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Synthesis, structural, and thermal characterization of a new binuclear copper(II) chelate complex bearing an amine-hardener for epoxy resins

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ABSTRACT

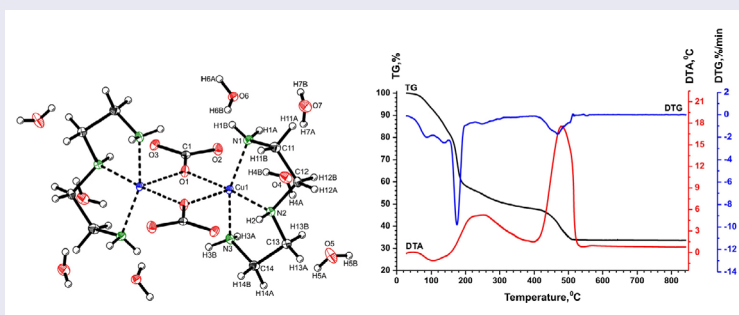
A new di(μ -carbonato)bis[aqua(diethylenetriamine)copper(II)] hexahydrate complex, $[\{\text{Cu}(\text{NH}(\text{C}_2\text{H}_4\text{NH}_2)_2)(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}]_2 \cdot 6\text{H}_2\text{O}$ (**1**), was synthesized by direct interaction of malachite with diethylenetriamine (*dien*). The crystals of **1** were characterized by X-ray powder diffraction and IR spectra, as well as structurally characterized. Compound **1** consists of $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}]_2$ discrete units whose CO_3^{2-} anions play the role of bridging ligands combining two Cu(II) chelate cores into a centrosymmetric dimer. The elongated octahedral environment of Cu^{2+} consists of three nitrogens of *dien* and an oxygen from CO_3^{2-} at the base of the bipyramid; the two apical positions of such polyhedron are occupied by an oxygen from an adjacent CO_3^{2-} and an O from H_2O . Combining the primary dimers into a framework is provided by $\text{O-H}\cdots\text{O}$ and $\text{N-H}\cdots\text{O}$ hydrogen bonds. The thermal behavior of **1** was investigated by differential thermal analysis. Thermal decomposition of **1** terminates at 400 °C, while the maximal combustion temperature of gaseous products is at 520 °C. Complex **1** may be an effective fire retardant and, at the same time, a curing agent for epoxy resins.

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1. Introduction

Transition metal complexes with polyamines are an important class of coordination compounds mainly owing to a chelating effect which causes formation of stable complexes possessing desired properties

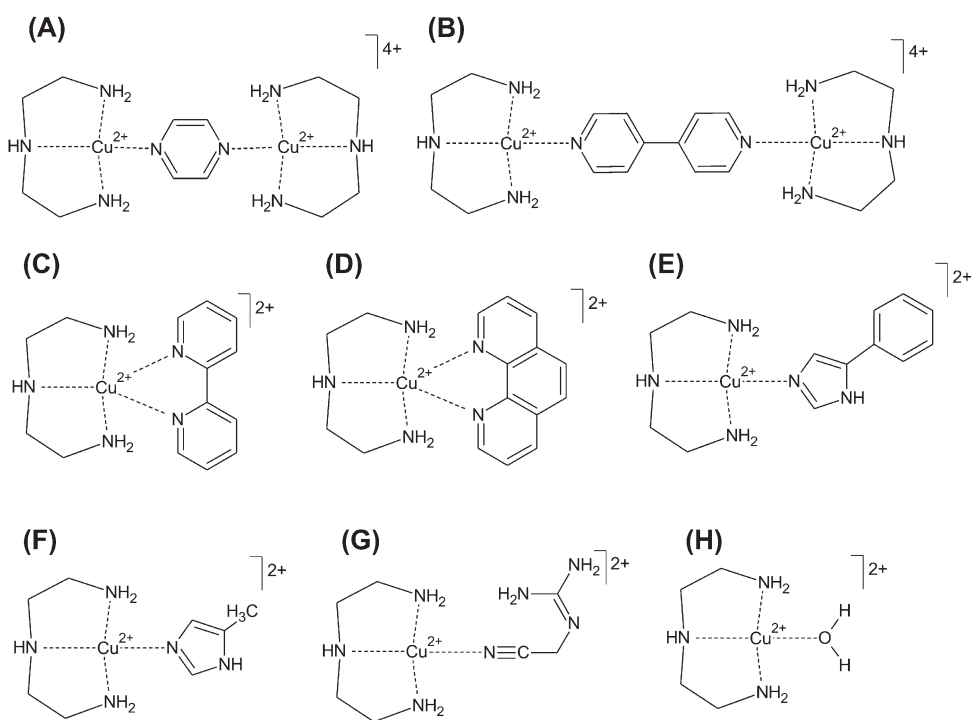
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[1] including as fire retardants and epoxy resin hardeners. Among the polyamines, diethylenetriamine (*dien*) is widely used as a curing agent in the production of epoxy resins, excellently contributing to curing the resin as three amino groups easily form networks cross-linking the polymer [2, 3]. Polymeric materials on the basis of epoxy resins, *viz.* thermoset polymers, are one of the most important polymer systems used in industry, ranging from simple two-part adhesives to high-tech applications [4, 5]. But, inherent combustibility of the epoxy polymers impedes their wider utilization. However, combustibility of epoxy-amine polymers can be appreciably decreased if the amine complexes of transition metals are used as fire retardants and epoxy curing agents simultaneously. In this regard, an important role belongs to Cu(II) chelate complexes with *dien* [6]. The ability of these chelate compounds to retard burning the polymers depends on the composition, the structure, and the type of copper salt participating in the complex formation. Crystalline copper(II) sulfate complex with *dien* is already used as fire retardant-hardeners of epoxy resins [7, 8] as this complex decreases the combustibility and enhances physicochemical and mechanical properties.

