

A Linear Trinuclear Copper(II) Complex Containing 4-Substituted (*m*-Phenol)-1,2,4-triazole: Synthesis, Crystal Structure, and Properties of Magnetism and Fluorescence

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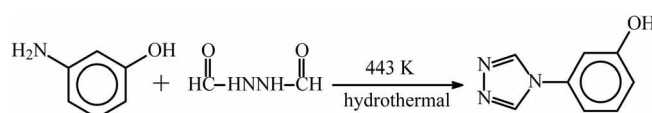
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The coordination complexes of 1,2,4-triazoles possess a great diversity of structures, which is connected to the di- or trinucleating properties of the neutral and anionic triazole ring. Substituted 1,2,4-triazoles have attracted great and growing interest in the coordination chemistry because of the fact that they can synthesize transition metal coordination complexes with the two bridging close adjacent nitrogen atoms, and can effectively transmit magnetic interaction between paramagnetic centers.¹ The chelating nitrogen donor atoms can support the very strong ligand field in ferrous complexes to induce a transition from the HS to the LS state on cooling or increasing pressure.² Among the design strategies for heterocycle-based organic blue emission molecular materials, introducing a heterocycle into a molecular structure is an efficient way to obtain excellent organic blue emission molecular materials because π -deficient and π -excessive heterocycles may respectively act as efficient acceptor and donor moieties.³ 1,2,4-triazole ring, a 6-electrons π -excessive system, has potential applications to achieve the heterocycle-based organic blue emission molecular materials. In view of the coordination characterizations of 1,2,4-triazole, we focus on the linear arrangements containing 4-substituted (*m*-phenol)-1,2,4-triazole (ptr) to synthesize new metal-organic polynuclear complexes. A linear trinuclear copper(II) complex $[\text{Cu}_3(\text{ptr})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6$ was obtained by successfully employed ptr reacting with $\text{Cu}(\text{ClO}_4)_2$, whose crystal structure was determined. fluorescent and magnetic properties of were characterized.

Experimental Section

Materials and physical measurements. All chemicals were used as purchased without further purification except that *m*-phenol-1,2,4-triazole (ptr) was prepared from the condensation reaction of diformylhydrazine with *m*-aminophenol according to literature method.⁴ The yield was improved by prolonging the reaction time at 170 °C for three days. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000-400 cm^{-1} and elemental analyses of C, H and N were carried out on a Vario EL III elemental analyzer. The electronic emission and excitation spectra recorded at room temperature were obtained on an Edinburgh FL/FS 920 TCSPC fluorescence spectrophotometer with excitation and emission slit at 5.0 nm, increment 1.0 nm and integration time 0.1 s.



Scheme 1. The synthesis of (*m*-phenol)-1,2,4-triazole.

Variable-temperature, solid-state direct current (DC) magnetic susceptibility data down to 2 K were collected on a Quantum Design PPMS60000 magnetometer in the our institute. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

Synthesis of (*m*-phenol)-1,2,4-triazole (ptr). (*m*-Phenol)-1,2,4-triazole was prepared by reacting the diformylhydrazine (6 mmol, 528 mg) and (*m*-amino)-phenol (6 mmol, 654 mg) in a Teflon-lined stainless steel autoclave in a furnace at 170 °C for 3 days, and then cooled to room temperature (Scheme 1). The product was isolated and washed with hot water and hot ethanol. Yield based on (*m*-amino)-phenol: 754 mg, 78%. Elemental analysis (%) for $\text{C}_8\text{H}_7\text{N}_3\text{O}$, Found (calcd): C, 59.61 (59.62); H, 4.29 (4.38); N, 26.18 (25.90). IR (cm^{-1} , KBr): 3136 (w), 3120 (w), 2954 (w), 2846 (w), 2743 (w), 1613 (s), 1533 (vs), 1494 (s), 1388 (w), 1381 (m), 1293 (s), 1204 (s), 1093 (m).

Synthesis of $[\text{Cu}_3(\text{ptr})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6$. To a solution of (*m*-phenol)-1,2,4-triazole (32 mg, 0.2 mmol) in a minimum of water was added 0.1 mmol of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (38 mg) aqueous solution yielding blue suspension. The block blue crystals were isolated by slow evaporation of the filtrate at room temperature for a couple of weeks. **Caution: perchlorate complexes are potential explosives. These complexes must be handled in small quantity and with great care.** Yield based on Cu: 29 mg, 46%. Elemental analysis (%), Found (calcd): C, 30.92 (30.96); H, 2.95 (2.92); N, 13.52 (13.54). IR data (in KBr, cm^{-1}): 3421 (vs), 2969 (w), 2918 (w), 1626 (s), 1400 (m), 1381 (m), 1119 (m), 1085 (m), 1049 (m), 880 (w), 779 (w), 671 (w), 621 (w), 465 (w).

