



## ORIGINAL ARTICLE

# A new copper(II) chelate complex with polyamines as fire retardant and epoxy hardener: Synthesis, crystal and electronic structure, and thermal behavior of (ethylenediamine-*N,N'*)-(diethylenetriamine-*N,N',N''*)-copper(II) hexafluoridosilicate



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Received 29 March 2018; accepted 27 August 2018

Available online 1 September 2018

## KEYWORDS

Copper(II) chelate complexes;  
Synthesis;  
Crystal structure;  
Electron-molecular structure;  
Differential thermal analysis

**Abstract** A new (ethylenediamine-*N,N'*)-(diethylenetriamine-*N,N',N''*)-copper(II) hexafluoridosilicate complex, [Cu(*eda*)(*deta*)]SiF<sub>6</sub> (**1**) (*eda* – ethylenediamine; *deta* – diethylenetriamine), was synthesized by direct interaction of anhydrous CuSiF<sub>6</sub> with polyethylenepolyamine (*pepa* – H<sub>2</sub>N [–C<sub>2</sub>H<sub>4</sub>NH–]<sub>*n*</sub>H, where *n* = 1 (*eda*) and 2 (*deta*)). The crystals of **1** were characterized by IR spectroscopy and X-ray diffraction. Compound **1** consists of SiF<sub>6</sub><sup>2–</sup> discrete anions and [Cu(*eda*)(*deta*)]<sup>2+</sup> complex cations whose Cu<sup>2+</sup> ions are chelated by *eda* and *deta*. The coordination polyhedron of Cu (II) atom is an elongated square pyramid which consists of four nitrogen atoms belonging to –NH<sub>2</sub> groups of *eda* and –NH<sub>2</sub> and –NH– groups of *deta* at the base of the pyramid and of one more nitrogen atom from –NH<sub>2</sub> group of *deta* at its apical position. *Ab initio* quantum-chemical calculations of chelation process were carried out for **1** by the restricted Hartree-Fock method using a 6-31G\* basis set. The influence of the chelate complex **1** upon its fire retardant properties was analyzed. The calculated electron-stereo-chemical parameters for **1** are in a good agreement with its

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<https://doi.org/10.1016/j.arabjc.2018.08.014>

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thermal parameters investigated by differential thermal analysis. The thermal decomposition of **1** is finished off at 368 °C and the maximal combustion temperature of gaseous decomposition products is 544 °C.

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## 1. Introduction

Coordination complexes of transition metals salts, in particular, of copper salts are known to use in many important chemical-technological processes of the transformation of organic substances for a long time (Temkin and Pozdeev, 2012; Mykhalichko et al., 2000). In view of it, the comprehensive study of cupric salts interaction with polyamines is of an exceptional scientific interest because the formation of Cu (II)←N coordination bonds along with the ability of polyamine molecules to chelate metal atoms should be regarded as one of the most important factors influencing onto amines combustibility lowering (Lavrenyuk et al., 2015, 2016a,b, 2018a–c). The practical significance of complexation processes is conditioned, first of all, by possibility of using the inorganic cupric salts as fire retardants which will be able very efficiently to prevent an ignition of various amines including the curing agents for epoxy polymers (Hamerton et al., 2002; Lavrenyuk et al., 2016a,b, 2018a–c). It is obviously that such property of the chelate complexes as ability to suppress burning the epoxy-amine polymers depends on the composition, the structure, and the type of cupric salt involved in the complexation.

Previously, the polyamine chelate complexes of CuSO<sub>4</sub> and CuCO<sub>3</sub> were already used as fire retardant-hardeners of epoxy resins (Lavrenyuk and Mykhalichko, 2015; Lavrenyuk et al., 2017). It was ascertained the coordination compounds of the above cupric salts can appreciably decrease the combustibility of modified epoxy-amine polymers and, at the same time, enhance their physicochemical and mechanical properties (Lavrenyuk et al., 2018a–c). Given the fact that among investigated complexes of cupric salts with polyamines the similar compounds with CuSiF<sub>6</sub> were not known, we have undertaken an attempt to study the interaction of polyethylenepolyamine with copper(II) hexafluoridosilicate whose anhydrous salt can play the role of fire retardant at the epoxy-amine composition elaboration with lowered combustibility.

The synthesis of [Cu(*eda*)(*deta*)]SiF<sub>6</sub> (**1**) (*eda* – ethylenediamine; *deta* – diethylenetriamine), structural and differential thermal analysis (DTA) as well as quantum-chemical calculations of its electron-molecular structure are reported in this article.

## 2. Experimental

### 2.1. Materials and methods

In order to obtain the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> chelate complex, the following chemicals were used: copper(II) hexafluoridosilicate hexahydrate – CuSiF<sub>6</sub>·6H<sub>2</sub>O (deep blue crystals,  $M = 313.5 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 2.21 \text{ g}\cdot\text{cm}^{-3}$ ) (Ray et al., 1973) and polyethylenepolyamine (*pepa*) – H<sub>2</sub>N[–C<sub>2</sub>H<sub>4</sub>NH–]<sub>*n*</sub>H, where *n* = 1 (*eda*) and 2 (*deta*) (yellowish transparent viscous liquid,

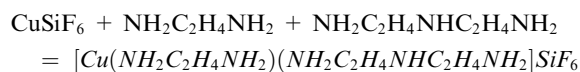
$\bar{M} = 81.5 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 0.927 \text{ g}\cdot\text{cm}^{-3}$ ,  $t_{\text{flash}} = 94 \text{ }^\circ\text{C}$ ,  $t_{\text{ignition}} = 97 \text{ }^\circ\text{C}$ ,  $t_{\text{self-ignition}} = 390 \text{ }^\circ\text{C}$ ) (Baratov and Korolchenko, 1990), IR (KBr cuvette, cm<sup>-1</sup>): 3372, 3254 and 3210 (ν<sub>NH</sub>); 2934, 2908 and 2790 (ν<sub>CH</sub>); 1600 (δ<sub>NH</sub>); 1460 (δ<sub>CH</sub>). All reagents were purchased through commercial sources and used as-received without further purification.