Previously, to study the structural consequences induced by substitution of anions in the *dien*-CuX-L system ($X = \text{SO}_4^{2-}$, $(\text{ClO}_4^-)_2$, $(\text{BF}_4^-)_2$, $(\text{NO}_3^-)_2$; $L = \text{H}_2\text{O}$, *pyrazine*, *2-methylimidazole*, *2-phenylimidazole*, *1,10-phenanthroline*, *2,2'-bipyridine*, *4,4'-bipyridine* and *2-cyanoguanidine*), a number of chelate complexes were synthesized and structurally investigated [9–15]. Scheme 1 summarizes the binuclear (A, B) and mononuclear (C–H) diethylenetriamine copper(II) chelate complexes.

In light of prior investigations, the study of the thermal behavior of the coordination compound obtained from the unstable copper(II) salt – CuCO_3 [16] and *dien* is particularly interesting, since crystals of this complex can be used as a fire retardant and curing agent of epoxy resins. Therefore, the results of synthesis of $[\{\text{Cu}(\textit{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2] \cdot 6\text{H}_2\text{O}$ (1), X-ray crystal structure determination (single crystal and powder), infrared spectroscopy (IR), and differential thermal analysis (DTA) are reported in this article.



Scheme 1. Overview of the binuclear **A, B** and the mononuclear **C–H** copper(II) chelate complexes with *dien*. **(A)** $[\text{Cu}_2(\textit{dien})_2(\textit{pyrazine})(\text{ClO}_4)_4]$ [9]. **(B)** $[\text{Cu}_2(\textit{dien})_2(4,4'\text{-bipyridine})(\text{ClO}_4)_4]$ [10]. **(C)** $[\text{Cu}(\textit{dien})(2,2'\text{-bipyridine})(\text{BF}_4)_2]$ [11]. **(D)** $[\text{Cu}(\textit{dien})(1,10\text{-phenanthroline})(\text{ClO}_4)_2]$ [11]. **(E)** $[\text{Cu}(\textit{dien})(2\text{-phenylimidazole})(\text{ClO}_4)_2]$ [12]. **(F)** $[\text{Cu}(\textit{dien})(2\text{-methylimidazole})\text{ClO}_4]\text{ClO}_4$ [13]. **(G)** $[\text{Cu}(\textit{dien})(2\text{-cyanoguanidine})(\text{NO}_3)_2]$ [14]. **(H)** $[\text{Cu}(\textit{dien})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$ [15].

2. Experimental

2.1. Materials and methods

For obtaining the binuclear copper(II) complex $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}_2]\cdot 6\text{H}_2\text{O}$ (**1**), the following chemicals were used: copper(II) carbonate hydroxide (malachite) – $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (bright green powder, $M = 221.11 \text{ g mol}^{-1}$, $d^{20} = 4.0 \text{ g cm}^{-3}$, $pK_s = 33.78$, $t_{\text{decomposition}} = 200 \text{ }^\circ\text{C}$ [17, 18]), and *dien* – $\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$ (colorless liquid, $M = 103.17 \text{ g mol}^{-1}$, $d^{20} = 0.955 \text{ g cm}^{-3}$, $n_D = 1.484$, $t_{\text{boiling}} = 204,1 \text{ }^\circ\text{C}$, $t_{\text{ignation}} = 97 \text{ }^\circ\text{C}$, $t_{\text{self-ignation}} = 350 \text{ }^\circ\text{C}$ [19], IR (KBr cuvette, cm^{-1}): 3372, 3254, and 3210 (ν_{NH}); 2934, 2908, and 2790 (ν_{CH}); 1600 (δ_{NH}); 1460 (δ_{CH}). All reagents have been purchased through commercial sources and used as received.

X-ray powder diffraction (XRPD) identification of the polycrystalline sample of **1** was carried out at room temperature on a HZG-4A diffractometer (Cu K_α -radiation, Bragg–Brentano geometry, angular range $5^\circ \leq 2\theta \leq 115^\circ$ with a step size of 0.02° and exposition time per point 20 s). The profile and structural parameters were refined by the Rietveld method using the package FullProf Suite [20]. Indexing of XRPD pattern was fulfilled automatically by the method described [21] using DICVOL91 software package [22]. The structure model was taken from single crystal data. The calculated data of the powder X-ray diffraction pattern are given in table 1.

IR absorption spectra were recorded from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1} on a Perkin Elmer SpectrumTwo FTIR spectrometer. IR measurements were performed with a solid sample of **1** pressed in spectroscopically pure KBr pellet, or a liquid sample of *dien* using a KBr cuvette.

