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Photocatalytic degradation of methylene blue with copper(II) oxide synthesized by thermal decomposition of Flubendazole complexes

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Graphical abstract





Thermal decomposition of Flubendazole copper(II) complexes gave Tenorite nanoparticles, which were as catalyst in the catalytic degradation of methylene-blue dye exposed to UV radiation.

Highlights:

- Nano-tenorite were synthesized from thermal decomposition of Flubendazole complexes.
- The polymorph and morphology of nano-particles were investigated by XRD and SEM.
- Photo-acceleration of the degradation process of methylene blue was reported.

- Electronic structures were assigned by the aid of TD-DFT calculations.
- Hybridization, electronic arrangements and M-L interactions were discussed.

Abstract

Novel copper(II) complexes of an anti-parasitic Flubendazole drug (FLU), $[Cu(FLU)_2X_2] \cdot yH_2O$ (X = Cl-(1), $C_2H_3O_2^-$ (3), and ClO_4^- (4), y = 1-4) and $[Cu(NO_3)(FLU)_2(OH_2)] \cdot NO_3 \cdot 2H_2O$ (2) were synthesized and characterized using elemental analysis, TG, IR, EPR, magnetic and conductance measurements. Geometry optimization and natural bond orbital analysis were performed at DFT/B3LYP/6-31G* level of theory. Electronic transitions were calculated by TD-DFT. Tenorite (CuO) nanoparticles with promising catalytic properties were prepared in air *via* the controlled thermal decomposition of 1-4. The polymorph and morphology of the prepared nano-tenorite particles were investigated by powder XRD and field emission scanning electron microscope. The catalytic degradation of methylene-blue dye exposed to UV radiation and in presence of CuO nanoparticles as a catalyst was studied at room temperature in water.

Key Words: Flubendazole; TD-DFT; Methylene-blue, Tenorite nanoparticles

Flubendazole (Scheme 1) is an anti-parasitic agent used for the treatment of various human and animal helminthoses **[1, 2]**.Recent reports suggested that FLU found an application in cancer treatment **[3]**. Its mode of action involves the destruction of cytoplasmic microtubules in the intestinal or absorptive cells of the parasite **[4]**.Inhibition of glucose uptake and depletion of glycogen stores follow lead to death of the parasite **[5]**.Several analytical techniques such as fluorescence spectroscopy **[6]**, liquid chromatography **[7]**, and polarography **[8]** were applied for determination of FLU in its pharmaceutical preparations. To the best of knowledge, the coordination behavior of FLU towards different metal ions has not been previously discussed in the literature.

Here, synthesis, spectroscopic and thermal characterization of Cu(II) complexes of FLU drug are reported both experimentally (see the supporting information for details) and theoretically **[9, 10]** and are correlated. Theoretical calculations were carried out by Gaussian 03 **[11]** suite of programs. In addition, a simple and nontoxic method for preparation of CuO nanoparticles based upon the thermal decomposition of the synthesized Cu (II) complexes has been explored. The morphology has been characterized by different physical methods such as XRD and FE-SEM. Finally, the degradation of MB by the catalytic performance of CuO nanoparticles has been investigated with the aid of the ultraviolet radiation.

The binary complexes $[Cu(FLU)_2X_2]$ ·yH₂O (X = Cl· (1), y = 4; C₂H₃O₂· (3), y = 1; X = ClO₄· (4), y = 3) and $[Cu(NO_3)(FLU)_2(OH_2)]$ ·NO₃·2H₂O (2) were prepared (see the supporting information for details). Elemental analysis (supporting information) data are in agreement with those calculated for the suggested structures. Lower conductance values were reported for 1, 3 and 4 (in DMF) compared with the reported values [12], while the higher one (100.10 ohm⁻¹ cm² mole⁻¹) of 2 suggests its ionic nature. IR bands observed at 3308, 1736, 1646 and 1595 cm⁻¹ are assigned to v(NH_{carb}), v(C=O_{carb}), v(C=O_{benzoyl}) and v(C=N), respectively. In complexes, the shift of v(NH_{carb}) and v(C=O_{benzoyl}) to higher values, 3374-3429 and 1636-1644 cm⁻¹, indicates that these groups remain intact. The v(C=O_{carb}) moves to lower wave numbers, which suggests its involvement in the chelation. As the effect of H-bond on the pyridine-type N is replaced by the complex formation, the position of v(C=N) in IR spectra of FLU and its complexes is the same [13, 14]. The new bands at 1301, 1388 and at 1347 cm⁻¹ in 2 are due to v₃(NO₃)modes of NO₃⁻ group [15], while those at 1352 and 1573 cm⁻¹ ($\Delta v = 221$ cm⁻¹)are taken as evidence for the monodentate mode of the acetate group [16].

