

Crystal Structure and Electrochemical Property of Tetrazole Complex of Copper [Cu(pta)₂(NO₃)₂(H₂O)₂] (pta = 1-Phenyl-1H-tetrazole)

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A new compound, [Cu(pta)₂(NO₃)₂(H₂O)₂] (pta = 1-phenyl-1H-tetrazole) has been synthesized and characterized by IR, elemental analysis and single-crystal X-ray diffractions. X-ray structural analysis reveals that each Cu atom is coordinated by two pta molecules, two nitrate ions and two water molecules to form octahedral coordination geometry. O(1w) atoms of the water molecules serve as H-donor to interact with the nitrate oxygen atoms O(2), O(3) (H-acceptor) and form 1D hydrogen-bond ladder chains. These chains then, construct a 2D network layer *via* π - π stacking interactions between the five-membered ring of tetrazole and the six-membered ring of benzene. The 3D framework was constructed through the hydrogen bonds of C(7)-H(7A)···O(3). The behaviour of cyclic voltammetry of the compound on three-electrode cell showed an irreversible process.

Keywords: 1-Benzyltetrazole, Hydrogen bond, Crystal structure, Cyclic voltammetry.

INTRODUCTION

Tetrazolium and its derivatives have important applications in medicine, agriculture and imaging technology [1-3]. In particular, tetrazole derivatives have been widely used in photosensitive materials, which has aroused researchers interest [4-6]. For example, 1-phenyl-5-mercapto-1,2,3,4-tetrazole is a photosensitive material widely used in domestic and foreign production. Various synthetic methods of tetrazole have been reported [7-10]. Tetrazolium derivatives have been widely used in medicine and life science due to their unique structure and acid-base characteristics. Many of the physical, chemical and biological properties of tetrazole are related to its abnormally high acidity and weak alkalinity [11-13]. In fact, most of the medicinal applications of tetrazole come from the acidity of the tetrazole ring. Tetrazole rings are often found in antihypertensive, antiallergic and antimicrobial agents or candidates, or in anticonvulsive drugs used to treat cancer or AIDS [14-16]. In addition, tetrazole can be used in agriculture as plant growth regulators, herbicides and fungicides or as a stabilizer in photography and photographic imaging [17]. At the same time, the tetrazolium derivatives are also used in explosives, missile propellant and air bag gas generator due to their high decomposition

enthalpy [18,19]. On the other hand, all tetrazolium derivatives have good coordination performance and can form stable complexes with various metal ions. This capability has been successfully applied to analytical chemistry, removing heavy metal ions from liquids and preventing corrosion of metal pairs in chemical systems, *etc.* [20-22].

However, tetrazolium metal compound has less research reports due to its potential explosive properties. In this paper, 1-phenyl-5-mercaptotetrazole was used as ligand to synthesize Fe, Co, Ni, Cu, Cd and other metal complexes, and the crystal structure of Cu complexes was obtained. By analyzing its crystal structure, it was found that title compound formed a three-dimensional network structure by π - π and hydrogen bonds interactions. In addition, a preliminary electrochemical study was conducted on the title compound and the cyclic voltammetry curve was measured. It was found that the electrochemical behaviour on the gold electrode was an irreversible redox process.

EXPERIMENTAL

All the chemicals were of analytical reagent grade and used directly without further purification. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared

spectra were recorded on a Nicolet 170SX spectrometer using pressed KBr plates in the 4000-400 cm^{-1} ranges. Electronic spectra were taken on a UV-Vis-NIR spectrophotometer.

Electrochemical experiments were carried out using an Autolab potentiostat/galvanostat (Eco Chemie, B.V., Utrecht, The Netherlands). Data acquisition and potentiostat control were accomplished with a computer, running the GPES software Version 4.9. A three-electrode cell was used in the experiments. The working electrode was gold electrode ($\Phi = 3$ mm). The counter electrode was a platinum wire. The reference electrode was an Ag|AgCl|KCl (1 M) and all potentials reported in this work were measured *versus* this electrode (236.3 mV at 25 °C). The electrochemical were all carried out in DMF solution containing 0.1 M TBAP (tetrabutylammonium perchlorate). The experiments were in a thoroughly anaerobic condition by bubbling with high-purity argon (99.999 %). All measurements were performed at room temperature (25 ± 2 °C).