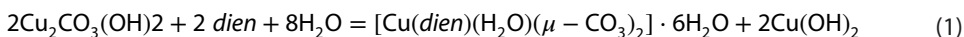
Thermal gravimetric analysis for crystalline phase of **1** was performed on a Q-1500D thermal analyzer (F. Paulik, J. Paulik, L. Erdey system) from 25 to $1000 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The experiments were carried out in dynamical regime in air. The weight of each solid-phase sample was 100 mg. Aluminum oxide was used as a standard.

Table 1. Crystal data and experimental details for monocrystalline and polycrystalline samples of **1**.

	Single-crystal	Powder
Empirical formula		$\text{C}_{10}\text{H}_{42}\text{Cu}_2\text{N}_6\text{O}_{14}$
Formula weight		$597.58 \text{ g mol}^{-1}$
Crystal system		Monoclinic
Space group		$P2_1/c$ (No. 14)
Unit cell dimensions (Å , $^\circ$)		
<i>a</i>	7.4793(1)	7.6504(4)
<i>b</i>	7.1731(1)	7.1991(3)
<i>c</i>	21.8567(3)	22.088(1)
β	98.129(2)	98.493(5)
Volume (Å^3), <i>Z</i>	1160.82(3), 2	1203.2(1), 2
Calculated density (g cm^{-3})	1.710	1.649
Absorption coefficient (mm^{-1})	1.908	–
<i>F</i> (0 0 0)	628.0	–
Crystal size	$0.6 \times 0.6 \times 0.2 \text{ mm}$	–
Crystal description	Dark-blue prism	Dark-blue powder
Temperature (K)	100(1)	293(2)
Wavelength (Å)	0.71073	1.54060
2θ range for data collection ($^\circ$)	5.98–58.96	5.00–115.00
Limiting indices	$-10 \leq h \leq 10; -9 \leq k \leq 9; -24 \leq l \leq 30$	–
Reflection collected	9039	3651
Independent reflections	2993 [$R(\text{int}) = 0.02$]	–
Parameters/restraints	229/0	104/0
Goodness-of-fit on F^2	1.009	–
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0177, wR_2 = 0.0496$	$R = 0.0819$
<i>R</i> indices (all data)	$R_1 = 0.0200, wR_2 = 0.0511$	–
Weighing scheme (<i>w</i>)	$[\sigma^2(F_o^2) + (0.0300P)^2 + 0.5933P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$	–
Largest diff. peak and hole (e Å^{-3})	0.412 and -0.286	–

2.2. Synthesis of **1**

$[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]\cdot 6\text{H}_2\text{O}$ (**1**) has been synthesized by the reaction of malachite with *dien*. Crystalline $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (2.21 g, 0.01 mol) was placed into a porcelain mortar, and 1.0 mL (0.01 mol) of *dien* and a bit of water were 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 a solid phase appeared according to the following reaction:



The obtained solid phase was dissolved in water and the insoluble residue of $\text{Cu}(\text{OH})_2$ was filtered off. Dark blue crystals of **1** suitable for X-ray structure determination were separated from the filtrate by solvent evaporation. Yield: 100% (with respect to *dien*), $\text{C}_{10}\text{N}_6\text{O}_{14}\text{H}_{42}\text{Cu}_2$ (597.58 g mol⁻¹). XRPD ($P2_1/c$; $a = 7.6504(4)$ Å, $b = 7.1991$ Å, $c = 22.088$ Å, $\beta = 98.493(5)^\circ$; $d(hkl)$, Å): 10.923 (0 0 2), 7.501 (1 0 $\bar{1}$), 7.282 (0 0 3), 7.199 (0 1 0), 5.830 (1 0 2), 5.684 (1 0 $\bar{2}$), 5.461 (0 0 4), 5.194 (1 1 $\bar{4}$), 5.120 (0 1 3), 4.960 (1 1 1), 4.905 (1 1 $\bar{2}$), and 4.776 (1 0 $\bar{4}$). IR (KBr pellet, cm⁻¹): 3470, 3252, and 3156 (ν_{NH}); 2960, 2926, and 2852 (ν_{CH}); 1614 (δ_{NH}); 1560 (δ_{CH}); 1452, 1416 (ν_{CO}); 824, 800 (δ_{CH}).

2.3. Crystallographic study

A single crystal of **1** was mounted on the Xcalibur diffractometer (Mo K_α -radiation, $\lambda = 0.71073$ Å, graphite monochromator) equipped with an Oxford Cryosystem cooler and a CCD detector. About 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 60 mm crystal-to-detector distance. After integration, the data were corrected for Lorentz and polarization effects [23]. Unit cell parameters were obtained by least-squares refinement based on reflection angles of $5.98 < 2\theta < 58.96$. Structure **1** was solved by direct methods applying SHELX software package [24]. Non-hydrogen atoms as well as hydrogens of water and amino groups were located by the Fourier difference synthesis and refined by the least-squares method in the full-matrix anisotropic (non-hydrogen atoms) and isotropic (hydrogens) approximation. The hydrogens of $-\text{CH}_2-$ groups were placed geometrically and refined as riding with C–H, 0.97 Å, and with isotropic temperature factors 1.2 times the U_{eq} value of the parent carbon. The crystal data, collected reflections, and parameters of the final refinement data for **1** are reported in table 1.