X-ray Crystallography. Data collection for the compound was performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at 293 K, corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique, and reduced using CrystalClear program.⁵ The structure was solved by direct method using SHELXTLTM package of crystallographic software⁶ and refined by full-matrix least-squares technique

Table 1. Crystal and experimental data

Empirical formula	C ₄₈ H ₅₄ Cl ₆ Cu ₃ N ₁₈ O ₃₆
Color and Habit	Blue block
Crystal Size (mm)	0.25 × 0.22 × 0.20
Crystal system	Rhombohedral
Space group	R-3
<i>a</i> (Å)	15.933(4)
<i>b</i> Å	15.933(4)
<i>c</i> (Å)	26.451(15)
<i>V</i> (Å ³)	5815(4)
<i>Z</i>	3
<i>F</i> _w	1862.41
<i>D</i> _{calcd} (Mgm ⁻³)	1.596
<i>μ</i> (mm ⁻¹)	1.120
<i>F</i> (000)	2835
<i>θ</i> (°)	3.45 to 27.50
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0987, 0.2594
<i>S</i>	1.061
(Δ/ <i>σ</i>) _{maximum}	0.003, 0.000
(Δρ) _{maximum} /eÅ ⁻³	1.018, -1.116

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

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

Cu1-N1	2.1384(16)	Cu2-O1W	2.100(3)
Cu2-N2	2.0545(19)		
N1A-Cu1-N1B	179.997(1)	N2C-Cu2-N2	91.58(8)
N1A-Cu1-N1	90.78(6)	N2B-Cu2-O1WB	89.95(10)
N1B-Cu1-N1	89.23(6)	N2C-Cu2-O1WB	176.08(10)
N1A-Cu1-N1C	90.78(6)	N2-Cu2-O1WB	91.98(11)
N1B-Cu1-N1C	89.23(6)	N2B-Cu2-O1WC	91.98(11)
N1-Cu1-N1C	89.23(6)	N2C-Cu2-O1WC	89.95(10)
N1A-Cu1-N1D	89.22(6)	N2-Cu2-O1WC	176.08(10)
N1B-Cu1-N1D	90.77(6)	O1WB-Cu2-O1WC	86.39(12)
N1-Cu1-N1D	179.998(1)	N2B-Cu2-O1W	176.08(10)
N1C-Cu1-N1D	90.78(6)	N2C-Cu2-O1W	91.98(11)
N1A-Cu1-N1E	89.22(6)	N2-Cu2-O1W	89.95(10)
N1B-Cu1-N1E	90.77(6)	O1WB-Cu2-O1W	86.39(12)
N1-Cu1-N1E	90.78(6)	O1WC-Cu2-O1W	86.39(12)
N1C-Cu1-N1E	180.00(7)	C1-N1-Cu1	127.88(16)
N1D-Cu1-N1E	89.22(6)	N2-N1-Cu1	124.42(12)
N2B-Cu2-N2C	91.58(8)	C2-N2-Cu2	127.73(17)
N2B-Cu2-N2	91.58(8)	N1-N2-Cu2	125.53(13)

Symmetry code: A = *x*-*y*+1/3, *x*-1/3, -*z*-2/3; B = -*x*+*y*-1, -*x*-1, *z*; C = -*y*+1, *x*-*y*, *z*; D = -*x*+4/3, -*y*-2/3, -*z*+2/3; E = *y*+1/3, -*x*-*y*+2/3, -*z*+2/3.

on *F*². All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C, N and O 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. Crystallographic data and the selected bond distances for the title complex are respectively listed in Table 1 and 2.