Preparation of $[\text{Cu}(\text{pta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$: 1-Phenyl-4,5-dihydro-1H-tetrazole-5-thiol was obtained by a known procedure and purified by ethanol [23]. 1-Phenyl-4,5-dihydro-1H-tetrazole-5-thiol (3.564 g, 0.02 mol) and NaOH (0.8 g, 0.02 mol) mixed and stirred at 0 °C in the solution of 1,4-dioxane for 0.5 h, then CS_2 (0.04 mol, 2.5 mL) was added dropwise. The reacting solution was stirred at > 5 °C for about 2 h. The yellow precipitate yielded and filtered. An aqueous solution 40 mL of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (4.83 g, 0.02 mol) and the yellow precipitate of xanthogenate $\text{phCN}_4\text{SCS}_2\text{Na}$ (0.02 mol) was mixed. The mixture was heated to reflux and kept for 4 h, then cooled to room temperature. The resultant solution was filtered and the green solution was concentrated from 40 mL to 20 mL under reduced pressure. The green prism single crystals suitable for X-ray analysis were obtained by slowly evaporating the solution in air about one night. Yield 4.31 g, 41.8 %. Elemental anal. calcd. (found) % for $\text{C}_{14}\text{H}_{16}\text{N}_{10}\text{O}_8\text{Cu}$: C, 32.56 (32.08); H, 3.10 (3.17); N, 27.13 (27.08). Selected IR data (KBr, ν_{max} , cm^{-1}): 3267 (m), 3102 (vs), 1594 (m), 1514 (vs), 1474 (w), 1356 (vs), 1229 (vs), 1087 (vs), 1053 (s), 1011 (s), 919 (w), 819 (m), 765 (vs), 689 (s).

Crystallographic study: The summary of key crystallographic information is given in Table-1. The cell dimensions were measured at 20 °C using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. A total of 2057 independent reflections were collected in the range of $2.06 < \theta < 26.96^\circ$, of which 1620 for reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. Both the structures were solved by direct methods and refined by least squares on F_{obs}^2 by using SHELXTL software package. All the non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. Final conventional $R(F) = 0.0339$ and $wR(F^2) = 0.0759$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma_2(\text{Fo}^2) + (0.0348\text{P})^2 + 0.1925\text{P}]$ where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$. The molecular graphics were plotted using SHELXTL.

RESULTS AND DISCUSSION

Crystal structures: Crystallographic analysis of complex, $[\text{Cu}(\text{pta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ revealed each copper(II) atom is coordinated to O, N atoms of two pta molecules, two nitrate ions

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT

Empirical formula	$\text{C}_{14}\text{H}_{16}\text{N}_{10}\text{O}_8\text{Cu}$
Formula weight	515.91
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 6.7090(13)$ Å, $\alpha = 99.72(3)^\circ$ $b = 7.6630(15)$ Å, $\beta = 98.77(3)^\circ$ $c = 10.2830(2)$ Å, $\gamma = 107.61(3)^\circ$
Volume (Å ³)	484.85
Z, Calculated density (Mg/m ³)	1, 1.767
Absorption coefficient (mm ⁻¹)	1.198
F(000)	263
Crystal size (mm)	$0.50 \times 0.23 \times 0.22$
Theta range for data collection (°)	2.06 to 26.96
Limiting indices	$0 \leq h \leq 7$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$
Reflections collected unique	2243/2057 [$R_{\text{int}} = 0.0211$]
Completeness to theta = 26.97	97.5 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2057/0/159
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0759$
R indices (all data)	$R_1 = 0.0577$, $wR_2 = 0.0840$
Largest diff. peak and hole ($e \cdot \text{Å}^{-3}$)	0.333 and -0.307

and two water molecules to form a regular centrosymmetric octahedral coordination geometry. The molecular structure of the complex is shown in Fig. 1. Selected bond lengths and bond angles are presented in Table-2. The Cu-O bond lengths vary from 1.988(2) to 2.408(2) Å, comparable with those of similar coordination complexes reported before [24,25]. The Cu-N distances are all 1.997(2) Å, which fall within the normal range, corresponding to the bond lengths in other six-coordinated Cu complexes [26]. The bond length of Cu(1)-O(1) is longer than the other coordination bond lengths of for Jahn-Teller elongation effect of Cu(II) center. So O(1) atoms occupy the axial position and O atoms of water and N atoms of pta occupy the equatorial positions. The bond angles of O(1w)#1-Cu(1)-O(1w), O(1)-Cu(1)-O(1)#1, N(1)#1-Cu(1)-N(1) are all 180°. Twenty-three atoms of 5-membered ring of tetrazole, benzene ring and Cu atom are nearly in one plane (P1) and the largest deviation from N(3) to the plane is 0.054 Å. The above plane (P1) is nearly perpendicular to the plane composed of Cu(1) atom, O(1) of the nitrate ion and O(1w) of water molecule, and the dihedral angle is 89.58°.