3. Results and discussion

3.1. Crystal structure description

The interaction of *dien* (a curing agent of epoxy resins) with non-combustible copper(II) carbonate (a fire retardant) predetermines the properties of $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]\cdot 6\text{H}_2\text{O}$ as fire retardant-hardener. In the compound under consideration, the nitrogen-containing tridentate ligand *dien* combines with cupric salt by forming the chelate complex where all three amine groups of the organic molecule are simultaneously bonded to Cu(II). As can be seen in figure 1, the chelate effect along with the bridging function of carbonate anion determines the structure of **1** as a discrete dimer – $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]$ which is similar to that of $[\{\text{Cu}(2,2'\text{-bipyridylamine})(\mu\text{-CO}_3)\}_2]\text{H}_2\text{O}$ [25–28]. In the binuclear chelate complexes, especially with a very peculiar coordination mode of carbonate bridge, the magnetic properties of the paramagnetic center, Cu(II) can intensify (or weaken) [26].

Like previous binuclear chelate complexes with the *dien* ligand $[(\text{dien})\text{Cu}(\mu\text{-L})\text{Cu}(\text{dien})](\text{ClO}_4)_4$ (L = pyrazine [9] and 4,4'-bipyridine [10]) (see scheme 1, **A** and **B**), **1** is also built from centrosymmetric discrete dimers $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]$. However, unlike **A** and **B**, where the bridging function corresponds to pyrazine or 4,4'-bipyridine, the role of the bridge in **1** is fulfilled by CO_3^{2-} . In the aforementioned binuclear complexes (**A** and **B**), the chelate core has a tetragonal coordination of Cu(II) generated by three N of *dien* and plus a fourth N atom of the corresponding $\mu\text{-L}$ molecule (the average lengths of

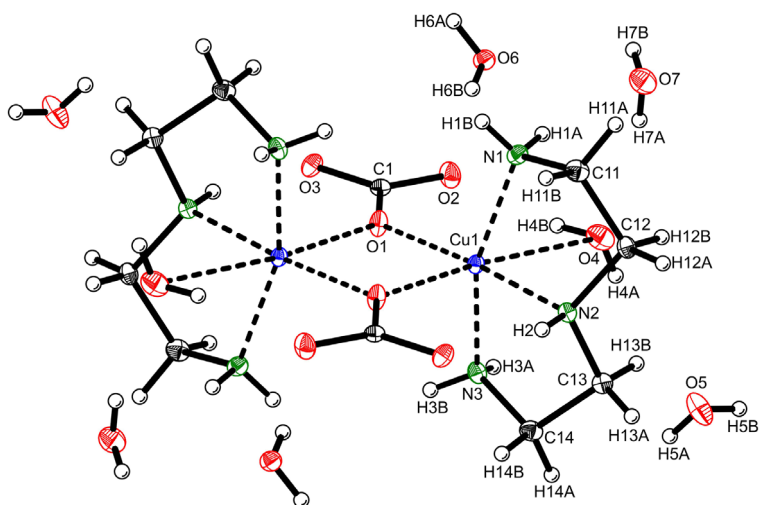


Figure 1. Atom numbering scheme of independent part of centrosymmetrical dimer in **1**. Thermal ellipsoids are displayed at the 50% probability level for non-hydrogen atoms.

the Cu–N bonds are 2.00 Å); the two apical positions of the coordination polyhedron are occupied by O of the ClO_4^- anions (the lengths of the axial Cu–O bonds is ≈ 2.60 Å).

Cu^{2+} in **1** is also six coordinate; the coordination sphere of Cu(II) consists of three N atoms of one tridentate molecule (*dien*), two O from two adjacent CO_3^{2-} anions and one water. The coordination polyhedron of Cu(II) to a first approximation can be figured as a distorted square pyramid where N1, N2, and N3 of the amine, together with O1 of the carbonate form the base of pyramid, while O1ⁱ of a nearby carbonate occupies the apical position (figure 2). In this case, O4 of water located at the farthest distance from copper was not included in the coordination sphere. Distances from each N to copper are almost identical, whereas axial Cu1–O1ⁱ bond is longer than that of the Cu1–O1 bond in the plane (table 2). The base of such square pyramid is non-planar; N1 and N3 are above the N1–N2–N3–O1 plane by 0.37 Å. We calculated a value of the τ parameter for the Cu(II) coordination environment (a coordination number of five) using the procedure proposed by Addison [29]; the geometry of the polyhedron is similar to the square pyramidal ($\tau_5 = 0.23$).

The coordination sphere of Cu(II) can be completed by one more oxygen (O4) of crystallized water (see figure 1). Thus, a distorted octahedron arises in the unit cell of **1** as a result of the additional coordination of O4 at another apical position on the opposite side of a square pyramid (Cu1–O4 2.939(1) Å). According to the Jahn–Teller effect [30], the less strong Cu1–O1ⁱ and Cu1–O4 bonds are mainly caused

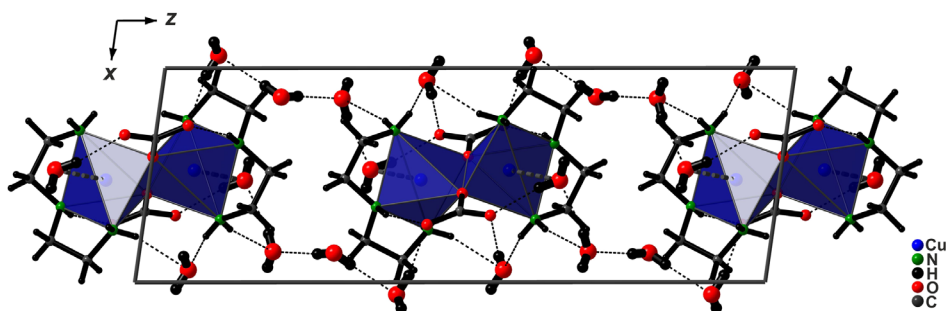


Figure 2. XZ plane projection of the crystal structure for **1**. The highlighted coordination polyhedron of Cu(II) is presented as a square pyramid.

