R</i> ₁ , <i>wR</i> ₂ indices (all)	0.1248, 0.1725

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

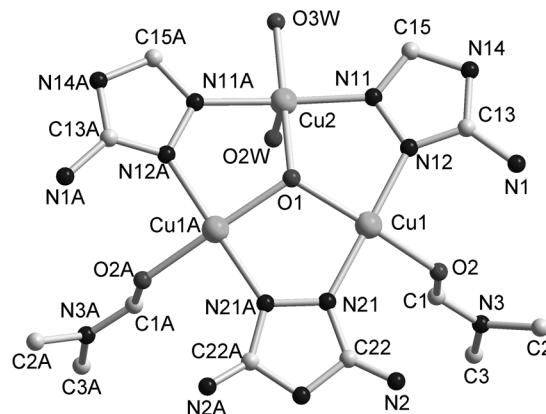
Table 2. Selected Bond Distances (Å) and Angles (°).

Cu1-N21 = 1.979(4)	Cu2-O1 = 2.019(4)
Cu1-O2 = 1.945(3)	Cu2-O3W = 2.001(8)
Cu1-N12 = 1.952(4)	Cu2-O2W = 2.324(10)
Cu1-O1 = 1.993(2)	Cu1...Cu1 = 3.348(2)
Cu2-N11 = 1.960(4)	Cu1...Cu2 = 3.3450(18)
N21-Cu1-O2 = 91.07(15)	N11-Cu2-O1 = 89.04(12)
N21-Cu1-N12 = 178.71(17)	N11-Cu2-O3W = 90.69(12)
O2-Cu1-N12 = 90.03(16)	O1-Cu2-O3W = 175.7(3)
N21-Cu1-O1 = 89.47(14)	N11-Cu2-O2W = 93.70(12)
O2-Cu1-O1 = 169.15(17)	O1-Cu2-O2W = 106.4(3)
N12-Cu1-O1 = 89.58(15)	O3W-Cu2-O2W = 77.9(4)
N11-Cu2-N11A = 172.6(2)	Cu1-O1-Cu1A = 114.73(18)
	Cu1-O1-Cu2 = 112.90(13)

Symmetry codes: *A* = *x*, *-y*+1/2, *z*.

Results and Discussion

Description of Crystal Structure. Single-crystal analysis reveals that the **1** contains a trimeric [Cu₃(Htrr)₂(trr)(OH)(DMF)₂(H₂O)₂]⁴⁺ polycation, four uncoordinated ClO₄⁻ and five lattice water molecules. Three Cu²⁺ centers with their six positive charges are balanced by one deprotonated trr⁻, one OH⁻, and four ClO₄⁻. The cyclic trinuclear unit comprises of two kinds of independent copper(II): quadrangular Cu1 and square pyramid Cu2. The quadriangular Cu1 lies 0.0961 Å off the plane, defined by two N atoms from two separated triazole entities and two O atoms from DMF and OH⁻; Cu2 displays a square pyramid geometry with $\tau = 0.052$ ($\tau = (\beta - \alpha)/60$, where α and β are the two biggest bond angles around Cu(II) center; $\tau = 0$ for ideal square pyramid; and $\tau = 1$ for ideal trigonal bipyramid),¹³ N11 and its symmetrical atom from two triazoles, O3W and OH⁻ constituting the basal square (*d*_{Cu2-N11} = 1.960(4)

**Figure 1.** The coordination sphere of Copper(II) atoms with atom labels. Hydrogen atoms are omitted for clarity. Symmetry codes: *A* = *x*, *-y*+1/2, *z*.

Å; *d*_{Cu2-O} = 2.001(8) and 2.019(4) Å) and O2W occupying the axial site (*d*_{Cu2-O2W} = 2.324(10) Å). The maximum deviation of Cu2 is 0.0449 Å from the best least-squares plane built by its coordination atoms. The slight distortion of the coordination geometries also can find evidences in the angles around Cu centers: N-Cu-O angles close to 90° (those around quadrangular Cu1 ranging 89.45(14) to 90.97(15)°, and those around Cu2 in basal plane from 89.47(14) to 91.07(15)°). In the trimeric unit, Cu1, Cu1A and Cu2 atoms are held together by two distinct bridges (Figure 1): (i) O1 of the tridentate hydroxy group, placed 0.2207 Å out of the least-square plane defined by the Cu₃ triangle, exhibiting a Cu₃(OH) pyramid. The bond-valence sum (BVS) of O1 is calculated to be 1.255 indicating that O1 is OH⁻ anion. The refined Cu-O(H) distances (1.993(2) and 2.019(4) Å) and Cu-O(H)-Cu angles (112.90(13) and 114.73(18)°) agree well with those found in similar structures containing pseudotetrahedral sphere of oxygen in Cu₃(OH) cores;^{7a,7c,7e,14} (ii) three (H)tr entities as bidentate μ₂-κN¹: κN² bridges, which bind three copper atoms into a 9-membered [(Cu-N-N)₃] ring and further divided into three 5-membered rings by μ₃-OH⁻. With a central pseudo-3-fold axis through the OH⁻, the three copper atoms in the cyclic trinuclear units fall at the corners of an almost equilateral triangle with Cu1...Cu1A distance of 3.348(2) Å and Cu1...Cu2 of 3.3450(18) Å.