The salient feature in the crystal packing of title compound is that there are some intermolecular, intramolecular hydrogen

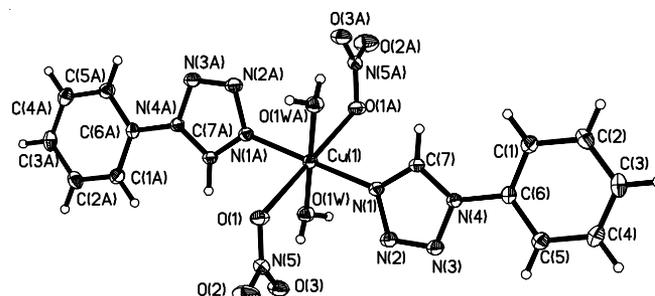


Fig. 1. Molecular structure of $[\text{Cu}(\text{pta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ showing the atom labeling scheme. Atoms are represented as thermal ellipsoids at 30 % level

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

Bond	Dist.	Bond	Dist	Angle	(°)	Angle	(°)
Cu(1)-O(1W)#1	1.988(2)	Cu(1)-O(1W)	1.988(2)	O(1W)#1-Cu(1)-O(1W)	180.0	O(1W)#1-Cu(1)-N(1)#1	91.81(9)
Cu(1)-O(1)	2.408(2)	Cu(1)-O(1)#1	2.408(2)	O(1)-Cu(1)-O(1)#1	180.0(1)	O(1W)-Cu(1)-N(1)#1	88.19(9)
Cu(1)-N(1)#1	1.997(2)	Cu(1)-N(1)	1.997(2)	N(1)#1-Cu(1)-N(1)	180.0	O(1W)#1-Cu(1)-N(1)	88.19(9)
O(1)-N(5)	1.248(3)	O(2)-N(5)	1.246(3)	O(1W)-Cu(1)-N(1)	91.81(9)	O(1W)-Cu(1)-O(1)	86.40(9)
O(3)-N(5)	1.250(3)	N(1)-C(7)	1.315(3)	O(1W)#1-Cu(1)-O(1)	93.60(9)	N(1)-Cu(1)-O(1)	91.24(8)
N(4)-C(7)	1.330(3)	N(4)-C(6)	1.440(3)	N(1)#1-Cu(1)-O(1)	88.76(8)	O(1W)-Cu(1)-O(1)#1	93.60(9)
				O(1W)#1-Cu(1)-O(1)#1	86.40(9)	N(1)-Cu(1)-O(1)#1	88.76(8)
				N(1)#1-Cu(1)-O(1)#1	91.24(8)	N(5)-O(1)-Cu(1)	125.99(8)
				C(7)-N(1)-Cu(1)	129.97(7)	N(2)-N(1)-Cu(1)	123.40(9)
				O(2)-N(5)-O(3)	118.9(2)	N(1)-C(7)-N(4)	108.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

bonds and π - π stacking interactions. The hydrogen bonding interactions of O-H...O form a 1D infinite supramolecular ladder chains along *c*-direction. The hydrogen bonds and bond angles list in Table-3. Two [Cu(pta)₂(NO₃)₂(H₂O)₂] molecule units are interconnected *via* intermolecular hydrogen bonds of O(1w)-H(2)...O(2) (the distance for donor and acceptor is 2.792 Å). The intermolecular hydrogen bonds of O(1w)-H(2)...O(2) and the intramolecular hydrogen bonds of O(1w)-H(1)...O(3) (the distance for D-A is 2.709 Å) construct the side of the ladder. Two water molecules, two nitrate ions and copper atom form crossbars. The planes that pta molecules located are nearly vertical to the plane of ladder chain. The supramolecular framework is shown in Fig. 2.

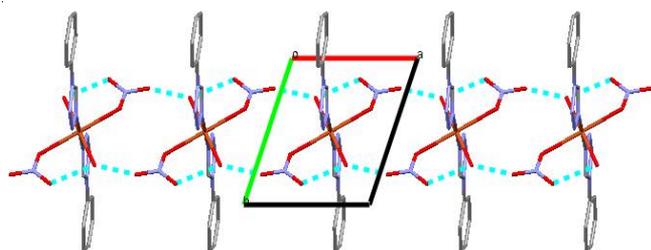


Fig. 2. A view of 1D infinite ladder chains formed by H-bonding (gray dotted lines) along the *c* axis, pta molecule and H atoms omitted for clarity

The pta molecules stagger in two paralleled hydrogen bond chains. Therefore, the 1D infinite supramolecular hydrogen bond chains construct two-dimension layer motif through π - π stacking interactions along *b*-direction in Fig. 3. There are four π - π stacking interactions between the five-membered ring of tetrazole (Cg1) and the six-membered ring of benzene (Cg2). The π - π interactions of the title compound list in Table-4. The face-to-face distances are from 3.578 to 3.742 Å. The planes, which the hydrogen bond ladder chains located, are nearly perpendicular to the 2D network plane. In addition, the ladders fused with the sheet through the metal atoms of copper.

