

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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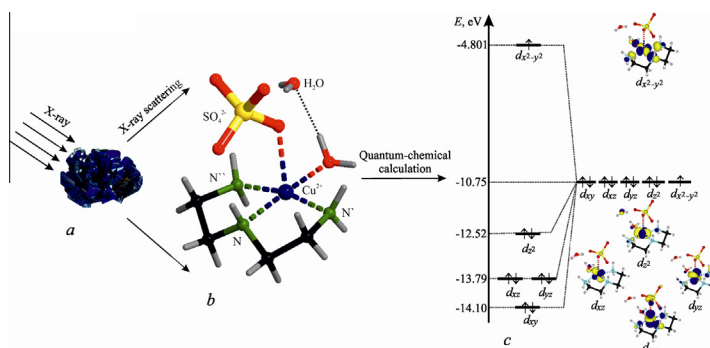
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HIGHLIGHTS

- 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 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 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*)H₂O]SO₄·H₂O 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 CuSO₄ 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 ([Cu₂(*deta*)₂(4,4'-bipyridine)(ClO₄)₂)(ClO₄)₂ [22], [Cu₂(*deta*)₂(pyrazine)(ClO₄)₄] [23], [Cu(*deta*)(2-methylimidazole)ClO₄](ClO₄) [24], [Cu(*deta*)(2-phenylimidazole)ClO₄](ClO₄) [25] and [Cu(*deta*)(1,10-phenantroline)](ClO₄)₂ [26]), copper(II) tetrafluoroborate ([Cu(*deta*)(2,2'-bipyridine)](BF₄)₂ [26]) and copper(II) nitrate ([Cu(*deta*)₂](NO₃)₂ [27], [Cu₂Cl₂(*deta*)₂](NO₃)₂ [28] and [Cu(*deta*)(2-cyanoguanidine)](NO₃)₂ [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 CuSO₄ 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*)H₂O]SO₄·H₂O 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: CuSO₄·5H₂O (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*)H₂O]SO₄·H₂O

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* – H₂N[–C₂H₄NH–]_nH, where $n = 2–6$) containing diethylenetriamine (*deta* – H₂NC₂H₄NHC₂H₄NH₂). Crystalline CuSO₄·5H₂O (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 ₄ H ₁₇ Cu ₁ N ₃ O ₆ S ₁
Formula weight	298.81 g mol ^{−1}
Color, shape	Blue-violet, prism
Crystal size	0.37 × 0.37 × 0.37 mm
Crystal system, space group	Triclinic, $P \bar{1}$
Unit cell parameters:	$a = 7.2819(4) \text{ \AA}$ $b = 8.4669(4) \text{ \AA}$ $c = 8.7020(3) \text{ \AA}$ $\alpha = 83.590(3)^\circ$ $\beta = 89.620(4)^\circ$ $\gamma = 84.946(4)^\circ$
Volume	$V = 531.09(4) \text{ \AA}^3$
Z	2
Calculated density	1.869 g cm ^{−3}
F(000)	310
Absorption coefficient	2.268 mm ^{−1}
$2\theta_{\min}/2\theta_{\max}$	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
$R_{\text{int}}, R_{\sigma}$	0.0086, 0.0121
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0193, wR_2 = 0.0544$
R indices (all data)	$R_1 = 0.0204, wR_2 = 0.0559$
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 F^2	1.000
Largest diff. peak and hole	0.366 and $-0.577 \text{ e \AA}^{-3}$

Table 2
The positional and displacement parameters of **1**.

Atom	x	y	z	$U_{eq}, \text{\AA}^2$ ^a
Cu1	0.71960(2)	0.85961(2)	0.69058(2)	0.00646(6)
S1	1.20306(4)	0.80561(4)	0.76287(4)	0.00597(8)
O1	0.6571(2)	1.0949(1)	0.6436(1)	0.0089(2)
O2	0.9187(2)	1.1939(1)	0.8136(1)	0.0127(2)
O3	1.0415(1)	0.9101(1)	0.6965(1)	0.0124(2)
O4	1.1591(1)	0.6397(1)	0.7881(1)	0.0119(2)
O5	1.3620(1)	0.8226(1)	0.6555(1)	0.0100(2)
O6	1.2548(1)	0.8613(1)	0.9121(1)	0.0141(2)
N1	0.7688(2)	0.6233(1)	0.7361(1)	0.0075(2)
N2	0.7452(2)	0.8218(1)	0.4671(1)	0.0080(2)
N3	0.6590(2)	0.8546(1)	0.9167(1)	0.0092(2)
C1	0.8010(2)	0.6503(2)	0.4598(2)	0.0117(3)
C2	0.7153(2)	0.5552(2)	0.5964(2)	0.0098(3)
C3	0.6716(2)	0.5728(2)	0.8805(2)	0.0092(3)
C4	0.7079(2)	0.6908(2)	0.9941(2)	0.0113(3)
H011	0.736(3)	1.137(3)	0.690(3)	0.021(5)
H012	0.665(4)	1.117(3)	0.550(3)	0.040(7)
H021	0.978(4)	1.117(3)	0.804(3)	0.026(6)
H022	0.879(3)	1.188(3)	0.891(3)	0.024(6)
HN11	0.887(3)	0.605(3)	0.752(2)	0.017(5)
HN21	0.644(3)	0.844(2)	0.421(2)	0.012(5)
HN22	0.830(3)	0.877(3)	0.427(3)	0.023(6)
HN31	0.537(3)	0.873(3)	0.915(2)	0.019(5)
HN32	0.712(3)	0.927(3)	0.970(2)	0.017(5)
H1A	0.934	0.631	0.464	0.014
H1B	0.759	0.618	0.363	0.014
H2A	0.582	0.564	0.586	0.012
H2B	0.760	0.443	0.602	0.012
H3A	0.718	0.466	0.922	0.011
H3B	0.540	0.574	0.861	0.011
H4A	0.634	0.672	1.086	0.014
H4B	0.837	0.678	1.024	0.014