Table 2. Selected bond lengths and angles for **1**.

Bond ^a	d (Å)	Angle	ω (°)
Cu1–N1	2.032(1)	N1–Cu1–N2	84.72(5)
Cu1–N2	2.006(1)	N1–Cu1–N3	158.94(5)
Cu1–N3	2.015(1)	N1–Cu1–O1	97.69(4)
Cu1–O1	1.939(1)	N1–Cu1–O1 ⁱ	102.38(4)
Cu1–O1 ⁱ	2.273(1)	N1–Cu1–O4	83.72(4)
Cu1–O4	2.939(1)	N2–Cu1–N3	102.38(4)
		N2–Cu1–O1	172.99(4)
		N2–Cu1–O1 ⁱ	93.96(4)
		N2–Cu1–O4	86.59(4)
		N3–Cu1–O1	94.76(4)
		N3–Cu1–O1 ⁱ	96.60(4)
		N3–Cu1–O4	77.39(4)
		O1–Cu1–O1 ⁱ	79.11(4)
		O1–Cu1–O4	100.20(4)
		O1 ⁱ –Cu1–O4	173.90(3)
C1–O1	1.307(2)	O1–C1–O2	119.0(1)
C1–O2	1.276(2)	O1–C1–O3	118.1(1)
C1–O3	1.282(2)	O2–C1–O3	123.0(1)
N1–C11	1.481(2)	N1–C11–C12	108.7(1)
N2–C12	1.476(2)	C11–C12–N2	107.5(1)
N2–C13	1.474(2)	C12–N2–C13	115.4(1)
N3–C14	1.482(2)	N2–C13–C14	107.6(1)
C11–C12	1.520(2)	C13–C14–N3	108.8(1)
C13–C14	1.522(2)		
N–H	0.82(2)–0.93(2)	H–N–H	101(2)–106(2)
C–H	0.92(2)–0.99(2)	H–C–H	103(1)–112(1)
O–H	0.73(2)–0.81(2)	H–O–H	101(2)–113(2)

^aSymmetry code: (i) 1 – x, 2 – y, 1 – z.

by electrostatic repulsion of the lone-electron pairs of the corresponding oxygens and the doubly occupied d_{z^2} orbital of copper(II).

The carbonate anion in **1** has a planar trigonal shape. Environment of C1 consists of O1, O2, and O3. Nevertheless, the values of the C–O bond lengths and the O–C–O bond angles are unequal. So, due to bridging of O1 connecting two copper(II) ions, the C1–O1 bond length somewhat exceeds the lengths of the C1–O2 and C1–O3 bonds, whose oxygens (O2 and O3) take part only in hydrogen bonds. The same applies to the bond angles of CO_3^{2-} , the O2–C1–O3 bond angle is 123.0(1)°, while O1–C1–O2 and O1–C1–O3 bond angles are 118.9(1)° and 118.1(1)°, respectively.

Thus, apart from bridging, the carbonate is hydrated by crystal water which, further, forms hydrogen bonds with adjacent water molecules and $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]$ dimeric units. Thus, **1**, by means of the carbonate and coordinated *dien* links external molecules of crystal water into the framework. As a consequence, the branched system of hydrogen bonds of $\text{H}_2\text{O}\cdots\text{OC}(\text{O})\text{O}\cdots\text{H}_2\text{O}$ (H6B \cdots O2 and H6A \cdots O3ⁱⁱ distances are 1.92(3) and 1.87(2) Å, respectively (symmetry code: (ii) 2 – x, 1 – y, 1 – z), forms in **1**. The cross-linked system of intramolecular and intermolecular N–H \cdots O bonds (table 3) also exercises considerable influence on the crystal structure. Consequently, the packing of $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]$ dimeric units into the crystalline framework of **1** (figure S1, Supp. info) can be explained by hydrogen bonds [31, 32].

3.2. XRPD identification and IR spectroscopy

Complex **1** has been characterized by XRPD (figure S2, Supp. info). The peaks of the simulated diffraction pattern are in agreement with the experimental XRPD pattern peak positions, indicating that the polycrystalline sample as a whole and the single crystals are the same compound. No other crystal phase except that of **1** has been found in the investigated sample.

Table 3. Distances (Å) and angles (°) in the hydrogen-bonding scheme for **1**.