Results and Discussion

Description of crystal structures. Attempts to synthesize linear chain compounds with triazole functionalities in conjunction with non-coordinating anions resulted in a series of isomorphous cations of composition [M₃(trz)₆(H₂O)₆]⁷⁺ (trz = 1,2,4-triazoles). Though the reactions of 4-substituted 1,2,4-triazoles with the metal salts of non-coordinating anions, such as ClO₄⁻, BF₄⁻, PF₆⁻ and SiF₆²⁻, yield either 1-D chain⁸ or linear trinuclear entities, the existence of the non-coordinating anions has no direct effect on the geometries of the polymers. The trimers have the same overall structure: three metal ions in a linear arrangement, linked to each other by two pairs of three bridging triazole ligands: the coordination sphere of the terminal metal ions always includes three water molecules. The principal structural features of the title compound with the atom labeling are given in Figure 1. The complex has a linear trinuclear structure with a crystallographic inversion center located on Cu1. In the arrangement, six ptr ligands act as bidentate ligands to link the Cu²⁺ centers *via* 1- and 2-positioned N atoms. The Cu1 center is coordinated to six N1 atoms from six separate ptr ligands. The bond angles between the neighboring N atoms and the central Cu1 are approximate right angles in a very narrow range of 89.22 and 90.78(6)°. The bond angles and nearly equal distances around Cu1 indicate that the octahedral formation of Cu1 is a near ideal geometry. The terminal Cu2 center and its symmetry-related atom are in distorted (4+2) octahedral environments including O1W and its symmetric atoms in the equatorial plane and axis

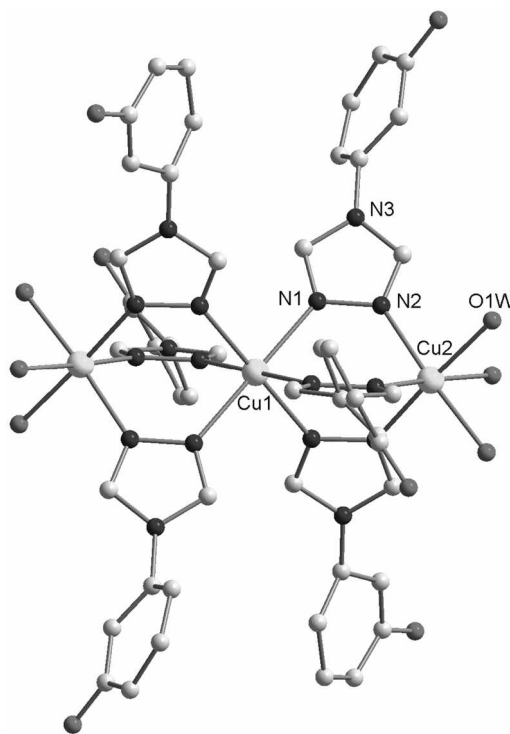


Figure 1. Structure of the polycation [Cu₃(ptr)₆(H₂O)₆]⁶⁺. Hydrogen atoms and ClO₄⁻ are omitted for clarity.

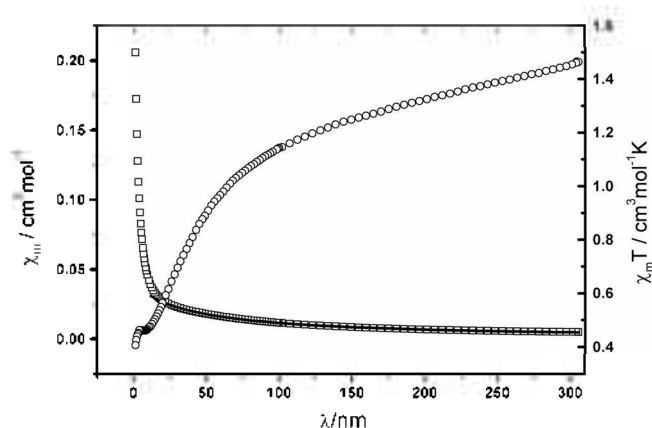


Figure 2. Plot of χ_m vs T and $\chi_m T$ vs T over 2-300 K at a field of 1T showing a Curie-Weiss paramagnetic behavior of the title complex (χ_m : square; $\chi_m T$: circle; non-linear fit: line).

position.