IR absorption spectra were recorded in the spectral range of 4000–500 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> on a Perkin Elmer Spectrum Two FTIR spectrometer. The IR measurements were performed with a solid sample of **1** pressed in spectroscopically pure KBr pellet, or a liquid sample of *pepa* using a KBr cuvette.

Thermal gravimetric analysis for crystalline phase of **1** was performed on a Q-1500D thermal analyzer (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 25 to 700 °C with a heating rate of 5 °C per minute. The experiments were carried out in dynamical regime in air atmosphere. The weight of each solid-phase sample amounted to 100 mg. Aluminum oxide was used as a standard.

### 2.2. Synthesis

[Cu(*eda*)(*deta*)]SiF<sub>6</sub> has been synthesized by direct interaction of anhydrous copper(II) hexafluoridosilicate with *pepa*. Polycrystalline CuSiF<sub>6</sub> (2.05 g, 0.01 mol) was placed into a porcelain mortar, and 1.75 cm<sup>3</sup> (0.02 mol) of *pepa* was added. The reaction mixture was triturated till the appearance of a homogeneous dark-blue liquid suspension. It was left for a few days at room temperature, and the solid phase appeared according to the following reaction:



Yield: 100% (with respect to CuSiF<sub>6</sub>), IR (KBr pellet, cm<sup>-1</sup>): 3416, 3238 and 3142 (ν<sub>NH</sub>); 2952, 2930 and 2886 (ν<sub>CH</sub>); 1584 (δ<sub>NH</sub>); 1454 (δ<sub>CH</sub>). Next the solid phase was dissolved in water. Dark-blue single crystals of **1** suitable for X-ray crystal structure determination were obtained out of the aqueous solution by recrystallization.

### 2.3. Crystal structure determination

A single crystal of **1** was mounted on the Xcalibur diffractometer (Mo K<sub>α</sub>-radiation, λ = 0.71073 Å, 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 were collected at 100.0(1) K using crystal-to-detector distance of 60 mm. After integration the data was corrected for Lorentz and polarization effects (Oxford diffraction, 2002). Unit cell parameters were obtained by the least-squares refinement based on reflection angles in the range 6.20° < 2θ < 59.06°. Structure **1** was solved by direct methods applying SHELX software package

(Sheldrick, 2008). Other non-hydrogen atoms were located from the Fourier difference synthesis and refined by the least-squares method in the full-matrix anisotropic approximation. The hydrogen atoms of  $-\text{NH}-$  and  $-\text{NH}_2$  groups also were located from the Fourier difference synthesis, while the hydrogen atoms of  $-\text{CH}_2-$  groups were placed geometrically. All of hydrogen atoms were refined as riding atoms with the C–H and N–H preset distances, 0.99 Å and 0.92 Å, respectively as well as with isotropic temperature factors of 1.2 times the  $U_{\text{eq}}$  values for the parent carbon or nitrogen atoms. The crystal data, collected reflections and parameters of the final refinement data for **1** are reported in Table 1. The positional and thermal displacement parameters are given in Table S1 (Supp. info). All images of the crystal structure of **1** were prepared using DIAMOND program (Brandenburg, 1998). The atom numbering system for the asymmetric part of **1** is represented in Fig. 1.

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

Empirical formula	$\text{C}_6\text{H}_{21}\text{N}_5\text{F}_6\text{Si}_1\text{Cu}_1$
Formula mass	368.91
Color, habit	Dark-blue, plate
Crystal dimensions (mm)	$0.3 \times 0.3 \times 0.1$
Crystal system	monoclinic
Space group	$P 1 2_1/n 1$
Z	4
$a$ (Å)	8.9945(4)
$b$ (Å)	9.6067(3)
$c$ (Å)	15.7357(8)
$\alpha$ (°)	90.00
$\beta$ (°)	91.460(4)°
$\gamma$ (°)	90.00
Collection ranges	$0 \leq h \leq 12; 0 \leq k \leq 13; -21 \leq l \leq 21$
Temperature (K)	100(2)
Volume (Å <sup>3</sup> )	1359.2(1)
$D_{\text{calcd}}$ (Mg·m <sup>-3</sup> )	1.803
Radiation	$\text{Mo } K_{\alpha}$ ( $\lambda = 0.71073$ Å)
Absorption coeff. ( $\mu$ ) (mm <sup>-1</sup> )	1.760
Absorption correction	Analytical numeric
$F(0\ 0\ 0)$	756
$\theta$ range for data collection (°)	3.10–29.53
Observed reflections	3490
Independent reflections	3490 ( $R_{\text{int}} = 0.0000$ )
Data/restraints/parameters	3490/0/172
Maximum shift/error	0.000/0.000
Goodness-of-fit on $F^2$	0.949
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0706, wR_2 = 0.0744$
$R$ indices (all data)	$R_1 = 0.1651, wR_2 = 0.0893$
Weighing scheme ( $w$ )	$[\sigma^2(F_o^2) + (0.0188P)^2]^{-1} + 0.0000P^{-1}$ , where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	N/A
Extinction coefficient	N/A
Largest diff. peak and hole ( $\bar{e} \cdot \text{Å}^{-3}$ )	0.667 and $-0.613$

## 2.4. Quantum-chemical calculation

The numerical simulation of the complexation processes in *eda-deta*-CuSiF<sub>6</sub> system was carried out by means of quantum-chemical analysis. 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 (HyperChem, 1995–2009; Frank, 1990). The base crystallographic data of CuSiF<sub>6</sub>·6H<sub>2</sub>O (Ray et al., 1973) and **1** were used for the design of [Cu(H<sub>2</sub>O)<sub>6</sub>]SiF<sub>6</sub> and [Cu(*eda*)(*deta*)]SiF<sub>6</sub> discrete clusters as well as for the construction of free *eda* and *deta* molecules.