H-bonds ^a	D–H	H···A	D···A	D–H···A
O4–H4B···O2	0.76(2)	1.95(2)	2.695(2)	167(2)
O6–H6B···O2	0.73(2)	1.92(3)	2.640(1)	172(3)
N2–H2···O3 ⁱ	0.85(2)	2.17(2)	2.994(2)	160(2)
O6–H6A···O3 ⁱⁱ	0.81(2)	1.87(2)	2.660(2)	166(2)
N3–H3A···O3 ⁱⁱⁱ	0.90(2)	2.07(2)	2.972(2)	167(2)
O7–H7A···O4	0.74(2)	2.06(2)	2.756(2)	158(2)
O7–H7B···O5 ^{iv}	0.78(2)	2.05(2)	2.826(2)	175(2)
O5–H5A···O6 ^v	0.76(2)	2.02(2)	2.776(2)	174(3)
N3–H3B···O6 ⁱⁱⁱ	0.82(2)	2.31(2)	3.063(2)	154(2)
N1–H1B···O6 ^{vi}	0.82(2)	2.31(2)	3.023(2)	145(2)
N1–H1A···O7	0.84(2)	2.27(2)	3.088(2)	162(2)
O5–H5B···O7 ^{vii}	0.77(2)	2.01(2)	2.785(2)	175(2)

^aSymmetry codes: (i) 1 – x, 2 – y, 1 – z; (ii) 2 – x, 1 – y, 1 – z; (iii) 1 – x, 1 – y, 1 – z; (iv) 1 + x, y, z; (v) –1 + x, y, z; (vi) x, 1 + y, z; (vii) 1 – x, –0.5 + y, 1.5 – z.

Besides XRPD, **1** was also identified by IR spectroscopy (figure S3, Supp. info). As a result of binding Cu(II) and *dien* into a chelate complex, a shift of N–H absorption bands is observed. Absorption bands caused by stretching and bending of NH₂ and NH groups of the coordinated and free *dien* molecule will interest us primarily [33, 34]. For free *dien* (figure S3(a), Supp. info), the high-frequency regions 3372 and 3254 cm⁻¹ are related to the stretching of –NH₂, whereas the band observed at 3210 cm⁻¹ is ascribed to stretching of –NH–; the observed oscillation frequency at 1600 cm⁻¹ is attributed to the bending of N–H bonds. After bonding of the *dien* with copper(II) carbonate (figure S3(b), Supp. info), one of the N–H absorption bands is shifted to high frequency at 3470 cm⁻¹, whereas two other bands are shifted to low frequency (3252 and 3156 cm⁻¹). The observed wavenumber at 1614 cm⁻¹ related to the bending of N–H bonds is also shifted to higher frequency.

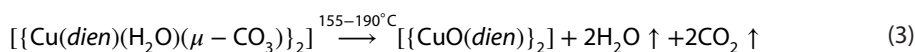
3.3. Thermal gravimetric analysis

The effectiveness of bonding a combustible organic amine with an incombustible inorganic salt in many respects predetermines the thermal stability of the diethylenetriamine copper(II) chelate complex as fire retardant-hardeners of epoxy resins. Therefore, the thermal behavior of **1** was studied by thermal gravimetric analysis. The curves of thermogravimetry (TG), differential thermogravimetry (DTG) and DTA are displayed in figure 3.

The TG curve for thermal decomposition of **1** is represented by four sections. The first involves 20–154 °C, accompanied by a loss of weight of 18.6 wt% and by the appearance of a minimum on the DTA curve. At this temperature interval (DTA curve), an endothermic process is observed with a temperature at 110 °C. This part of the curve is related to dehydration of the crystal water which can be written as:



The second stage of the thermal decomposition is from 155 to 190 °C ($\Delta m = 21.6$ wt%). The loss of coordinated water and, concurrently, the break down of the inorganic part of complex take place in this temperature range:



The third stage of the thermal decomposition occurs from 191 to 400 °C and is accompanied by the appearance of two successive exothermic effects at the DTA curve. The loss of weight at this stage amounts to 11.6 wt% from the partial thermal-oxidative destruction of $[\{\text{CuO}(\textit{dien})\}_2]$, with a concurrent dehydrogenization of the coordinated *dien*.

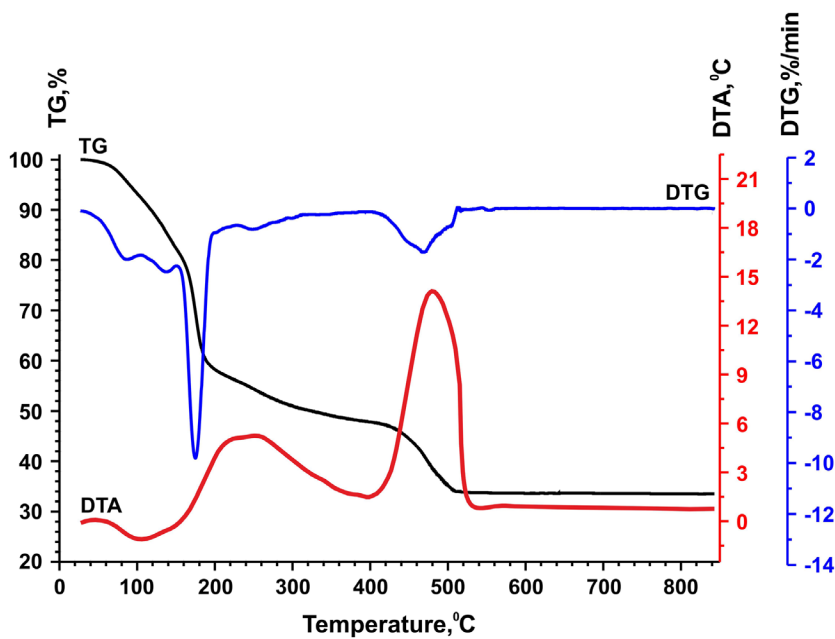


Figure 3. TG, DTG, and DTA curves of polycrystalline 1.