^a $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (\bar{a}_i \bar{a}_j)$, for H atoms – U_{iso} .

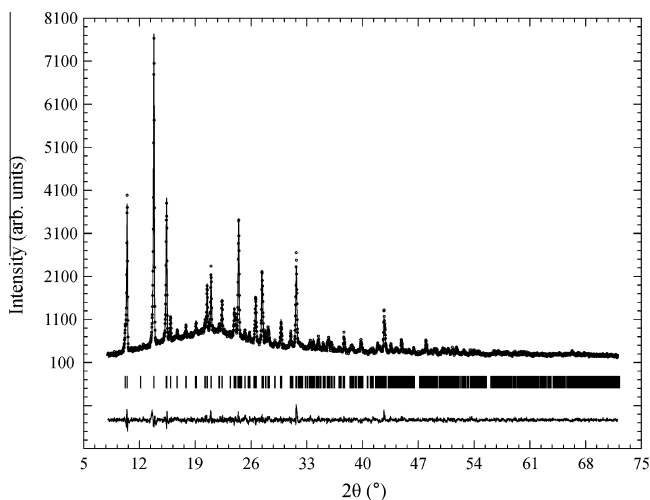


Fig. 1. Experimental (circles), calculated (continuous line) and difference (continuous line at the bottom of the figure) diffractograms of the polycrystalline sample of **1**. Vertical lines show the positions of the reflections.

Single crystal X-ray diffraction analysis

A single crystal of **1** was mounted on the Xcalibur diffractometer (Mo $K\alpha$ -radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator) equipped with an Oxford Cryosystem cooler and a CCD detector. 180 ω oscillation images with a frame width of 0.5° and an exposure time of 20 s was collected at 100.0(1) K using crystal-to-detector distance of 60 mm. After integration the data were corrected for Lorentz and polarization effects [30]. Unit cell parameters were obtained by a least-squares refinement based on reflection angles

Table 3
Crystal data and experimental details for the polycrystalline sample of **1**.

Unit cell parameters	$a = 7.3043(2) \text{ \AA}$ $b = 8.5456(3) \text{ \AA}$ $c = 8.7152(3) \text{ \AA}$ $\alpha = 83.789(3)^\circ$ $\beta = 89.433(5)^\circ$ $\gamma = 85.064(5)^\circ$
Volume	$V = 538.801(9) \text{ \AA}^3$
Calculated density	1.842 g cm^{-3}
Preferred orientation parameter, $[hkl]$	$0.972(6), [011]$
Scan range 2θ	$20\text{--}110^\circ$
Step	0.020°
Exposition time	20 s
Profile parameters U, V, W	$0.227(16), -0.112(7), 0.0222(8)$
Mixing parameter η	0.809(14)
Asymmetry parameters A_1, A_2	$0.050(2), 0.0306(7)$
R indices	$R_B = 0.0489, R_F = 0.0476, R_p = 0.0455,$ $R_{wp} = 0.0589$
χ^2	1.82

Table 4
Results of the quantum-chemical calculation of energies.

Particle composition	Total energy (kJ mol^{-1})	Integrated energy of all bonds (kJ mol^{-1})
$[\text{Cu}(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$	620049.48	10085.29
$\text{SO}_4^{2-} \cdot \text{H}_2\text{O}$	250730.28	1957.91
$\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$	180110.01	7105.54
H_2O	47319.49	684.52

in the range $6.4 < 2\theta < 58.7^\circ$. Structure **1** was solved by direct methods applying SHELX software package [31]. Other non-hydrogen atoms as well as the hydrogen atoms of water molecules and amino groups were located from the Fourier difference synthesis and refined by least-squares method in the full-matrix anisotropic (non-hydrogen atoms) and isotropic (hydrogen atoms) approximation. The methylene hydrogen atoms were placed geometrically and refined as riding atoms with C–H, 0.97 \AA , and with isotropic temperature factors of 1.2 times the U_{eq} value of the parent carbon atoms. The crystallographic data for the compound **1** as well as details of

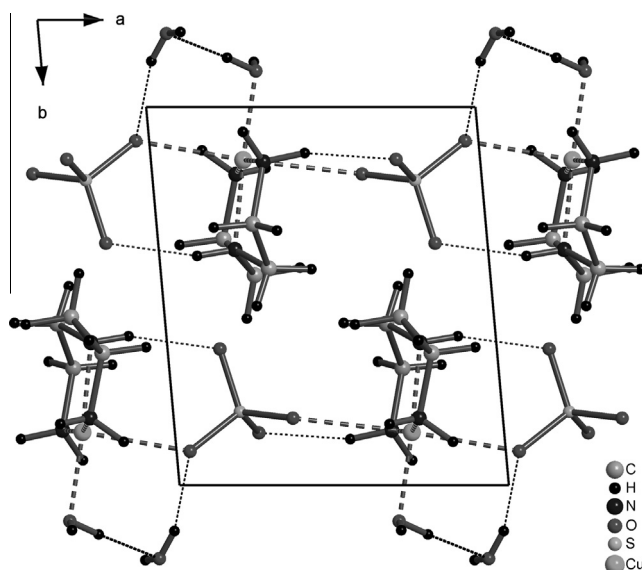


Fig. 2. Projection of structure **1** along the crystallographic direction $[001]$.