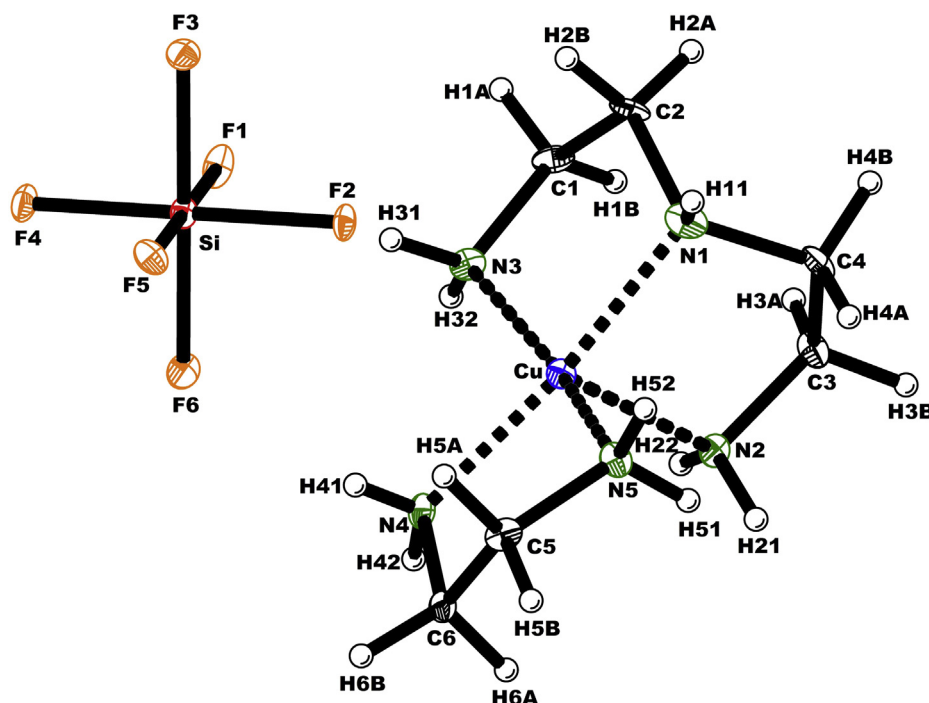
Calculation of a charge density distribution on atoms for discrete clusters was performed without geometrical optimization of structural fragments whereas the geometry of free molecules was optimized. All calculations were carried out under the hypothesis that the presented clusters (like the free molecules) are isolated and are in vacuum. The results of the quantum-chemical calculation of energy effects of the *pepa*-CuSiF<sub>6</sub> interaction are given in Table 2; the exhaustive information about the charge density redistribution on the atoms in above particles is represented in Table S2 (Supp. info).

## 3. Results and discussion

### 3.1. X-ray crystal structure description

The interaction of *pepa* (a curing agent of epoxy resins) with noncombustible copper(II) hexafluorosilicate (a fire retardant) in many respects predetermines the fire retardant-hardener properties for the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> complex whose crystal structure is displayed in Fig. 2. In **1**, polyamine molecules – *eda* and *deta* – coordinate to inorganic cupric salt, forming the chelate complex where all amine groups of the organic ligands are simultaneously bonded to central atom – Cu(II). As can be seen in Fig. 1, the chelation mode determines the structure of **1** that is composed of discrete complex cations resembling those in the [Cu(*deta*)(*eda*)](BF<sub>4</sub>)<sub>2</sub> (Valdes-Martinez et al., 2006), [Cu(*deta*)(*eda*)](ClO<sub>4</sub>)<sub>2</sub> (Duan-Jun 1993; Ullah et al., 1996; Patel et al., 2007), as well as in the [Cu(*deta*)(2,2-bipyridine)](BF<sub>4</sub>)<sub>2</sub>, [Cu(*deta*)(1,10-phenantroline)](ClO<sub>4</sub>)<sub>2</sub> (Patel et al., 2005) and [Cu(*deta*)(tetramethylethylenediamine)]Br<sub>2</sub>·H<sub>2</sub>O (Saleemh et al., 2017). Similarly, cations of **1** have the same stoichiometry ([Cu(*deta*)(*eda*)]<sup>2+</sup>) and together with SiF<sub>6</sub><sup>2-</sup> anions are main building blocks its crystals.

The bond lengths and bond angles for **1** are listed in Table 3. The Cu<sup>2+</sup> ion is pentacoordinated by N atoms (two N atoms from bidentate *eda* + three N atoms from tridentate *deta*) in the titled structure. The coordination sphere around the central atom is an elongated square pyramid in which N4, N5 atoms from *eda* and N1 and N3 atoms from *deta* form the bottom of the polyhedron, and another nitrogen atom, N2, from *deta* occupies the apical position. The Cu–N bond lengths in the pyramid base are close and these range from 2.008(4) to 2.043(4) Å; the axial Cu–N2 bond is more lengthy (2.223(3) Å). It should be noted that the bottom of the square pyramid is not planar. The N3 and N5 atoms are above of the N1–N3–N4–N5 plane. Therefore, a  $\tau$  parameter for coordination environment of Cu(II) (coordination number = 5) was



**Fig. 1** The atom numbering system for the asymmetric part of **1**. Thermal ellipsoids are displayed at the 30% probability level for non-hydrogen atoms.