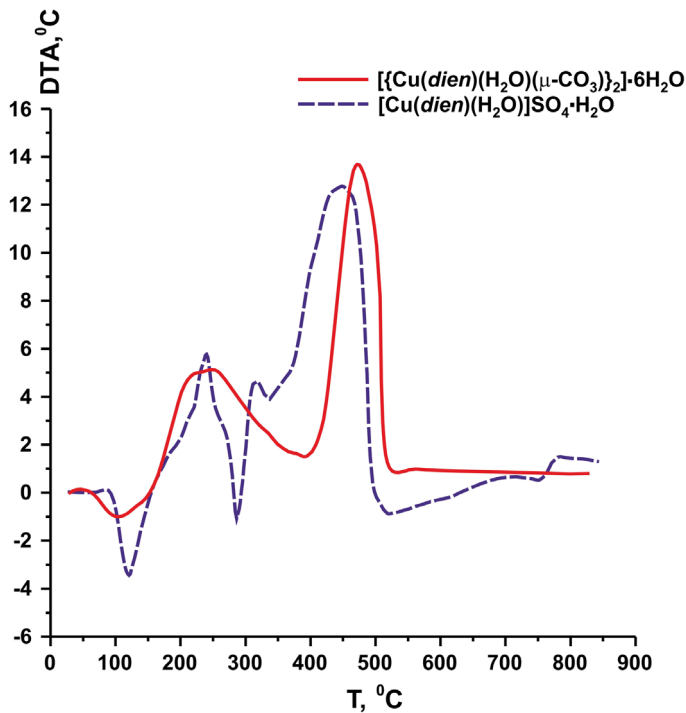
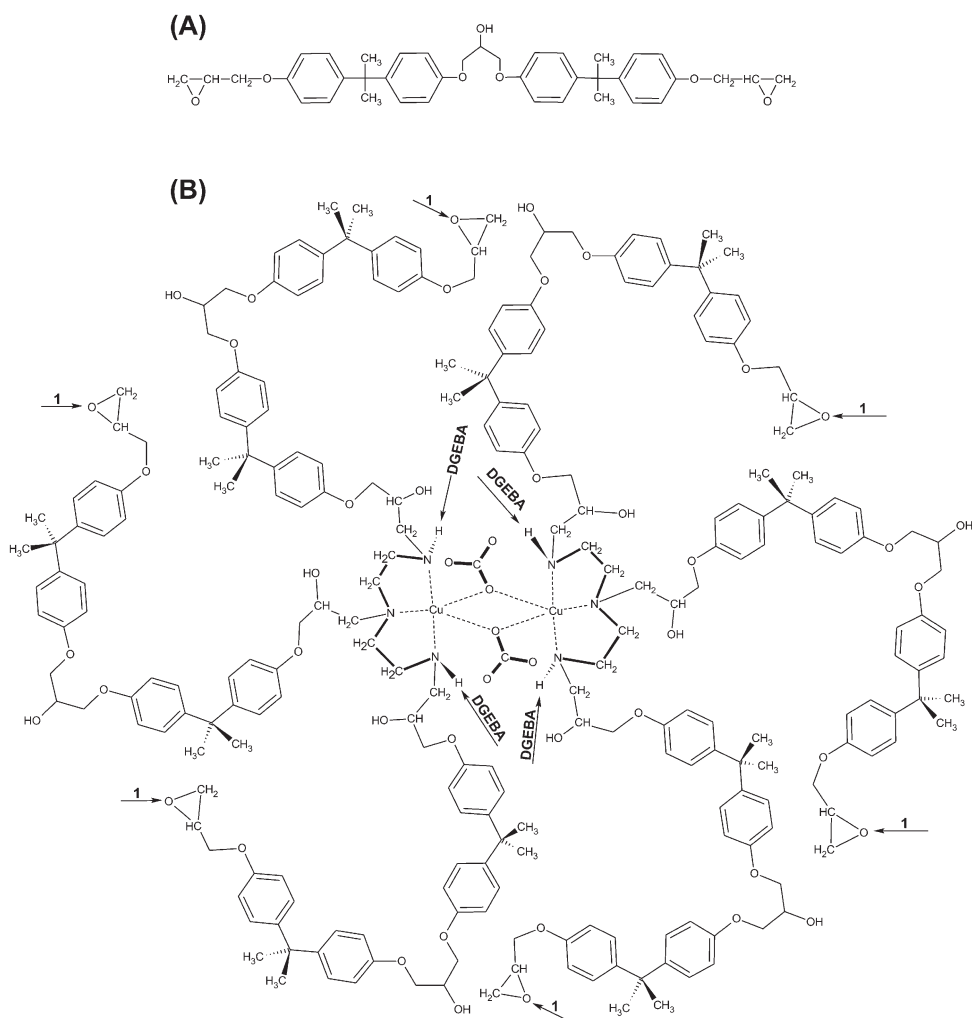


Figure 4. DTA curves for $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}_2]\cdot 6\text{H}_2\text{O}$ (1) (solid line) and $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]\text{SO}_4\cdot \text{H}_2\text{O}$ [8] (dotted line).