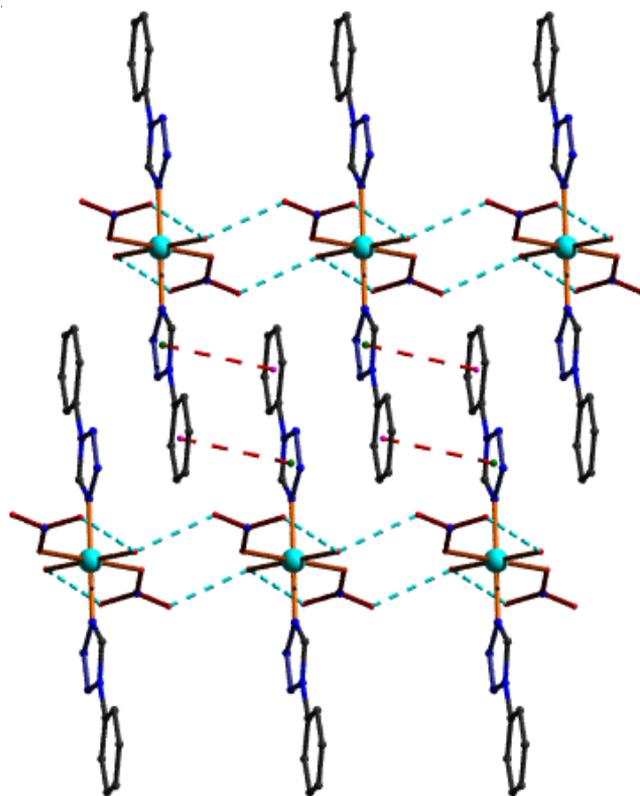


Fig. 3. A molecular packing diagram along the *b* axis. Intermolecular hydrogen bonds are shown with turquoise lines. Intermolecular π - π interactions are shown with thick red lines

The layer motifs were connected to three dimensions supramolecular architectures through the intermolecular hydrogen bonds of C(7)-H(7A)...O(3) (D-A distance is 3.168 Å) in Fig. 4. The C atoms of tetrazole serve as the donor and the O of nitrate radical serve as acceptor.

Electrochemical studies: The cyclic voltammetry behaviour of the title complex is studied and the result is shown in Fig. 5. The title complex had a pair of redox peaks at -0.820 V and

 TABLE 3
 HYDROGEN BOND GEOMETRY (Å, °) FOR THE TITLE COMPOUND

Donor-H...Acceptor	symm	D-H	H...A	D...A	D-H...A H...A
Intra O(1W) - H(1)...O(3)		0.7797	1.9708	2.7088	157.80
O(1W) - H(2)...O(2)	1+x, y, z	0.8228	2.0117	2.7926	158.25
Intra C(5) - H(5A)...N(3)		0.9300	2.4770	2.8004	100.53
C(7) - H(7A)...O(3)	x,-1+y,z	0.9300	2.2884	3.1680	157.56

ring(i)	ring(j)	symm	Cg-Cg	CgI_perp	CgJ_perp
Cg(1)	Cg(2)	-X,-Y,-Z	3.578	3.387	3.318
Cg(1)	Cg(2)	1-X,-Y,-Z	3.742	3.284	3.385
Cg(2)	Cg(1)	1-X,-Y,-Z	3.578	3.318	3.387
Cg(2)	Cg(1)	1-X,-Y,-Z	3.742	3.385	3.284

^aCg(1)=N(1)-N(2)-N(3)-N(4)-C(7); Cg(2)=C(1)-C(2)-C(3)-C(4)-C(5)-C(6); Cg-Cg = Distance between ring Centroids.
CgI_Perp = Perpendicular distance of Cg(I) on ring J CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