**Table 2** Results of the quantum-chemical calculation of the energy effects.

Particle	Total energy (kJ·mol <sup>-1</sup> )	Binding energy (kJ·mol <sup>-1</sup> )	Sum of energies of all chemical bonds (kJ·mol <sup>-1</sup> )
<i>eda</i>	-106323.2	-13053.7	4117.6
<i>deta</i>	-178338.0	-22399.2	7109.0
[Cu(H <sub>2</sub> O) <sub>6</sub> ][SiF <sub>6</sub> ]	-839370.0	-13331.0	5373.9
[Cu( <i>eda</i> )( <i>deta</i> )]SiF <sub>6</sub>	-838822.2	-41406.4	12491.2

calculated using the procedure proposed by Addison et al. (1984). The obtained value ( $\tau_5 = 0.16$ ) unambiguously fixes the pentahedron shape which has proved considerably closer to square-pyramid than to trigonal-bipyramid.

Nevertheless, the coordination sphere of Cu(II) can be complemented by one more F atom of neighboring hexafluorosilicate anion (see Fig. 2). Thus, a distorted square bipyramid arises in unit cell of **1** in consequence of supplementary coordination of the central atom by atom of F2 that occupies another apical position on the opposite side of a square pyramid (Cu–F2 3.086(3) Å). Observed loosening of Cu–N2 and Cu–F2 bonds is mainly caused by electrostatic repulsion of electron lone pair of nitrogen atom or fluorine atom from electron pair located on  $d_{z^2}$  atomic orbital (AO) of Cu<sup>2+</sup> ion (Jahn-Teller effect (Tanaka et al., 1979)).

The SiF<sub>6</sub><sup>2-</sup> anions have an almost ideal octahedral shape (see Table 3 and Fig. 2). The bulky SiF<sub>6</sub><sup>2-</sup> units are incorporated into crystalline framework of **1** where these crosslink the cation stacks by N–H...F hydrogen bonds (the branched system of the hydrogen bonds for **1** is presented in Table 4). These hydrogen bonds impart a directed character to the ionic interaction Cat<sup>2+</sup>...An<sup>2-</sup>. The examined hydrogen bonds are a striking

example of especial influence of the directed ionic interaction on the crystal structure forming (Desiraju, 2000, 2002).

### 3.2. IR spectroscopy

Besides X-ray structure analysis, **1** was also identified by IR spectroscopy (Fig. 3). Due to the fact that cupric salt is able to interlink the polyamine molecules into chelate complex, one can observe the shifts of N–H absorption bands after complexing. Therefore, the absorption bands caused by the stretching and bending of NH<sub>2</sub> and NH groups of the coordinated and free molecules of polyamine will interest us primarily (Nakamoto, 2009). So, for free *pepa* (Fig. 3, A) the high-frequency region 3372 and 3254 cm<sup>-1</sup> is related to the stretching of –NH<sub>2</sub> whereas the band observed at 3210 cm<sup>-1</sup> is ascribed to the stretching of –NH–; the observed oscillation frequency at 1600 cm<sup>-1</sup> is attributed to the bending of N–H bonds. After bonding of the *pepa* (*eda* + *deta*) with CuSiF<sub>6</sub> (Fig. 3, B), one of the N–H absorption bands is shifted to the high-frequency region observed at 3416 cm<sup>-1</sup> whereas two other bands are shifted to the low frequency region (3238 and 3142 cm<sup>-1</sup>). The observed wavenumber at

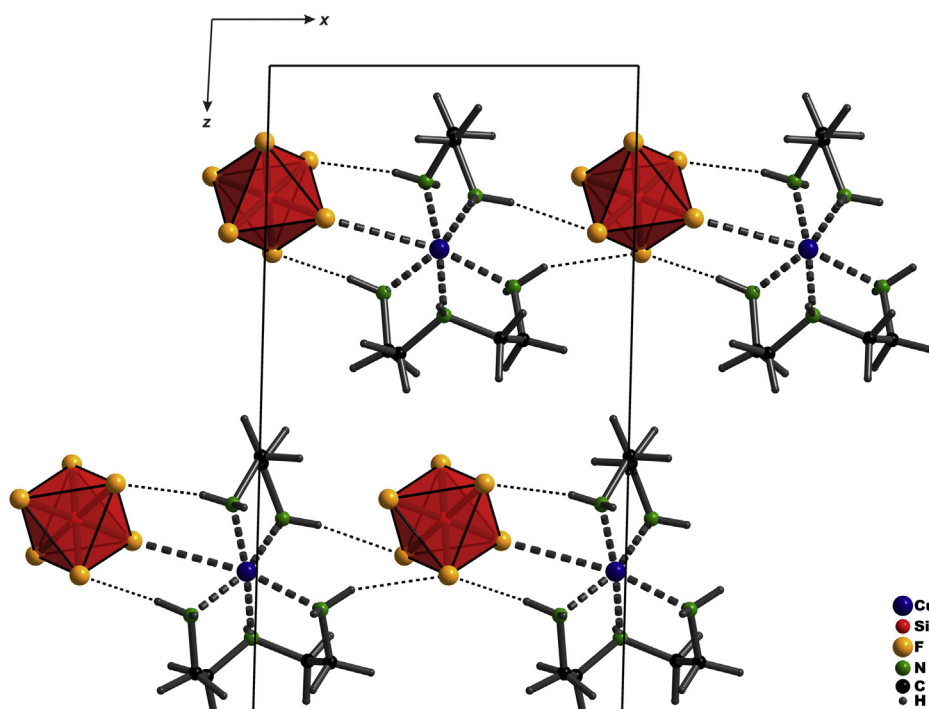


Fig. 2 Crystal structure projection of **1** onto  $xz$  plane. Hydrogen bonds are depicted by dot line.