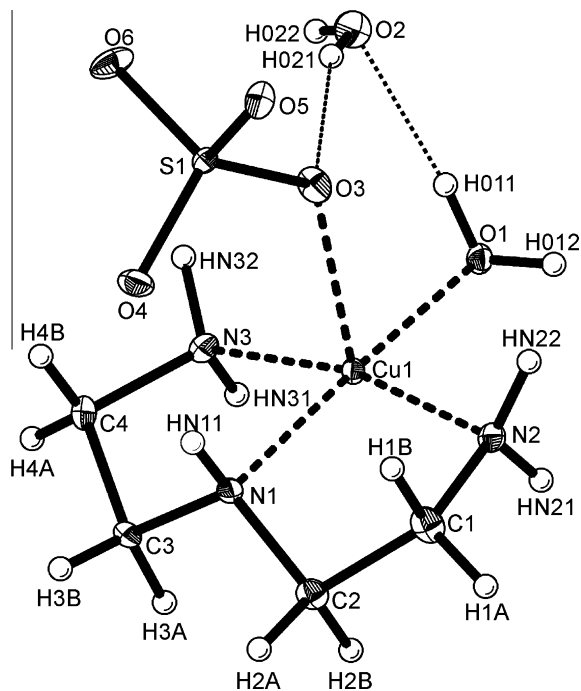


Fig. 3. Numbering system of the $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ discrete unit in **1**. Thermal ellipsoids are shown with the 50% probability level for non-hydrogen atoms.

the structural refinement are listed in the Table 1. The positional and thermal displacement parameters are printed in the Table 2. The figures were prepared using DIAMOND program [32].

Powder X-ray diffraction analysis

The powder X-ray diffraction pattern (Fig. 1) of the polycrystalline sample of **1** has been obtained for phase identification. The experiment was carried out at room temperature on the DRON-3 M diffractometer (Cu $K\alpha$ -radiation, Bragg–Brentano geometry, angular range $8 \leq 2\theta \leq 72^\circ$, step 0.02° and exposition time per point 20 s).

The profile and structural parameters were refined by the Rietveld method using the package of program FullProf Suite [33]. Structure model was taken from single crystal data. The

Table 5
The bond lengths and bond angles in **1**.

Bond	<i>d</i> (Å)	Angle	ω (°)
Cu1–N1	1.997(1)	N1–Cu1–O1	177.15(5)
Cu1–N2	2.010(1)	N1–Cu1–N2	85.58(5)
Cu1–N3	2.011(1)	N1–Cu1–N3	85.07(5)
Cu1–O1	2.001(1)	N1–Cu1–O3	94.51(4)
Cu1–O3	2.421(1)	N2–Cu1–N3	166.88(5)
S1–O3	1.487(1)	N2–Cu1–O3	89.82(4)
S1–O4	1.461(1)	N3–Cu1–O3	100.07(4)
S1–O5	1.489(1)	O1–Cu1–N2	94.18(5)
S1–O6	1.491(1)	O1–Cu1–N3	94.70(5)
N1–C2	1.471(2)	O1–Cu1–O3	88.32(4)
N1–C3	1.478(2)	O3–S1–O4	110.49(6)
N2–C1	1.482(2)	O3–S1–O5	108.94(6)
N3–C4	1.487(2)	O3–S1–O6	108.63(6)
C1–C2	1.522(2)	O4–S1–O5	110.77(6)
C3–C4	1.522(2)	O4–S1–O6	110.21(6)
O1–H011	0.83(3)	O5–S1–O6	107.72(6)
O1–H012	0.82(3)	C2–N1–C3	116.6(1)
O2–H021	0.76(3)	N1–C2–C1	106.7(1)
O2–H022	0.73(2)	N1–C3–C4	106.7(1)
N1–HN11	0.87(2)	N2–C1–C2	108.3(1)
N2–HN21	0.84(2)	N3–C4–C3	108.1(1)
N2–HN22	0.86(2)	H011–O1–H012	111(3)
N3–HN31	0.89(2)	H021–O2–H022	109(3)
N3–HN32	0.92(2)	HN11–N1–C2	110(1)
C1–H1A	0.97(1)	HN11–N1–C3	109(1)
C1–H1B	0.97(1)	HN21–N2–HN22	113(2)
C2–H2A	0.97(1)	HN31–N3–HN32	111(2)
C2–H2B	0.97(1)	H1A–C1–H1B	108(1)
C3–H3A	0.97(1)	H2A–C2–H2B	109(1)
C3–H3B	0.97(1)	H3A–C3–H3B	109(1)
C4–H4A	0.97(1)	H4A–C4–H4B	108(1)
C4–H4B	0.97(1)		

Table 6
Hydrogen bonds parameters (in Å and °).