The TG curve of **1** (Fig. S1a⁺) shows two decomposition stepsat 192 and 690 °C due loss of hydrated $4H_2O+Cl$ and pyrolysis of two FLU molecules with overall mass amounts to 86.91% (calcd. 87.57%) and CuO+2C as a residue **[17].** For **2** (Fig. S1b⁺), four decomposition stages at 54, 186, 465 and 834 °C are observed. Two hydrated water molecules are desorbed in the first step. The elimination of coordinated $H_2O + 2 NO_3 + 2FLU$ takes place in the next stages and results in formation of Cu+CuO as a final residue,

7.86% (calcd. 8.24%). Incomplete degradation was observed in case of the acetato complex **3**(Fig. S1c†), with overall mass loss amounts to 77.76% (calcd. 88.92%), assuming the formation of CuO+C as a residue at 1000 °C. Complex **4** (Fig. S1d†) is thermally decomposed *via* five steps (49, 251, 335, 505 and 955 °C). The 1st step is responsible for desorption of three hydrated water molecules. The following stages give up a residue of CuO+C, 10.45% (calcd. 9.71%) through loss of two FLU and two perchlorate groups.

The observed effective magnetic moment (μ_{eff}) values, were found to be (1.80-2.06) μ_B (298 K) for the complexes (1-4). These values are expected for non-interacting Cu(II) ions (S=½; t⁶_{2g}e³_g), and in the acceptable range for copper complexes (1.60-2.2 μ_B) [18]. Room temperature powdered ESR spectra of 1-4were recorded at X-band frequency, Fig. S2†. The chloride complex 1shows a slightly rhombic spectrum, with three g values, g₁ = 2.003, g₂ = 2.188, g₃ = 2.282. The parameter R{R = (g₂ - g₁)/(g₃ -g₂) for rhombic systems} is found to be 1.968, i.e. R>1, which is characteristic for Cu(II) trigonal bipyramidal complexes [19]. The spectrum of 2 displays an isotropic signal with g_{ave}=2.131. The ESR spectra of 3 and 4 are axial with two well-defined g₁₁ = 1.780, 2.073 and g₁ = 2.078, 2.189, respectively and g₁ > g₈ (2.0023) suggesting that d_{z²} orbital is the most populated ground state. Therefore the stereochemistry around the metal centre is proposed to be compressed trigonal bipyramidal with D_{3h} symmetry [20].

The fully optimized geometries of complexes (**1-4**) and the numbering of atoms are shown in Fig. 1. The atomic coordinates are presented in Table S1. Complexes (**1-4**) adopt distorted trigonal-bipyramidal geometry. The basal plane is defined by carbamate oxygen atom [Cu-O(34)=2.306 Å (**1**); 2.174 Å (**2**); 2.326 Å (**3**); 2.142 Å (**4**)] and two chlorine atoms [Cu-Cl(66)=2.413 Å and Cu-Cl(67)=2.267 Å] (**1**), two acetate groups [Cu-O(44)=1.915 Å and Cu-O(45)=1.946 Å] (**3**) or two perchlorate groups [Cu-O(44)=2.164 Å and Cu-O(45)=1.963 Å] (**4**). In case of **2**, three oxygen atoms; monodentate nitrate ligand [Cu-O(44) = 1.955 Å], water [Cu-O(45) = 2.137 Å] and carbamate group [Cu-O(34) = 2.174 Å], constitute the basal plane of the metal center. In each complex, the axial positions are occupied by two pyridine-type nitrogen atoms [Cu-N(10) = 1.997Å (**1**), 1.973Å (**2**), 2.059 Å (**3**), 1.967 Å (**4**); and Cu-N(15) = 2.032 Å (**1**), 1.977Å (**2**), 2.085Å (**3**), 2.009 Å (**4**)]. The N(10)-Cu-N(15) angle somewhat deviate from the linearity and is equal 168.8, 172.4 and 171.2^efor **1**, **2** and **4**, respectively. This deviation leads to formation of an irregular