$1584\text{ cm}^{-1}$  related to the bending of N—H bonds is also shifted to low frequency region.

### 3.3. Electron-molecular structure

The complexing in *pepa* –  $\text{CuSiF}_6$  system is accompanied by some changes in the electronic parameters of coordinated *eda* and *deta* molecules in comparison with ones in uncoordinated state. The carried out quantum-chemical calculations have revealed that the electron density of nitrogen atoms within coordination core efficiently shifts to the Cu(II) atom owing to chelate effect. So, the values of charge density ( $\delta$ ) on amine nitrogen atoms of uncoordinated *eda* and *deta* molecules are  $-0.266$ ,  $-0.381$ ,  $-0.393\bar{e}$  for N1, N2, N3 atoms and  $-0.366$ ,  $-0.360\bar{e}$  for N4, N5 atoms, respectively, and the  $\delta$  value on Cu atom in copper(II) hexafluoridosilicate hexahydrate equals to  $-0.575\bar{e}$  (Fig. 4, A–C). However, the electron density on  $-\text{NH}_2$  and  $-\text{NH}-$  groups of *eda* and *deta* molecules is decreased (the  $\delta$  values are  $-0.026$ ,  $-0.148$ ,  $-0.114\bar{e}$  for N1, N2, N3 atoms and  $-0.094$ ,  $-0.087\bar{e}$  for N4, N5 atoms, respectively) after the  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  formation while the electron density on copper(II) atom, conversely, is increased (the  $\delta$  value is  $-0.672\bar{e}$  for Cu atom) (Fig. 4, D).

The above-mentioned distribution of electron density within the coordination core results in the degeneracy elimination of the  $3d$ -AOs in the  $\text{Cu}^{2+}$  ion. According to theory of crystal field advanced in (Van Vleck, 1932), the degenerated  $3d$ -AOs are split influenced by the square-pyramidal crystal field. The constructed diagram of molecular orbitals (MOs) for  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  and  $3d$ -AOs splitting by the square-pyramidal crystal field for chelated  $\text{Cu}^{2+}$  ion are represented

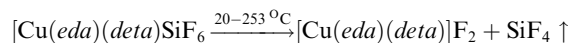
in Fig. 5. Taking into account the chelate effect, the split parameters of the  $3d$ -AOs by the square-pyramidal crystal field acquire next sequence in **1**; the energy levels are disposed in the following way (in ascending order):  $d_{xy} < d_{yz} < d_{xz} < d_{z^2} < < d_{x^2-y^2}$  (see Fig. 5).

### 3.4. Thermal behavior

The bonding efficiency of a combustible organic polyamine with an incombustible inorganic salt largely predetermines the thermal stability of the  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  chelate complex – fire retardant-hardener of epoxy resins. Therefore, the thermal behavior of **1** was studied by thermal gravimetric analysis. The curves of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) are displayed in Fig. 6.

The TG curve of the thermal decomposition of **1** is represented by four sections. The first involves the temperature range from 20 to 160 °C. It is accompanied by a loss of weight of 13.4 wt% and by the appearance of a minimum on the respective section of the DTA curve. At this temperature interval (DTA curve) an endothermic process is observed at 112 °C.

The second stage of the thermal decomposition lies in the temperature range from 160 to 253 °C ( $\Delta m = 14.3\text{ wt}\%$ ) with an endothermic minimum at 212 °C. The stepwise break-down of the inorganic part of complex takes place at these two temperature intervals:

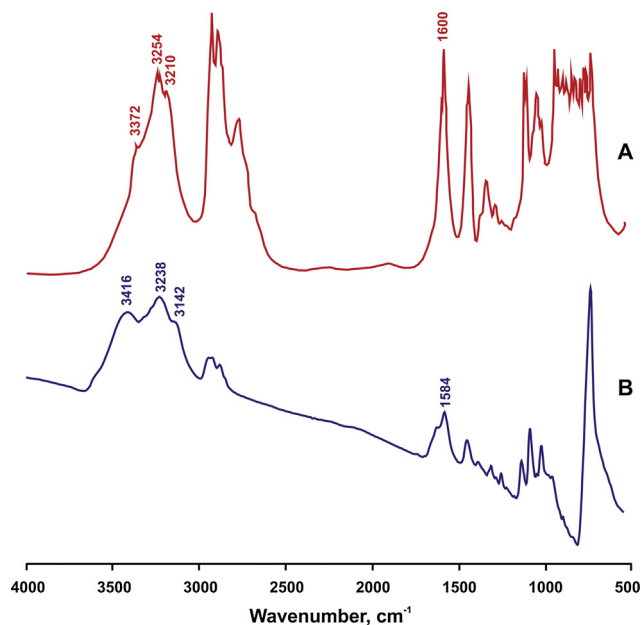


The third stage of the thermal decomposition occurs in the temperature range from 253 to 368 °C and is accompanied by the appearance of exothermic and endothermic effects on the