The magnetic behavior of $[\text{Cu}_3(\text{ptr})_6(\text{H}_2\text{O})_6]_2(\text{ClO}_4)_6$ is shown in Figure 2 in the form of χ_m vs T and $\chi_m T$ vs T plots. The product $\chi_m T$ decreases on cooling and the title compound follows the Curie-Weiss law $\chi_m = 1.598/(T+39.7)$ in the temperature range of 30-300 K, whose magnetic behaviors indicate overall antiferromagnetic interaction between adjacent copper(II) ions. The $\chi_m T$ value is $1.44 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature, slightly larger than the spin-only value ($1.12 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for tricopper(II) complexes. The title compound is a symmetrical linear trinuclear complex, thus the corresponding magnetic susceptibility data were represented by Equation (1) [the Hamiltonian being $H = -2J[S_1 \cdot S_2 + S_2 \cdot S_3]$, assuming that the exchange integral between the neighboring copper(II) are identical ($J_{12} = J_{23} = J$) and the integral between the terminal copper(II) is zero ($J_{13} = 0$),⁹ where χ_m is magnetic susceptibility per tricopper(II), N is Avogadro's number, β is Bohr's magneton, k is Boltzmann's constant and J is the isotropic exchange parameter. The best least-squares fit of the theoretical equation to experimental data leads to $g = 1.89$, $J/k = -21.2$ K and the agreement factor $R = 3.90 \times 10^{-3}$ [$R = \sum |(\chi_m T)_{\text{obs}} - (\chi_m T)_{\text{calc}}|^2 / \sum (\chi_m T)_{\text{obs}}^2$]. The negative J value suggests that antiferromagnetic interaction exists in the compound, which is in agreement with the result of the fit obtained from the Curie-Weiss law.

$$\chi_m = \frac{N\beta^2 g^2}{4kT} \cdot \frac{1 + \exp(-2J/kT) + 10\exp(J/kT)}{1 + \exp(-2J/kT) + 2\exp(J/kT)} \quad (1)$$

Polynuclear copper(II) complexes containing triazoles have been investigated because of the diverse magnetic properties with the J values ranging from -118 [2b] to 1.99 cm^{-1} [8d]. The superexchange integral J between adjacent metal ions comes from the contributions of the sum of both ferromagnetic (J_F) and antiferromagnetic (J_{AF}). There mainly exist two factors to control the value of J . Firstly, the σ -overlap density between the Cu(II) ions and ligand molecular orbitals is the main pathway to govern the super-

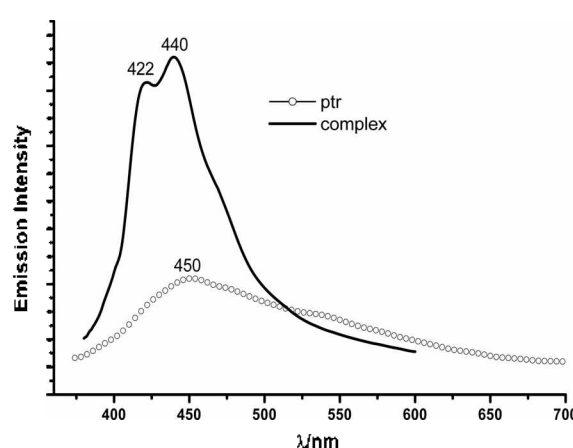


Figure 3. The solid-state electronic emission spectra of the title compound ($\lambda_{\text{ex}} = 361 \text{ nm}$) and the free ptr ligand ($\lambda_{\text{ex}} = 370 \text{ nm}$) recorded at room temperature.

exchange interaction. When metal atoms are bridged by polyatomic extended ligands like 1,2,4-triazoles, J_{AF} will hold the predominance increasing with the ratio to the square of the overlap integral between magnetic orbitals centered on nearest neighbor metal ions.¹⁰ Therefore, the 1,2,4-triazole rings twisting out of the equatorial plane formed by the two Cu(II) ions involved, is also expected to decrease the overlap of the magnetic orbitals in the bridging region.¹¹ Secondly, the Cu-N-N angles play an important role in the exchange interaction: a symmetric bridging model with the Cu-N-N angles close to 135° allows a larger antiferromagnetic interaction than the more asymmetric bridging model in a $\text{Cu}(\text{N-N})_2\text{Cu}$ framework.¹² It is consistent with the calculation made by A. Escuer [13b], showing that the antiferromagnetic component of J reaches its maximum for the parameters M-N-N 135° and N-M-N 90° . Though the N-Cu-N angles are around the 90° , but the Cu-N-N angles ($125.53(13)$ and $124.42(12)^\circ$) are large deviations from 135° decrease the value of J_{AF} . The overall result shows antiferromagnetic interaction between adjacent Cu(II) centers. Both antiferromagnetic and ferromagnetic interactions are reported in the complexes containing triazole ligands, indicating additional structural factors determining the sign and magnitude of J should be taken into consideration.