H-bonds ^a	D–H	H···A	D···A	D–H···A
O1–H011···O	0.83(2)	1.85(2)	2.668(2)	169(2)
O2–H021···O3	0.76(3)	2.09(3)	2.788(2)	152(3)
N1–HN11···O4	0.87(2)	2.06(2)	2.899(2)	162(2)
N3–HN31···O6 ⁱ	0.89(2)	2.07(2)	2.940(2)	167(3)
N2–HN21···O1 ⁱⁱ	0.84(2)	2.27(2)	3.086(2)	166(2)
N2–HN22···O3 ⁱⁱⁱ	0.86(2)	2.27(2)	3.077(2)	158(2)
O1–H012···O5 ⁱⁱⁱ	0.82(3)	1.81(2)	2.620(2)	169(2)
O2–H022···O6 ^{iv}	0.73(2)	1.99(2)	2.707(1)	169(3)
N3–HN32···O6 ^{iv}	0.92(2)	2.19(2)	3.078(2)	161(2)

^a Symmetry codes: (i) $-1+x, y, z$; (ii) $1-x, 2-y, 1-z$; (iii) $2-x, 2-y, 1-z$; (iv) $2-x, 2-y, 2-z$.

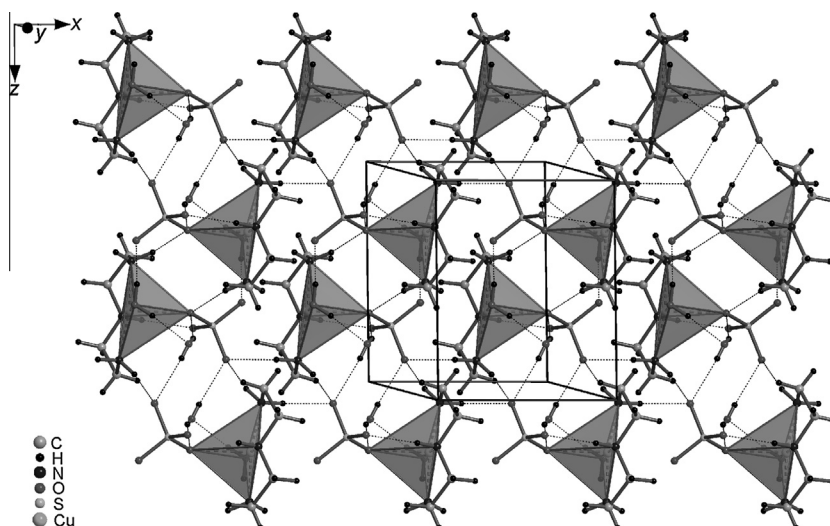


Fig. 4. Crystal packing of **1** into layers oriented perpendicularly to the $[010]$ direction with presented square-pyramidal coordination of Cu(II). Hydrogen bonds are shown as dotted lines.

calculation results of the powder X-ray diffraction pattern are given in Table 3.

Quantum-chemical analysis

Numerical modeling of the electronic structure and construction of the molecular orbitals (MO) diagram [34] were carried out for **1**. The *ab initio* quantum-chemical calculations (the restricted Hartree–Fock method with a basis set 6-31*G) were performed using the HyperChem program version 8.0.6 [35]. Initial crystallographic data about the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [36] and **1** were used for the designing of $\{[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}\}$ and $\{[\text{Cu}(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}\}$ discrete clusters as well as for the constructing of free diethylenetriamine molecule. Calculation of charge density on atoms was performed without optimization of these structural fragments. All calculations were carried out under the hypothesis that the presented clusters and *deta* molecule exist as isolated particles in vacuum. The results of the quantum-chemical calculation of the binding energy in discrete cluster of **1** and in its segregate particles are given in Table 4.

Results and discussion

Crystal structure of $[\text{Cu}(\text{deta})(\text{H}_2\text{O})\text{SO}_4 \cdot \text{H}_2\text{O}$

It is known that under certain conditions the nitrogen-containing tridentate ligands (e.g. diethylenetriamine) can be linked with cupric salts into the chelate complexes where all three amine groups of organic molecule are fastened (σ bonds) to the central Cu(II) atom by forming peculiar heterocyclic rings. At the same time, the chelate effect predetermines the structure of formed complexes having the general composition $\text{CuX}_2 \cdot \text{deta} \cdot \text{L}$ (X – ClO_4^- , BF_4^- , NO_3^- ; L – co-ligands). The chelate complexes described in articles [22–29] can be illustrated as examples. The same as in the aforementioned complexes, in the discussed $[\text{Cu}(\text{deta})(\text{H}_2\text{O})\text{SO}_4 \cdot \text{H}_2\text{O}$ (**1**) complex, whose crystal structure is shown in Fig. 2, all N atoms of the three amino-groups presented in the diethylenetriamine is simultaneously coordinated with one copper(II) atom. Likewise to the cationic chelate complexes $[\text{Cu}(\text{deta})(1,10\text{-phenantroline})](\text{ClO}_4)_2$, $[\text{Cu}(\text{deta})(2,2'\text{-bipyridine})](\text{BF}_4)_2$ [26] and $[\text{Cu}(\text{deta})(2\text{-cyanoguanidine})](\text{NO}_3)_2$ [29], the cations of complex **1** have composition $[\text{Cu}(\text{deta})(\text{H}_2\text{O})]^{2+}$ and are main building blocks in the crystal structure, whereas counterions consist from the hydrated sulfate anions.