Scheme 2. The bisphenol A diglycidyl ether molecule (DGEBA) **A** and the polymeric framework of the epoxyamine composite modified by CuCO_3 **B**.

The fourth stage of thermal destruction from 400 to 520 °C corresponds to 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 maximum at 480 °C. The weight loss at this final stage is 14 wt%.

3.4. Fire retardant-hardener properties of $[\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)]_2 \cdot 6\text{H}_2\text{O}$

One must consider the chemical influence of copper(II) carbonate on the flammability of the modified epoxy-amine polymers. *Dien*- CuCO_3 interaction results in the formation of **1** and exerts direct influence on the combustibility of the coordinated amine. So, if the ignition point for free *dien* is 97 °C then the coordinated *dien* complex **1** does not inflame at all. In other words an inflammable *dien* (a curing agent of epoxy resins) after bonding to copper(II) carbonate (a fire retardant) turns into a practically incombustible substance. In this connection it will be interesting to compare the thermal behavior of **1** with $[\text{Cu}(\text{dien})(\text{H}_2\text{O})\text{SO}_4 \cdot \text{H}_2\text{O}]$ [8] whose solid phase is used as fire retardant of epoxy resins [7]. The DTA curves of these complexes are presented in figure 4. The curves clearly reveal that the thermal properties

of $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}_2]\cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{dien})(\text{H}_2\text{O})\text{SO}_4]\cdot \text{H}_2\text{O}$ are similar. So, the thermal decomposition of crystalline **1** finishes at 400 °C while the maximal combustion temperature of the gaseous products is at 520 °C. For $[\text{Cu}(\text{dien})(\text{H}_2\text{O})\text{SO}_4]\cdot \text{H}_2\text{O}$ these temperatures are 340 and 500 °C, respectively.

A similar tendency takes place in flammability of the epoxy resins. The ignition point of epoxy–amine polymer after adding CuSO_4 increases from 314 to 358 °C. However, when the carbonate copper(II) salt is added the flammability of the epoxy resin shifts to 371 °C. The cause of this is related to the extra chemical bonds formed in the course of epoxy–amine polymerization with participation of the cupric salt. The results of quantum-chemical calculations of the binding energy in a square-pyramidal core of Cu(II) performed for $[\text{Cu}(\text{dien})(\text{H}_2\text{O})\text{SO}_4]\cdot \text{H}_2\text{O}$ [15] revealed that the total energy of three Cu–N and two Cu–O bonds is 337.32 kJ mol⁻¹. After addition of the copper(II) complex, e.g. $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}_2]\cdot 6\text{H}_2\text{O}$ (**1**), to the epoxy oligomer, bisphenol A diglycidyl ether (DGEBA), the coordinated *dien* polymerizes as shown in scheme 2.

As a result, the polymeric framework which forms within this compositional matrix contains the chemically connected incombustible inorganic salt – CuCO_3 . The coordination bonds that arise between Cu(II) of such salt and N atoms of the curing agent are responsible for the flammability suppression of the epoxy–amine composite. To break down these coordination bonds, a significant amount of thermal energy should be used up. It is important to notice that final combustion of pyrolytic residue of the epoxy resin which only contains the *dien* is completed at 900 °C. However, combustion of the pyrolytic residue for epoxy resin hardened by the *dien* copper(II) complex ceases at 660 °C (for CuSO_4) or 690 °C (for CuCO_3). It can testify to self-extinguishing nature of burning of epoxy–amine composites filled with cupric salts. Thus, it allows considering **1** as a vastly effective fire retardant-hardener for combustibility suppressing of epoxy–amine composites.

4. Conclusion

A new complex $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}_2]\cdot 6\text{H}_2\text{O}$ (**1**), whose crystal phase can be used as a fire retardant-hardener of epoxy resins, was obtained by the reaction of malachite and *dien*. $[\{\text{Cu}(\text{dien})(\text{H}_2\text{O})(\mu\text{-CO}_3)_2\}_2]\cdot 6\text{H}_2\text{O}$ consists of discrete units where the CO_3^{2-} anions are bridging ligands, connecting the coordination cores of Cu(II) into centrosymmetric dimers, while the *dien* molecules chelate. Crystal packing of **1** into a framework is ensured by the formation of O–H⋯O and N–H⋯O hydrogen bonds. The chelate effect determines the thermal behavior of solid **1**. Thus, thermal analysis of **1** shows that the decomposition of crystals ends at 400 °C, while the maximum combustion temperature of the gaseous products is 520 °C. It allows the use of this crystalline complex as fire retardant-hardener of epoxy-amine polymers contributing to a decreased combustibility. Work directed towards the use of **1** in the production of self-extinguishing epoxy–amine composites is under way. The results of these investigations will form the basis of future publications.

Supplementary material

CCDC reference number 1442321 contains the supplementary crystallographic data for **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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223336033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

Disclosure statement

No potential conflict of interest was reported by the authors.

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