Bond	<i>d</i> , Å	Angle	$\omega$ , °
Cu—N1	2.043(4)	N1—Cu—N2	82.7(1)
Cu—N2	2.223(3)	N1—Cu—N3	85.5(2)
Cu—N3	2.008(4)	N1—Cu—N4	172.2(2)
Cu—N4	2.014(4)	N1—Cu—N5	95.4(1)
Cu—N5	2.018(4)	N2—Cu—N3	97.1(1)
		N2—Cu—N4	105.1(1)
Si—F1	1.708(3)	N2—Cu—N5	99.8(1)
Si—F2	1.684(3)	N3—Cu—N4	92.5(2)
Si—F3	1.690(3)	N3—Cu—N5	163.1(1)
Si—F4	1.681(3)	N4—Cu—N5	84.3(1)
Si—F5	1.679(3)	F1—Si—F2	89.5(1)
Si—F6	1.697(3)	F1—Si—F3	89.2(1)
		F1—Si—F4	88.9(1)
N1—C2	1.489(6)	F1—Si—F5	179.4(1)
N1—C4	1.479(5)	F1—Si—F6	89.7(1)
N2—C3	1.465(5)	F2—Si—F3	90.5(1)
N3—C1	1.465(6)	F2—Si—F4	178.4(1)
C1—C2	1.512(6)	F2—Si—F5	90.2(1)
C3—C4	1.531(6)	F2—Si—F6	90.1(1)
		F3—Si—F4	89.8(1)
N4—C6	1.463(6)	F3—Si—F5	90.3(1)
N5—C5	1.482(5)	F3—Si—F6	178.7(2)
C5—C6	1.526(6)	F4—Si—F5	91.4(1)
		F4—Si—F6	89.6(1)
		F5—Si—F6	90.7(1)
		C2—N1—C4	115.9(4)
		N1—C2—C1	110.3(4)
		N1—C4—C3	112.4(4)
		N2—C3—C4	109.7(4)
		N3—C1—C2	109.3(4)
		N4—C6—C5	106.8(4)
		N5—C5—C6	107.9(4)

DTA curve. The loss of weight amounts to 39.9 wt% at this stage. In this temperature interval, the partial thermal-oxidative destruction of the amine part of the complex (*i.e.*, a dehydrogenization of the coordinated *eda* and *deta* with a concurrent combustion of H<sub>2</sub>) takes place.

The fourth stage of a thermal destruction takes place in the temperature range from 368 to 544 °C and corresponds to a complete combustion of the pyrolytic residue of organic constituents of the complex. It is accompanied by the appearance of a pronounced exothermic effect on the DTA curve with a



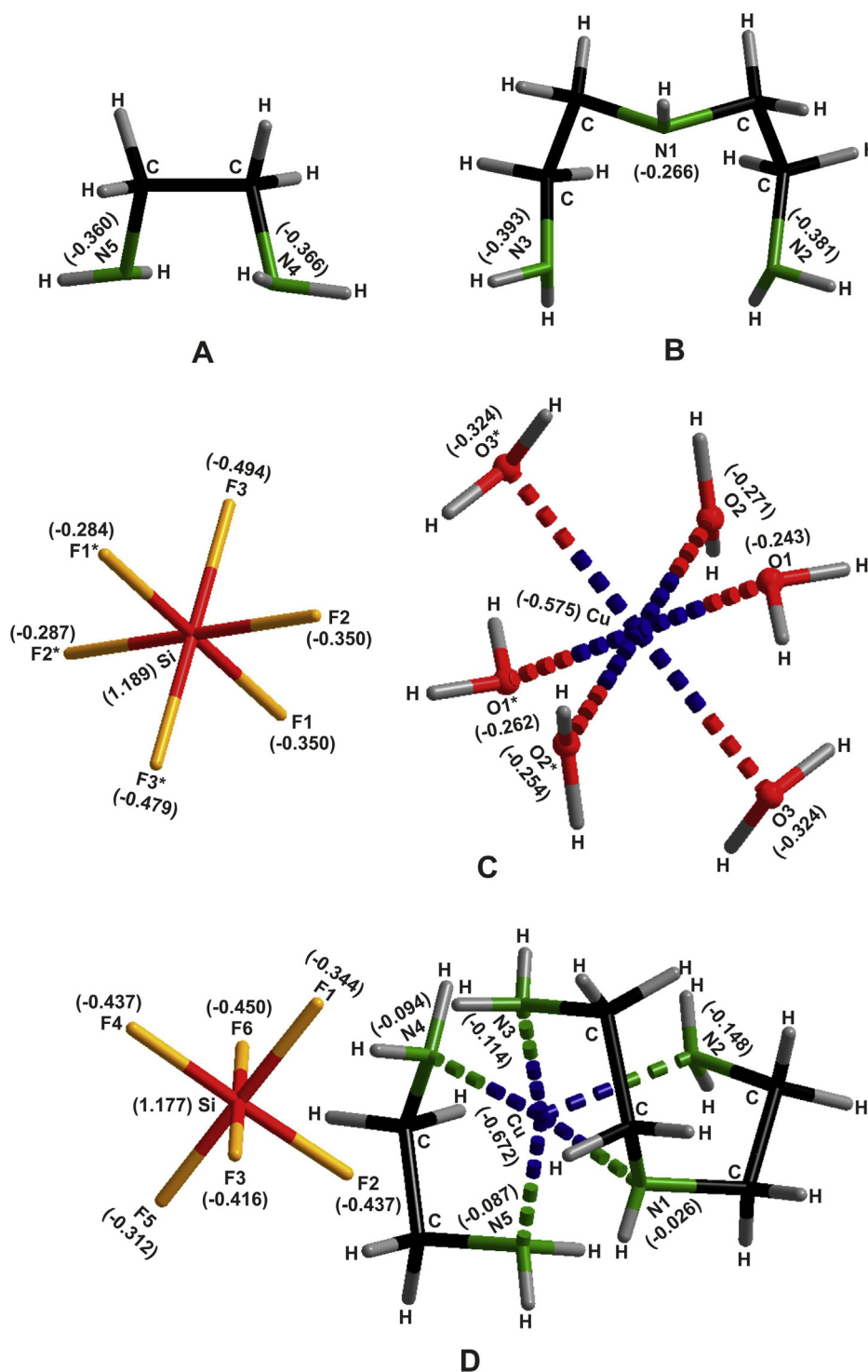
**Fig. 3** IR spectra of *pepa* (A) and **1** (B).

maximum at 488 °C. The weight loss amounts to 15.3 wt% at this final stage.