The independent part of the crystal structure of the complex **1** with the atomic numbering scheme is displayed in Fig. 3; the bonds lengths and bonds angles are listed in the Table 5. The Cu^{2+} ion in **1** is pentacoordinated by three N atoms of one tridentate molecule (*deta*) and two O atoms (H_2O and SO_4^{2-}). The coordination sphere around the central Cu(II) atom is a distorted square pyramid where three N atoms (N1, N2 and N3) of *deta* molecule and O1 atom of water molecule form the basal plane, while O3 atom of sulfate anion occupies the apical position. Distance from each of three N atoms to the copper(II) ion are almost identical (Cu1–N1 1.997(1), Cu1–N2 2.010(1) and Cu1–N3 2.011(1) Å); axial Cu–O bond is much longer than Cu–O bond in a plane (Cu1–O3 2.421(1) and Cu1–O1 2.001(1) Å, respectively). The Cu1 atom deviation from the basal plane of ligands in the direction of apical O3 atom is negligible ~ 0.1 Å.

It should be noted that coordination sphere of Cu(II) can be supplemented by one more O atom of sulfate anion from the adjacent structural fragment (see Fig. 2). Thus, a square bipyramid arises in unit cell of **1** as a result of additional coordination of central atom Cu1 by atom O5ⁱ (symmetry code: (i) $-1 + x, y, z$) that occupies

another apical position on the opposite side of a square pyramid (Cu1–O 5ⁱ 2.673(1) Å). The Cu1–O3 and Cu1–O5ⁱ bonds are less strong and impairment of their attractive force are mainly caused by electrostatic repulsion of electron lone pairs of corresponding oxygen atoms and d_{z^2} atomic orbital (AO) of copper(II) atom that

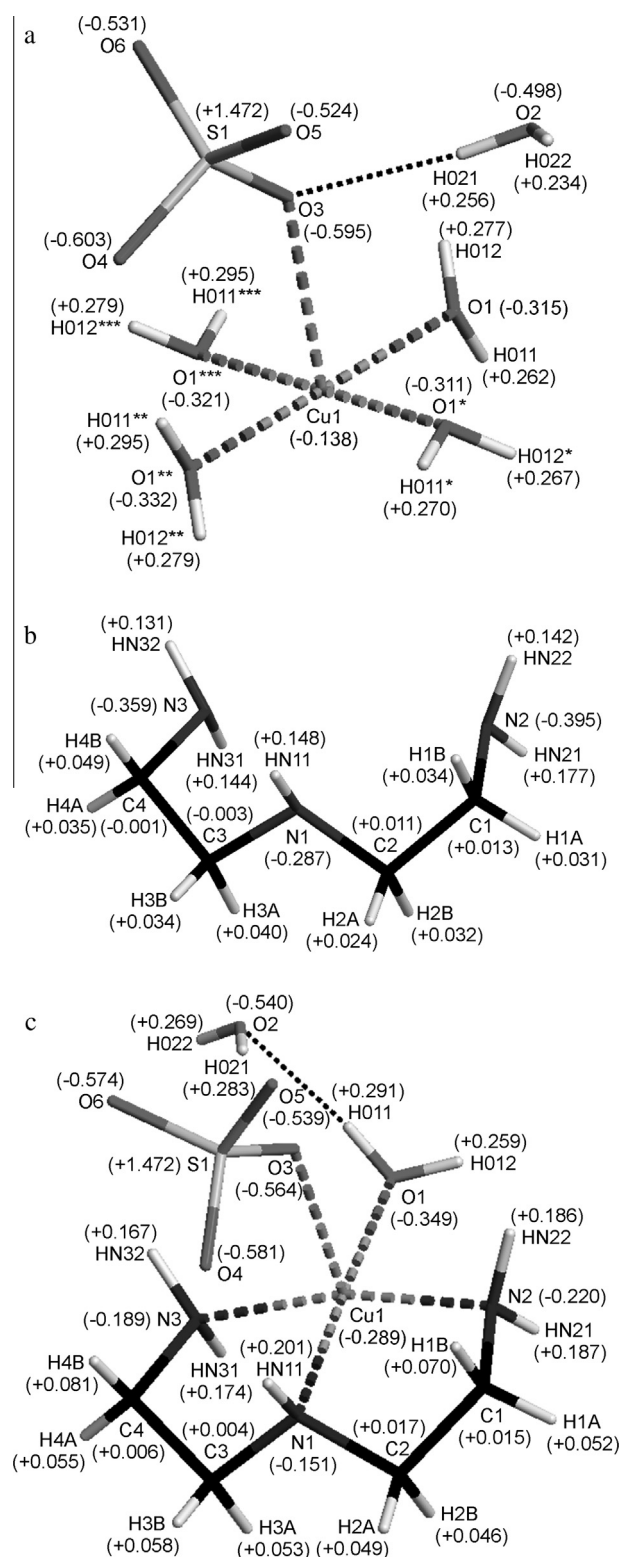


Fig. 5. Charge density ($\pm e$) distribution on the atoms in the $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (a), *deta* (b) and $[\text{Cu}(\text{deta})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$ (c).

are also occupied by pair of electrons (consequence of Jahn–Teller effect [37]).

