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CHEMICAL SCIENCES

USING THE $[Cu(H_2NC_2H_4NH_2)_2(H_2O)Cl]Cl$ CHELATE COMPLEX AS AN EFFICIENT FLAME RETARDANT-HARDENER FOR EPOXY RESINS

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Polyamine chelate complexes of transition metals are an important class of coordination compounds mainly due to a chelating effect that results in formation of the thermal stable complexes [1–3] with desired properties including properties of flame retardants and epoxy hardeners [4–11]. Along with the great number of polyamines, ethylenediamine (*eda*) is also used as a curing agent to produce epoxy polymers. In turn, the epoxy-polymer materials are one of the most important classes of polymers used today in the industry, starting from simple two-part adhesives to high-tech applications. However, the inherent combustibility of epoxy polymers prevents their wider use. Nevertheless, the combustibility of polymer materials based on epoxy resins can be significantly reduced if polyamine transition metal complexes are used for the production of epoxy-amine composites. In this regard, the chelate complex of non-combustible copper(II) chloride with *eda* is of particular interest. Given above, we were studied the interaction of polyethylenepolyamine (*pepa*) with copper(II) chloride to obtain the crystalline complex $[Cu(eda)_2(H_2O)(Cl)]Cl$ (**1**) (*eda* is *pepa* component), to more precise determine its crystal structure and DFT calculate its electron characteristics.

Aqua-bis(ethylenediamine)-chloro-copper(II) chloride complex, **1**, was synthesized by direct interaction of $CuCl_2 \cdot 2H_2O$ with *pepa* (*pepa* is polyethylenepolyamine containing ethylenediamine (*eda*)). Crystals of **1** were characterized by IR spectra and structurally studied. Compound **1** consists of $[Cu(eda)_2(H_2O)(Cl)]^+$ discrete complex cations whose Cu^{2+} ions is chelated by two *eda*; the complex cation (Figure) is elongated square bipyramid, the ligands being the two bidentate *eda* molecules, the water molecule, and the chloride ion. Combining Cu(II) polyhedrons along with external Cl^- ions into a framework is provided by O–H…Cl and N–H…Cl hydrogen bonds. Quantum-chemical calculations of chelation process were carried out with the restricted Hartree-Fock method using a 6-31G* base set. The DFT-calculated electron-stereo-chemical parameters are in a good agreement with its possibility to be a flame retardant and a hardener epoxy resins simultaneously.

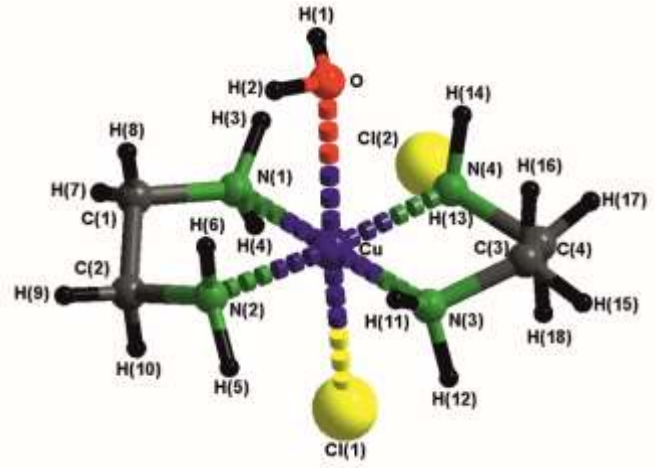
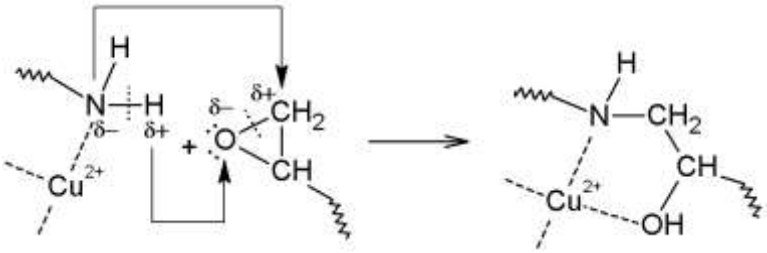


Figure. Atom numbering scheme of independent part of the complex **1**.

Cu(II)–(*eda*) chelating results in the N–H bonds polarization and, as consequence of it, increases electrophilic ability of the H atoms of $–NH_2$ groups. This as well as possible facilitates the electrophilic addition of the H atom to the O atom of the oxirane ring and, concurrently, promotes the nucleophilic attack of the N atom onto C atom of the epoxy group (Scheme). Thus, DFT analysis of the charge distribution on atoms in **1** clearly shows that *eda* coordinated on Cu(II) is a more effective curing agent of epoxy resins than *eda* in free.



Scheme. Curing of epoxy with fire retardant-hardener (**1**).

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