At the very end, we would like to consider the chemical influence of the *pepa*–CuSiF<sub>6</sub> interaction and the complex **1** formation on the combustibility of the coordinated polyamine. So, if the ignition point for free *eda* and *deta* is 45 °C and 97 °C, respectively then the coordinated *eda* and *deta* in **1** do not inflame at all. In other words, a combustible curing agent of epoxy resins (*pepa*), which is made up of the highly inflammable *eda* and inflammable *deta* after bonding to copper(II) hexafluoridosilicate (a fire retardant) turns into a practically incombustible substance. Undoubtedly, the reason for this is the additional chemical bonds that arise between the combustible organic molecules (*eda* and *deta*) and the incombustible inorganic salt (CuSiF<sub>6</sub>). To break down the Cu(II) ← N bonds, a considerable part of the heat energy coming from the ignition source must be expended. Moreover, in order to get a flame, it is necessary that *eda* and *deta* form a mixture of gaseous polyamines with air in which concentration of the saturated vapor *eda* and *deta* was greater than the bottom concentration limit of the flame spread (Hurley, 2016). How-

H-bonds [a]	D—H	H...A	D...A	D—H...A
N1—H11...F6 <sup>i</sup>	0.92(5)	2.03(5)	2.938(5)	165(4)
N2—H21...F1 <sup>ii</sup>	0.92(5)	2.40(4)	3.229(5)	150(4)
N2—H21...F4 <sup>ii</sup>	0.92(5)	2.35(5)	3.180(4)	150(4)
N2—H22...F5 <sup>iii</sup>	0.92(5)	2.25(5)	3.079(5)	149(4)
N3—H32...F2 <sup>iii</sup>	0.92(5)	2.24(5)	3.057(5)	147(4)
N4—H41...F6	0.92(5)	1.99(4)	2.903(4)	171(4)
N4—H42...F2 <sup>iii</sup>	0.92(5)	2.38(5)	3.047(4)	129(4)
N4—H42...F3 <sup>iii</sup>	0.92(5)	2.12(5)	2.980(5)	155(4)
N5—H51...F3 <sup>ii</sup>	0.92(5)	2.24(4)	3.098(4)	156(4)
N5—H52...F1 <sup>i</sup>	0.92(5)	1.99(5)	2.886(4)	162(4)

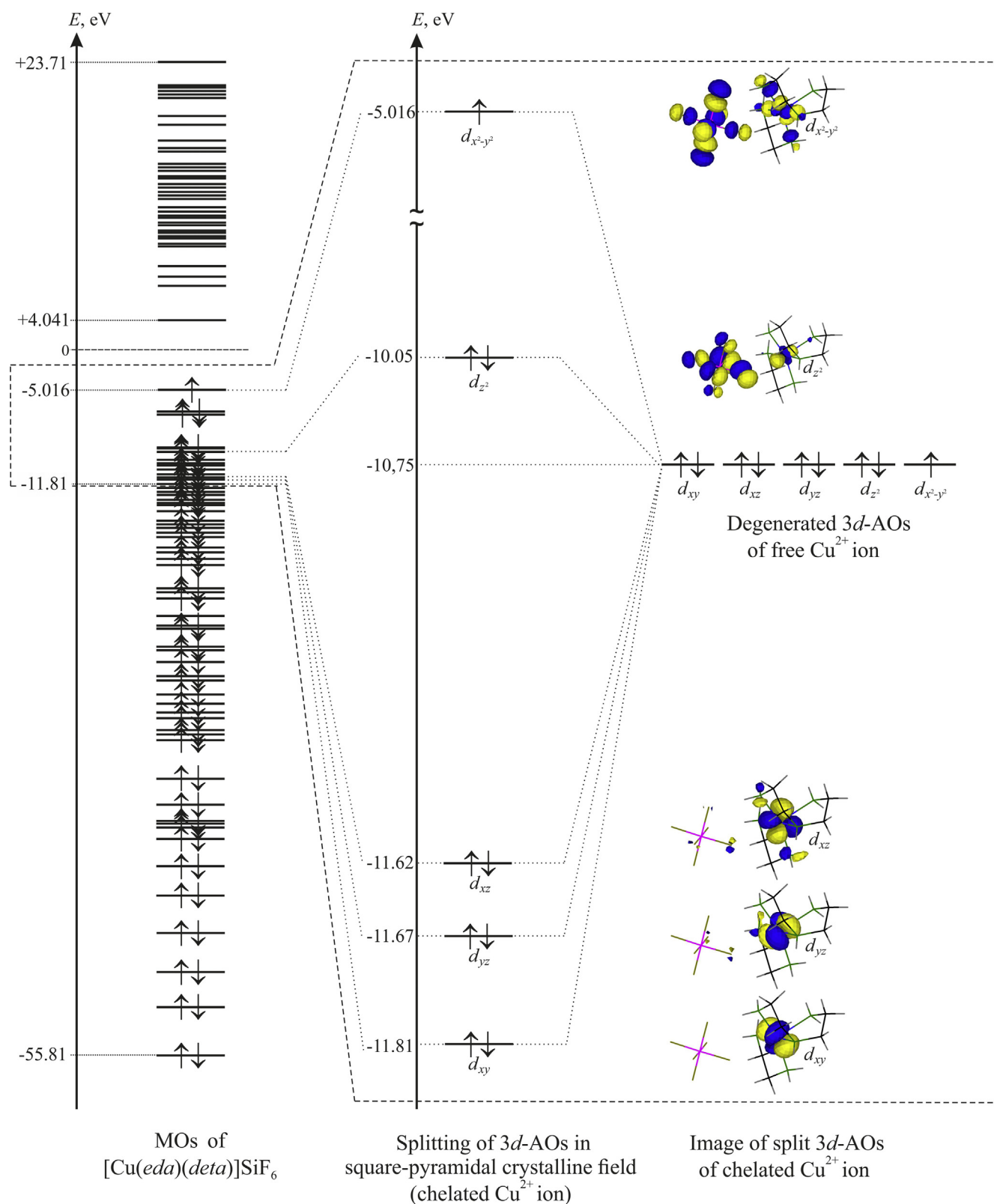
[a] Symmetry codes: (i) 3/2−*x*, −1/2 + *y*, 3/2−*z*; (ii) 1 + *x*, *y*, *z*; (iii) 3/2−*x*, 1/2 + *y*, 3/2−*z*.



