

# A new copper(II) chelate complex with tridentate ligand: Synthesis, crystal and molecular electronic structure of aqua-(diethylenetriamine-N, N', N'')-copper(II) sulfate monohydrate and its fire retardant properties



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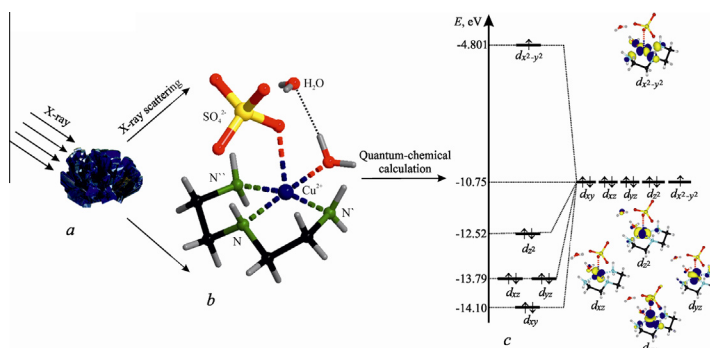
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## HIGHLIGHTS

- The crystals of a new chelate compound of  $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$  (1) have been synthesized.
- The X-ray (single crystal and powder) structure of 1 has been determined.
- The molecular electronic structure of 1 has been calculated by quantum-chemical method.
- The fire-retardant properties of 1 in solid state have been considered.

## GRAPHICAL ABSTRACT

X-ray and quantum-chemical investigation of **1**: (a) view of the synthesized single crystals; (b) discrete unit of copper(II) chelate complex; (c) 3d-AOs splitting by square-pyramidal crystal field in chelate-bonded  $\text{Cu}^{2+}$  ion.



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## ABSTRACT

The crystals of a new aqua-(diethylenetriamine-N, N', N'')-copper(II) sulfate monohydrate have been synthesized by direct interaction of solid copper(II) sulfate pentahydrate with diethylenetriamine (*deta*). The crystal structure of  $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$  (1) has been determined by X-ray diffraction methods at 100 K and characterized using X-ray powder diffraction pattern: space group  $P\bar{1}$ ,  $a = 7.2819(4)$ ,  $b = 8.4669(4)$ ,  $c = 8.7020(3)$  Å,  $\alpha = 83.590(3)$ ,  $\beta = 89.620(4)$ ,  $\gamma = 84.946(4)^\circ$ ,  $Z = 2$ . The environment of the Cu(II) atom is a distorted, elongated square pyramid which consists of three nitrogen atoms of the *deta* molecule and oxygen atom of the water molecule in the basal plane of the square pyramid (the average lengths of the in-plane Cu–N and Cu–O bonds are 2.00 Å). The apical position of the coordination polyhedron is occupied by complementary oxygen atom of the sulfate anion (the length of the axial Cu–O bond is 2.421(1) Å). The crystal packing is governed by strong hydrogen bonds of O–H...O and N–H...O types. The *ab initio* quantum-chemical calculations have been performed by the restricted Hartree–Fock method with a basis set 6-31\*G using the structural data of  $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ . It has been ascertained that the degenerate *d*-orbitals of the  $\text{Cu}^{2+}$  ion split under the co-action of both the square-pyramidal coordination and the chelation. It is significant that visually observed crystals color (blue-violet) of the

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[Cu(*deta*)H<sub>2</sub>O]SO<sub>4</sub>·H<sub>2</sub>O complex is in good agreement with the calculated value of wavelength of visible light ( $\lambda = 5735 \text{ \AA}$ ) which is closely related to the energy of the absorbed photon ( $\Delta = 2.161 \text{ eV}$ ). Furthermore, the stereo-chemical aspect of influence of the CuSO<sub>4</sub> upon combustibility of modified epoxy-amine polymers has been scrutinized.

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## Introduction

The study of a complexation of salts of transition metals (in particular, of copper salts in the oxidation states +1 and +2) with polyamines in a combination with determination their crystal and molecular electronic structure is one of major research trends of modern chemistry. Currently, complexes of this type are commonly used as catalysts [1–6] and models of the active centers of copper-containing enzymes [7,8]. They also serve as a basis for new types of luminescent materials [9,10] and are constituent of polymeric matrices of epoxy resins having the decreased combustibility [11] as well as they possess many other useful properties [12–17]. So, it is well-known that copper salts for a long time have used as catalysts of many transformations of various derivatives of hydrocarbons [18]. However, besides catalytic activity, salts of copper(I) and copper(II) also can be used for effective suppression of the inflammation of nitrogen-containing hydrocarbons (e.g. amines, nitriles) [11]. The crucial role in the process of suppressing of a flame belongs to chemical interaction which, in many respects, predetermines formation of virtually non-flammable copper(II) complex. From this point of view, the copper–nitrogen interlinking should be considered as a principal cause of effective inhibition of burning of nitrogen-containing hydrocarbons occurring in the presence of copper salts. It opens up new vistas of using of copper salts in production of self-extinguishing epoxy-amine composites [19]. On the other hand, the structural multiplicity of copper complexes known in the literature [20,21] is illustrated by large quantity of Cu–N type interactions where nitrogen-containing polydentate ligands demonstrate exceptional ability to form chelate complexes in which the arisen heterocyclic fragments stabilize the structure as a whole. In this regard, it would be interesting to study the interaction between solid cupric salts and polyamines, to research the influence of the electronic structure of inorganic substances and denticity of organic ligands onto stoichiometry and stereochemistry of nascent chelate complexes as well as to discuss ability of copper(II) salts to the suppress of flammability of epoxy-amine resins.