Due to the existence of abundant donors and acceptors, plentiful of hydrogen bondings are expected to form among the cyclic trinuclear units, ClO₄⁻ and lattice water. A 1D supramolecular chain is formed by hydrogen bondings (O1W...O2W = 2.936(12); O1W...O13 = 2.870(10); N1-H...O14 = 2.992(13) Å), which is further connected into 2D grid via hydrogen bondings (N2-H...O21 = 2.907(16); O1W...O24 = 2.952(11) Å). A final 3D supramolecular architecture is shaped by hydrogen bondings (O4W...O24 = 2.830(11); N2-H...O11 = 3.099(16); N1-H...O14 = 3.036(13) Å (Figure 2).

Fluorescence. Compared to the interest of cyclic trinuclear copper(II) in magnetism, up to present, less work has been performed on the optical properties. Compound **1** and free Htrr show luminescent features in the solid-state fluorescent spectra at room temperature (Figure 3). Excitation of **1** with λ_{ex} =

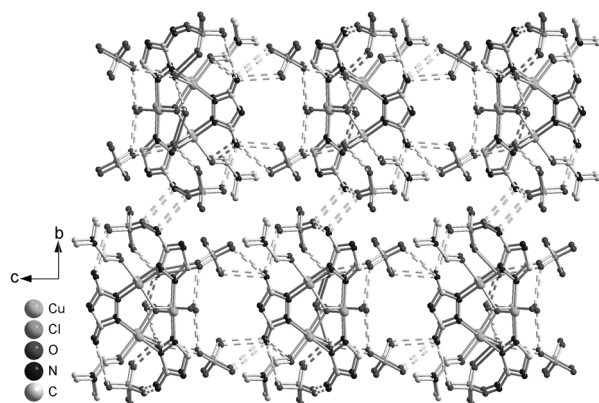


Figure 2. The 3D supramolecular architecture in **1**.

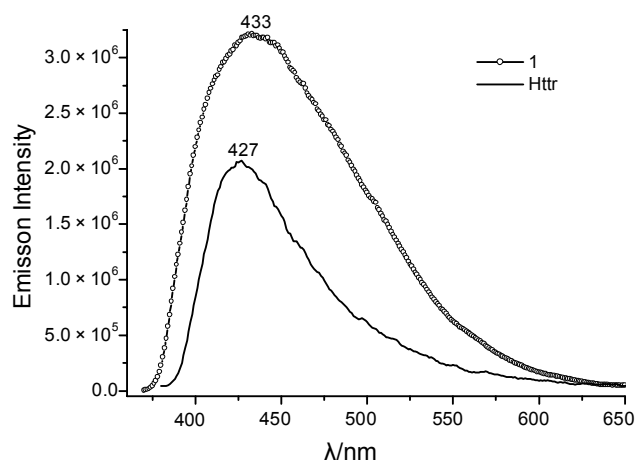


Figure 3. The solid-state electronic emission spectra of compound **1** ($\lambda_{\text{ex}} = 343$ nm) and the free ligand Httr ($\lambda_{\text{ex}} = 360$ nm) recorded at room temperature.

343 nm produces pale blue fluorescence at 433 nm. Compared to the free ligand of Httr (the emission at 427 nm with $\lambda_{\text{ex}} = 360$ nm), the similar emission of **1** with only 6 nm red-shifting, can be assigned as an intra-ligand $\pi-\pi^*$ transition of Httr. The emission of **1** is different from those Httr-containing complexes (mainly around 420 or 460 nm),¹⁵ implying the structural factors affect the emission peaks. Because of the location of **1** out of the blue light region (435–480 nm), it may not be regarded as a good candidate for blue emission molecular materials. Further investigations in cyclic trinuclear compounds with other metal centers may be helpful in searching blue emission molecular materials.

In summary, this paper describes the synthesis, structure, and fluorescence of a trinuclear Cu(II) compound containing deprotonated ttr[−] ligands as bridges. The trinuclear Cu(II) compound shows a cyclic trinuclear Cu₃(OH) core with $\mu_3\text{-OH}^-$ and $\mu_2\text{-}\kappa\text{N}^1\text{:}\kappa\text{N}^2$ triazole bridges. The structure is stabilized by hydrogen bondings formed among the cyclic trinuclear Cu₃(OH) core, ClO₄[−] and water molecules. The fluorescent characterization exhibits a similar emission peak at 433 nm as free Httr, assigned to an intra-ligand $\pi-\pi^*$ transition of Httr.

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Supporting Information Available. The synthetic route of Httr, 1D and 2D supramolecular motifs of the title compound are available on request from the correspondence authors.

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