The sulfate anion in **1** is characterized by tetrahedral shape. Environment of S1 atom consists of O3, O4, O5 and O6 atoms. The values of the S–O bond and O–S–O bond angles on average are 1.48 Å and 109°, respectively (see Table 5). Besides, the sulfate anion is hydrated by crystal water which, in addition, forms hydrogen bond with the coordinate water. Thus, the complex cation, $[\text{Cu}(\text{deta})\text{H}_2\text{O}]^{2+}$, by means of the aqueous ligand links the external sulfate anion through the bridged molecule of crystal water. In a result of this, the discrete unit of $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}$ with respective intramolecular hydrogen bonds is formed (see Fig. 3). As a consequence, the cross-linking system of extremely strong hydrogen bonds $\text{O}_3\text{S}-\text{O}\cdots\text{H}_2\text{O}\cdots\text{H}-\text{OH}$ ($\text{H}021\cdots\text{O}3$ and $\text{H}011\cdots\text{O}2$ distances are 2.09(3) and 1.85(2) Å, respectively) is formed in **1** (Table 6). Apart from intramolecular H-bonds, the branched system of strong intermolecular $\text{O}-\text{H}\cdots\text{O}$ bonds ($\text{H}012\cdots\text{O}5^{\text{iii}}$ distance is 1.81(2) Å (symmetry code: (iii) $2-x, 2-y, 1-z$) as well as $\text{N}-\text{H}\cdots\text{O}$ bonds (see Table 6) exert the still more significant influence on the crystal structure forming. Seemingly, the packing of $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}$ discrete units into layers also can be explained by hydrogen bonds [38,39]. The $\{[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}\}_n$ layer, oriented perpendicularly to the [010] direction, is shown in Fig. 4.

Molecular electronic structure of $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}$

The $\text{Cu}(\text{II})-(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)$ chelation is accompanied by some changes in the electronic parameters of coordinated *deta* molecule in comparison with those in uncoordinated *deta* molecule. The performed quantum-chemical calculations reveal that the electron density of nitrogen atoms within coordination chelate-core efficiently shifts to the central copper atom owing to chelation effect. So, the value of charge density (δ) on amine nitrogen atoms of uncoordinated *deta* molecule are -0.287 , -0.395 and -0.359 e for N1, N2 and N3 atoms, respectively, and the δ value on Cu1 atom in $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}$ unit fragment of the copper(II) sulfate equals to -0.138 e (Fig. 5a and b). However, the electron density on amine nitrogen atoms of coordinated *deta* molecule in formed $[\text{Cu}(\text{deta})(\text{H}_2\text{O})]\text{SO}_4\cdot\text{H}_2\text{O}$ unit fragment of **1** is lowered owing to chelation (the δ value are -0.151 , -0.220 and -0.189 e for N1, N2 and N3 atoms, respectively) while electron density on Cu(II) atom, contrariwise, is increased (the δ value is -0.289 e for Cu1 atom) (Fig. 5c). Thus, due to chelation, the lone pairs of electrons of N atoms of amino-groups as well as aqueous O atom more efficiently overlap with the four of six unoccupied hybrid $sp^3 d_{x^2-y^2} d_{z^2}$ AOs of the central Cu^{2+} ion which are directed toward vertices of basal square. Furthermore, the overlaps between two other unoccupied hybrid orbitals and lone pairs of electrons of O