Previously, crystals of Cu(II) chelate complexes with tridentate ligands (diethylenetriamine – *deta*) were obtained and structurally characterized mostly for copper(II) perchlorate ([Cu<sub>2</sub>(*deta*)<sub>2</sub>(4,4'-bipyridine)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> [22], [Cu<sub>2</sub>(*deta*)<sub>2</sub>(pyrazine)(ClO<sub>4</sub>)<sub>4</sub>] [23], [Cu(*deta*)(2-methylimidazole)ClO<sub>4</sub>](ClO<sub>4</sub>) [24], [Cu(*deta*)(2-phenylimidazole)ClO<sub>4</sub>](ClO<sub>4</sub>) [25] and [Cu(*deta*)(1,10-phenantroline)](ClO<sub>4</sub>)<sub>2</sub> [26]), copper(II) tetrafluoroborate ([Cu(*deta*)(2,2'-bipyridine)](BF<sub>4</sub>)<sub>2</sub> [26]) and copper(II) nitrate ([Cu(*deta*)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [27], [Cu<sub>2</sub>Cl<sub>2</sub>(*deta*)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [28] and [Cu(*deta*)(2-cyanoguanidine)](NO<sub>3</sub>)<sub>2</sub> [29]). Distinguishing feature of all these extremely stable complexes is formation of the pentatomic rings within the coordination core of Cu(II) where *deta* partially surrounds and strongly connects the central atom (the chelate effect). Given the fact that among investigated complexes of cupric salts and *deta* the analogous complexes with CuSO<sub>4</sub> were not known, we undertook an attempt to study interaction of *deta* with copper(II) sulfate whose anhydrous salt, by the way, has been employed by us as a fire-retardant agent for development of self-extinguishing epoxy-amine polymers [19]. Therefore synthesis, X-ray crystal structure determination (single crystal and powder) of [Cu(*deta*)H<sub>2</sub>O]SO<sub>4</sub>·H<sub>2</sub>O chelate complex

(1) and the quantum-chemical calculations of its molecular electronic structure as well as the stereo-chemical aspect of influence of the copper(II) sulfate upon combustibility of modified epoxy-amine polymers are described in this article.

## Experimental

### Materials

The chemicals: CuSO<sub>4</sub>·5H<sub>2</sub>O (copper vitriol) and the mixture of polyethylenepolyamines (epoxy hardener) containing diethylenetriamine (*deta*) were obtained from commercial sources and used as-received without further purification.

### Synthesis of [Cu(*deta*)H<sub>2</sub>O]SO<sub>4</sub>·H<sub>2</sub>O

The crystals of aqua-(diethylenetriamine-N, N', N'')-copper(II) sulfate monohydrate (1) have been synthesized by direct interaction of solid copper(II) sulfate pentahydrate with the mixture of polyethylenepolyamines (*pepa* – H<sub>2</sub>N[–C<sub>2</sub>H<sub>4</sub>NH–]<sub>n</sub>H, where  $n = 2–6$ ) containing diethylenetriamine (*deta* – H<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>). Crystalline CuSO<sub>4</sub>·5H<sub>2</sub>O (1.25 g, 5 mmol) has been placed into a porcelain mortar and 1 mL of the mixture of *pepa* was added to it. Content of the mortar was triturated till the appearance of a homogeneous blue-violet liquid suspension. This thick liquid was left for a few days at the room temperature to obtain blue-violet crystals of the title compound.

**Table 1**  
Crystal data and experimental details for the single crystal sample of 1.

Empirical formula	C <sub>4</sub> H <sub>17</sub> Cu <sub>1</sub> N <sub>3</sub> O <sub>6</sub> S <sub>1</sub>
Formula weight	298.81 g mol <sup>−1</sup>
Color, shape	Blue-violet, prism
Crystal size	0.37 × 0.37 × 0.37 mm
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Unit cell parameters:	<i>a</i> = 7.2819(4) Å <i>b</i> = 8.4669(4) Å <i>c</i> = 8.7020(3) Å $\alpha$ = 83.590(3)° $\beta$ = 89.620(4)° $\gamma$ = 84.946(4)°
Volume	<i>V</i> = 531.09(4) Å <sup>3</sup>
<i>Z</i>	2
Calculated density	1.869 g cm <sup>−3</sup>
<i>F</i> (000)	310
Absorption coefficient	2.268 mm <sup>−1</sup>
$2\theta_{\min}/2\theta_{\max}$	6.38/58.68°
Limiting indices	$-9 \leq h \leq 9, -11 \leq k \leq 11, -11 \leq l \leq 9$
Measured reflections	4323
Unique reflections	2585
Used in refinement reflections	2475
Free parameters	172
<i>R</i> <sub>int</sub> , <i>R</i> <sub>σ</sub>	0.0086, 0.0121
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0193, w <i>R</i> <sub>2</sub> = 0.0544
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0204, w <i>R</i> <sub>2</sub> = 0.0559
Weighing scheme	$w = [\sigma^2(F_o^2) + (0.0375P)^2 + 0.3418P]^{-1}$ , where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.000
Largest diff. peak and hole	0.366 and −0.577 e Å <sup>−3</sup>

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