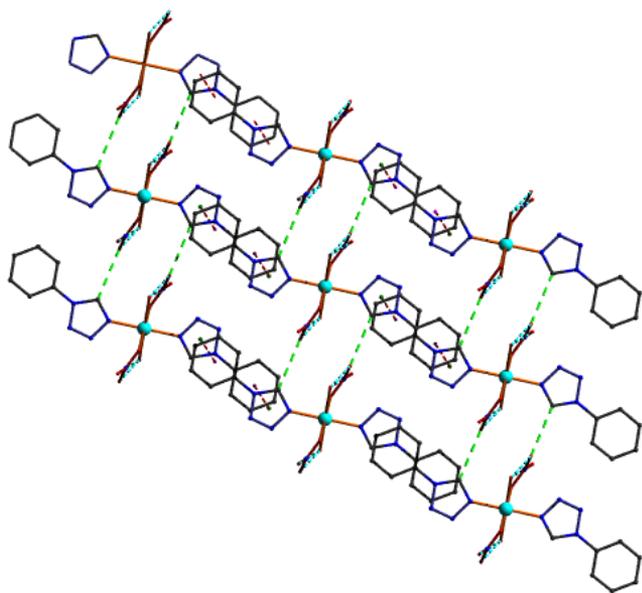
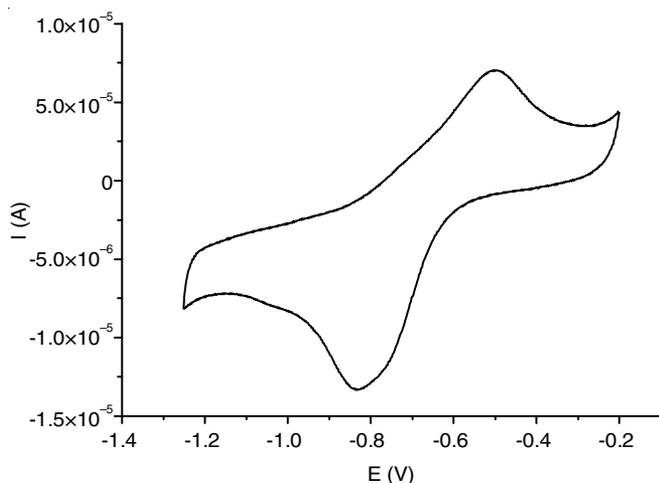
Fig. 4.A view of the 3-D crystal stacking along the *a* axis

Fig. 5. Cyclic voltammograms of the title complex in DMF solution containing 0.1 M TBAP at a scan rate of 50 mV/s

-0.508 V, and the formal potential (E°) was calculated to be -0.664 V, with the formula $E^{\circ} = (E_{pc} + E_{pa})/2$. The separation of the cathodic and anodic peak potential, $\Delta E = 0.312$ V, $i_{pa}/i_{pc} = 1.67$ indicated that the electrochemical behaviour of the title complex on gold electrode was an irreversible process. Fig. 6 shows the cyclic voltammogram obtained by scanning at different rates. It can be seen that the peak current increases with the increase of scanning rate and has a good linear relationship (Fig. 6).

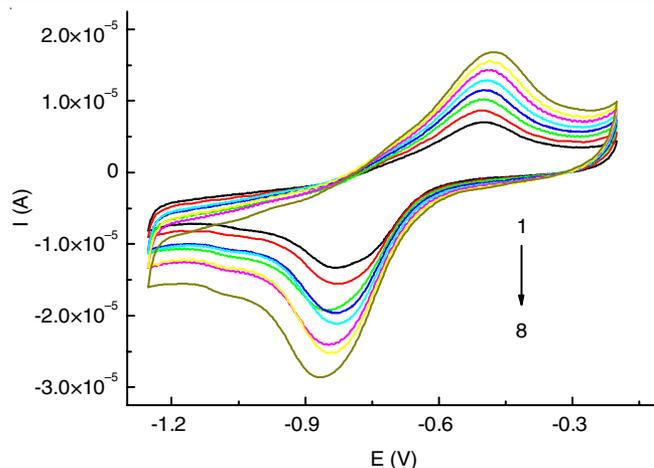


Fig. 6. Cyclic voltammograms of the title complex in DMF solution containing 0.1 M TBAP at a scan rate from 0.05-0.12 V/s

Conclusion

Tetrazolium compound has less research reports due to its potential explosive properties. A series of tetrazolium metal complexes were obtained by the synthesis of desulfhydryl. The single crystals of $\text{Cu}(\text{pta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ were obtained. By analyzing its crystal structure, we found that the complex formed a three-dimensional network structure by supramolecular forces such as intermolecular hydrogen bonds and π - π interaction. In addition, a preliminary electrochemical study was conducted on the title complex, and the cyclic voltammetry curve was measured. It was found that the electrochemical behaviour on the gold electrode was an irreversible redox process.

Supplementary materials

"CCDC-708642 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email:deposit@ccdc.cam.ac.uk".

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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