The fluorescent studies of 1,2,4-triazoles are very limited in contrast to the studies of magnetic properties. The title compound reported here show luminescent feature in the solid-state electronic emission spectrum at room temperature as given in Figure 3. It shows a dual broad emission: a high-energy band around 422 nm and a lower energy emission around 440 nm excited at 361 nm. Compared to the free ligand (blue fluorescence with the emission at 450 nm with $\lambda_{\text{ex}} = 370 \text{ nm}$),¹³ the emission peak at 440 nm is assigned to the π - π^* transition of the triazole rings. The other emission around at 422 nm can be assigned as ligand-to-metal transfer (LMCT).

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Supplementary material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-289958). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

- (a) van Koningsbruggen, P. J.; Haasnoot, J. G.; Kooijman, H.; Reedijk, J.; Spek, A. L. *Inorg. Chem.* **1997**, *36*, 2487. (b) Liu, J. C.; Fu, D. G.; Zhuang, J. Z.; Duan, C. Y.; You, X. Z. *J. Chem. Soc., Dalton Trans.* **1999**, 2337.
- (a) Gütlich, P.; Hauser, A.; Spierring, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024. (b) Kahn, O.; Kröber, J.; Jay, C. *Adv. Inorg. Chem.* **1992**, *4*, 718.
- Abbotto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Org. Lett.* **2002**, *4*, 1495.
- (a) Wiley, R. H.; Hart, A. J. *J. Org. Chem.* **1953**, *18*, 1368. (b) Foces-Foces, C.; Cabildo, P.; Claramunt, R. M.; Elguero, J. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1160.
- Rigaku *CrystalClear 1.3.6*. Software User's Guide for the Rigaku R-Axis, Mercury and Jupiter CCD Automated X-ray Imaging System; Rigaku Molecular Structure Corporation: Utah, USA, 2002.
- Siemens *SHELXTLTM* Version 5 Reference Manual; Siemens Energy & Automation Inc.: Madison, Wisconsin, USA, 1994.
- (a) Antolini, L.; Fabretti, A. C.; Gatteschi, D.; Giusti, A.; Sessoli, R. *Inorg. Chem.* **1991**, *30*, 4858. (b) Kolnaar, J. J. A.; van Dijk, G.; Kooijman, H.; Spek, A. L.; Ksenofontov, V. G.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 2433. (c) Garcia, Y.; Guionneau, P.; Bravic, G.; Chasseau, D.; Howard, J. A. K.; Khan, O.; Ksenofontov, V.; Reiman, S.; Gütlich, P. *Eur. J. Inorg. Chem.* **2000**, *39*, 1531. (d) Liu, J. C.; Song, Y.; Yu, Z.; Zhuang, J. Z.; Huang, X. Y.; You, X. Z. *Polyhedron* **1999**, *18*, 1491. (e) Vreugdenhil, W.; Haasnoot, J. G.; Reedijk, J.; Wood, J. S. *Inorg. Chim. Acta* **1990**, *167*, 109.
- (a) Drabent, K.; Ciunik, Z. *Chem. Commun.* **2001**, 1254. (b) Garcia, Y.; Koningsbruggen, P. J.; Bravic, G.; Chasseau, D.; Kahn, O. *Eur. J. Inorg. Chem.* **2003**, 356. (c) Garcia, Y.; van Koningsbruggen, P. J.; Bravic, G.; Guionneau, P.; Chasseau, D.; Cascarano, G. L.; Moscovici, J.; Lambert, K.; Michalowicz, A. *Inorg. Chem.* **1997**, *36*, 6357.
- (a) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313. (b) Brown, D. B.; Wasson, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2526.
- Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalle, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.
- Colacio, E.; Costes, J. P.; Kivekäs, R.; Laurent, J. P.; Ruiz, J. *Inorg. Chem.* **1992**, *31*, 774.
- (a) Slangen, P. M.; van Koningsbruggen, P. J.; Goubitz, K.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1994**, *33*, 1121. (b) Escuer, A.; Vicente, R.; Mernari, B.; Gueddi, A. E.; Pierrot, M. *Inorg. Chem.* **1997**, *36*, 2511.
- (a) Liu, B.; Li, B.; Zhang, X. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1677. (b) Liu, B.; Xu, L.; Guo, G. C.; Huang, J. S. *J. Mol. Struct.* **2006**, *825*, 79. (c) Liu, B.; Xu, L.; Guo, G. C.; Huang, J. S. *Inorg. Chem. Commun.* **2006**, *9*, 687. (d) Xu, L.; Guo, G. C.; Liu, B.; Fu, M. L.; Huang, J. S. *Acta Cryst. E60* **2004**, O1060.