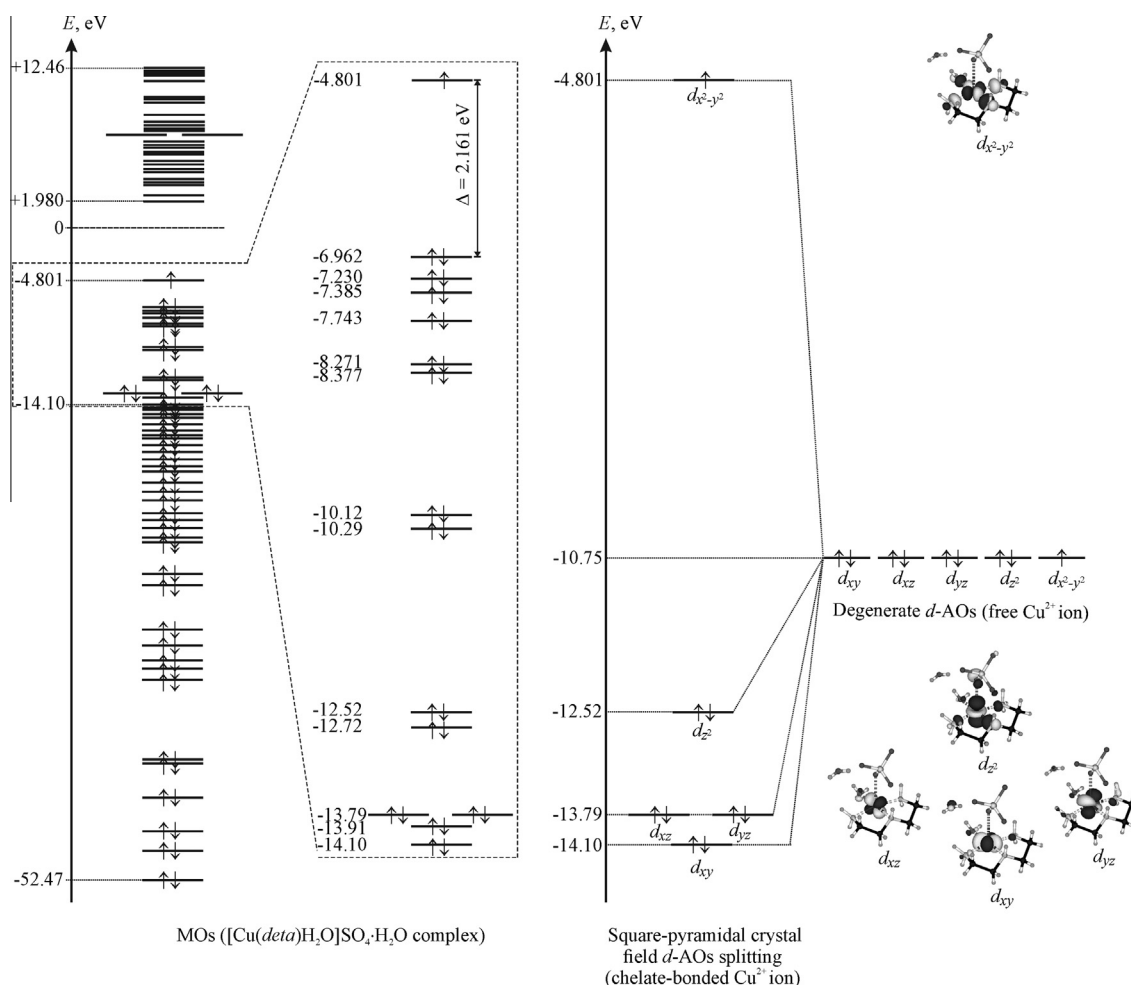


Fig. 6. The $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}$ MOs diagram (on the left) and 3d-AOs splitting by square-pyramidal crystal field in chelate-bonded Cu^{2+} ion (on the right).

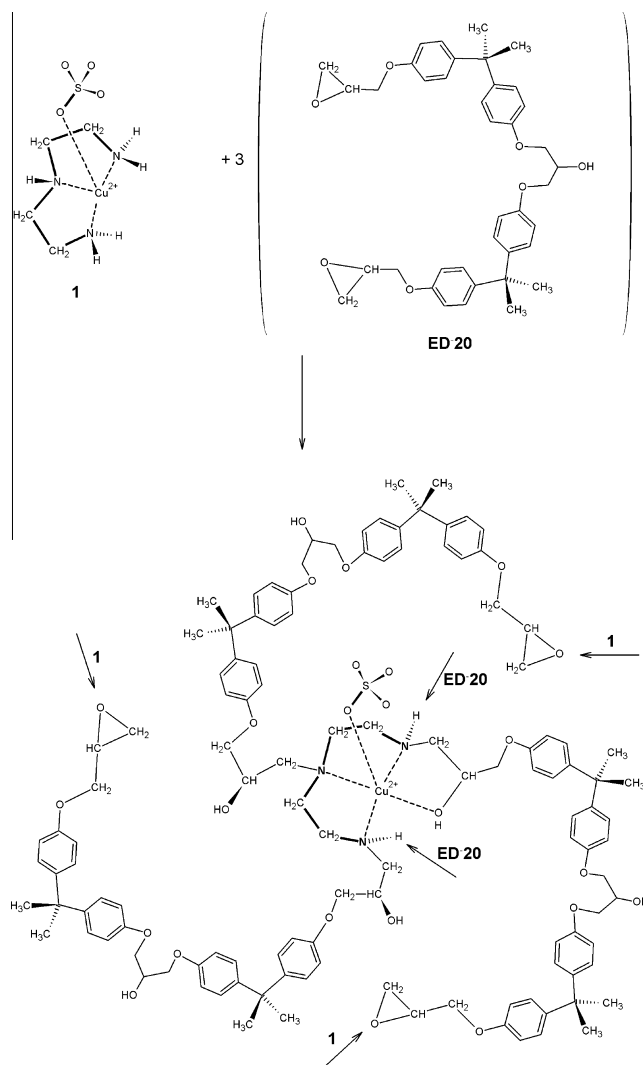
atoms of SO_4^{2-} ions as well take place, connecting Cu1 atom with apical atoms O3 and O5¹, but, nevertheless, less efficiently. Therefore the initial octahedral surrounding of the metal atom (six identical $sp^3 d_{x^2-y^2} d_{z^2}$ -hybrid AOs of Cu(II) atom are directed to octahedron vertexes) is strongly distorted. It acquires the shape of the extended square bipyramid or, rather, square pyramid. As a result, the square-pyramidal field of the ligands simultaneously with chelate effect predetermines the elimination of degeneracy of the 3d-AOs of Cu^{2+} ion in **1**. The $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ MOs diagram and 3d-AOs splitting by square-pyramidal crystal field with their 3D-image in chelate-bonded Cu^{2+} ion are represented in Fig. 6. According to theory of crystal field advanced in [40], the degenerate d-AOs in square-pyramidal crystal field are split into several sets with different energy and such crystal-field splitting parameters: the twice degenerate d_{xz} , d_{yz} AOs and d_{xy} AO are characterized by the lowest and lower energy whereas d_{z^2} and $d_{x^2-y^2}$ AOs possess higher and the highest energy, respectively.