**Fig. 4** Charge density ( $\pm \delta, \bar{e}$ ) distribution on the atoms in *eta* (A), *deta* (B),  $[\text{Cu}(\text{H}_2\text{O})_6]\text{SiF}_6$  (C),  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  (D).

ever, even at temperature exceeding 450 °C, ignition of *eda* and *deta* was not observed above the surface of melted down complex **1**. It is not less interesting to compare the thermal behavior of complex **1** with such behavior for *pepa*. Unlike *pepa*, whose total weight loss is observed in the temperature range from 20 to 170 °C, the complex **1** fully degrades at a lot more

temperature (544 °C). Consequently, the polyamine molecules through Cu(II)—N bonds firmly hold in the complex, therefore their instantaneous vaporization and further ignition becomes difficult. Obviously, the complexation is the main cause of a fire retarding effect at burning of nitrogen-containing hydrocarbons.



**Fig. 5** The MOs diagram for  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  (on the left) and splitting of 3d-AOs by square-pyramidal crystal field for chelated  $\text{Cu}^{2+}$  ion (on the right).



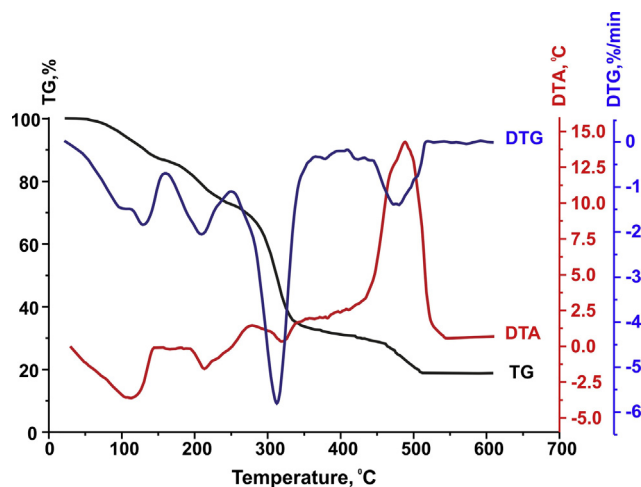


Fig. 6 TG, DTG and DTA curves of polycrystalline sample of **1**.

#### 4. Conclusions

A new chelate complex –  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  (**1**), whose crystal phase can be used as fire retardant and epoxy hardener simultaneously, was obtained by direct reaction of dehydrated salt of  $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$  and polyamines – *eda* and *deta*. Complex **1** consists of discrete complex cations –  $[\text{Cu}(\text{eda})(\text{deta})]^{2+}$ , where the *eda* and *deta* molecules act as chelate agents, and  $\text{SiF}_6^{2-}$  anions. The  $\text{Cu}^{2+}$  ion of  $[\text{Cu}(\text{eda})(\text{deta})]^{2+}$  unit is pentacoordinated by five N atoms of *eda* and *deta*. It predetermines the geometry of Cu(II) coordination polyhedron having the distorted square pyramid shape. Packing of **1** into the crystal framework is ensured by the formation of N–H...F hydrogen bonds. Quantum-chemical analysis of an electron-molecular structure of **1** revealed that a synergism of square-pyramidal crystal field effect and chelate effect results in the splitting of the degenerate  $3d$ -AOs of the  $\text{Cu}^{2+}$  ion on two sets of the energy levels; one set has lower energy ( $d_{xy} < d_{yz} < d_{xz}$ ) while another set has higher energy ( $d_{z^2} < d_{x^2-y^2}$ ). The chelate effect also predetermines the thermal behavior of solid complex **1**. So the thermal tests have displayed that the decomposition of crystal complex of **1** is finished at 368 °C while the maximum temperature of the gaseous products of combustion runs up to 544 °C. It makes possible the use of the crystals as fire retardant-hardener of epoxy resins. Further elaborations aimed at utilization of this complex at the making the self-extinguishing epoxy-amine composites are under way and their results will soon be published.

#### Appendix A. Supplementary material

CCDC 1831147 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](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.arabjc.2018.08.014>.

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