Owing to the chelate effect, the square-pyramidal crystal-field splitting parameters acquire somewhat other arrangement sequence of the split d-AOs (the energy levels are situated in the following way (in ascending order): $d_{xy} <$ twice degenerate d_{xz} , $d_{yz} < d_{z^2} < d_{x^2-y^2}$ (see Fig. 6)). The size of the gap between energy levels of d_{z^2} and $d_{x^2-y^2}$ orbitals is very large and amounts to 7.719 eV. The certain part of energy levels occupy this gap. As a result, the one more gap ($\Delta = 2.161$ eV) arises within electron-molecular system between energy levels of corresponding MO (-6.962 eV) occupied by electronic pair and of $d_{x^2-y^2}$ AO (-4.801 eV) with unpaired electron. It exactly correlates with the energy of visible light ($\lambda = 5735$ Å), which is sufficient in order that one electron could jump from the lower energy level to the higher energy level acquiring excited state. This difference in energy between the ground state and the excited state is equal to the energy of the absorbed photon related with certain wavelength of the light. That is why blue-violet ($\lambda = 4170$ Å) color of the crystals of **1** is observed.

Fire retardant properties of $[\text{Cu}(\text{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$

In this section, it would be desirable to scrutinize the chemical influence (chelation) of cupric salts upon flammability of epoxy-amine composites [19]. The experiments earlier performed by us, concerning measurements of ignition points, confirm once again that chemical interaction of organic amine with cupric salt directly has an influence on combustibility of amine. So, if the ignition point for uncombined diethylenetriamine amounts to 97 °C, then diethylenetriamine in chelate complex of **1** non-inflames up to the extent of temperature 510 °C. In other words, inflammable diethylenetriamine (a hardener of epoxy resins) after interlinking with cupric sulfate turns into practically incombustible substance. The same tendency is observed in case of flammability of epoxy resins: the ignition point of epoxy-amine polymer after adding anhydrous cupric sulfate increases from 314 °C to 358 °C. The cause of it is in the supplementary chemical bonds which form in the course of epoxy resin polymerization at participation of cupric sulfate linked with diethylenetriamine. It is necessary to notice that total energy of three Cu–N bonds and two Cu–O bonds which form the square-pyramidal coordination core equals 337.32 kJ mol⁻¹ (see Table 4). Thus, after addition of the epoxy hardener linked with anhydrous cupric sulfate to the epoxy diene oligomer (ED-20), the coordinated *deta* molecule polymerizes in Scheme 1.

As a result of such polymerization, the epoxy-amine resin possessing suppressed combustibility was developed. The polymeric framework which forms within this compositional matrix contains the chemically connected incombustible inorganic salt



Scheme 1.

of copper(II). Assuredly, the strong coordination bonds that arise between metal atoms of incombustible CuSO_4 and N atoms of the amine hardener are responsible for the flammability suppression of the epoxy-amine composite. Indeed, the considerable amounts of a flame thermal energy should be used up as long as the coordination bonds (Cu–N and Cu–O) will undergo destruction. That is why epoxy-amine composites filled by transition metals become highly resistant to free flame influence.

Conclusions

Analysis of the experimental data obtained during the studying of the interaction of copper(II) sulfate pentahydrate with diethylenetriamine and at the crystal structure determination of the complexation product (the aqua-(diethylenetriamine-N, N', N'')-copper(II) sulfate monohydrate (**1**)) as well as information gained from the quantum-chemical calculation of the molecular electronic structure of **1** reveals the specific features of the coordination chemistry of copper(II) chelate complexes and the peculiarities of the behavior of nitrogen-containing tridentate ligands as the chelating agents.

Formation of the coordination sphere of the Cu^{2+} ion having an electron configuration of the valence level $[\text{Ar}]3d^9 4s^0$, is caused by pentacoordination of the metal center with three N atoms of one

deta molecule (of chelating agent) and by two O atoms of water molecule and sulfate anion. It predetermines the architecture of Cu(II) coordination polyhedron having the shape of the distorted square pyramid.

The geometrical parameters of the square-pyramidal polyhedron of Cu(II) atom are in good agreement with the Jahn–Teller principle and are the result of the mutual strengthening of two individual effects (of square-pyramidal crystal field effect and chelate effect). This synergism causes the splitting of the degenerate $3d$ -AOs of the Cu^{2+} ion onto four sets of the energy levels ($d_{xy} < \text{twice degenerate } d_{xz} \text{ and } d_{yz} < d_{z^2} < d_{x^2-y^2}$). The peculiar molecular electronic structure of $[\text{Cu}(\textit{deta})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ in many respects predetermines existence of rather steady blue-violet crystals of copper(II) chelate complex of **1**. In addition, such high stability of this chelate compound in solid state is responsible for the decrease of combustibility of epoxy-amine resins filled by CuSO_4 .

Supplementary data

CCDC reference number 1010826 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk.

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