structure. According to NBO analysis, the electronic arrangement of Cu(II) in complex **1** is $[Ar]4s^{0.39}3d^{9.18}4p^{0.48}5p^{0.01}$. The occupancies of Cu 3d are: $d_{xy}^{1.954}d_{xz}^{1.759}d_{yz}^{1.891}d_{x^2-y^2}^{1.608}d_{z^2}^{1.973}$. For **2**, and **3**, the electronic configurations of Cu atom in **2** and **3** are $[Ar]4s^{0.32}3d^{9.14}4p^{0.36}$ and $[Ar]4s^{0.35}3d^{9.15}4p^{0.35}5p^{0.01}$, respectively. For complex **4**, the electronic arrangement of Cu is $[Ar]4s^{0.31}3d^{9.14}4p^{0.37}5p^{0.01}$, distributed as 18 core electrons, 9.825 valence electrons (on 4s, 3d, and 4p atomic orbitals) and 0.012 Rydberg electrons (mainly on 5p orbital). The second order interaction energy (E^2) values **[21, 22]**, for **1**, are 0.46, 0.09, 0.10, 0.29 and 0.18 Kcal mol⁻¹ for LP(1)N10 \rightarrow RY*(5)Cu, LP(1)O34 \rightarrow RY*(4)Cu, LP(1)Cl67 \rightarrow RY*(2)Cu, LP(1)N15 \rightarrow RY*(5)Cu and LP(1)Cl66 \rightarrow RY*(2)Cu, respectively. Similar values are observed for the complexes (**2-4**), as tabulated in Table S2.

The UV-vis. absorption spectra of (1-4) exhibit the highest energy band at 317-323 nm corresponding to the internal ligand transitions. Both 1 and 4display MLCT band at 22727 and 26667 cm⁻¹, respectively. The spectra of complexes 1-4 show broad absorption bands with a maximum in the visible range (11111-13245 cm⁻¹) assigned to $2E' \rightarrow {}^{2}A_{1}$ 'transitions in trigonal bipyrimidal complexes [23]. In order to understand the transitions occurring in the studied complexes, TD-DFT calculations were performed [24]. The spectrum of 1 shows five transitions at 441, 420, 399, 386 and 306 nm, which are mainly assigned to $H \rightarrow L$, $H - 1 \rightarrow L$, $H - 2 \rightarrow L$, $H - 3 \rightarrow L$ and to $H \rightarrow L + 1/L + 2(H: HOMO and L: LUMO)$. The TD-DFT spectrum of 2exhibits three main bands at 471, 431 and 300 nm with oscillator strengths of 0.0007, 0.0005 and 0.6552, corresponding to $H/H - 1 \rightarrow L$, $H - 2/H - 4 \rightarrow L$ and $H \rightarrow L + 1/L + 2$ transitions. Four transitions at 413, 366, 355 and 304 nm are observed in the calculated spectrum of complex 3 owing to &-spin H to &-spin L+1, H- $2/H - 1/H \rightarrow L$ and $H - 1 \rightarrow L/L + 1$ transitions. The absorption bands at 549, 518, 487 and 302 nm, in complex 4, are allocated for $H \rightarrow L$, $H - 3/H - 2 \rightarrow L$ and $H \rightarrow L + 1/L + 2$, in that order.

CuO nanoparticles were prepared by heating complexes (**1-4**) in an electric furnace (700 °C) under the ambient air condition before cooling to room temperature. Their XRD diffraction peaks are in agreement with the reported JCPDS card no. 04-015-5866, characteristic for CuO tenorite nanoparticles, as shown in Fig.S3[†]. Samples **1** and **4** are contaminated with CuCl (nantokite) (JCPDS card no. 04-007-3881). CuO nanoparticles are almost spherical, as shown in the FE-SEM images, (Fig. 2). The influence of

the type of the coordinated anion has been reflected in the size of the nanoparticles. The diameter of some nanoparticles is less than300 nm (1), 200 nm (2), 250 nm (3) and 225 nm (4). Therefore, the thermal decomposition of the nitrato complex 2 gives rise to the smallest copper oxide nanoparticles. The sizes of the current nanoparticles are comparable to those of reported copper oxide nanoparticles prepared under the thermal decomposition conditions [25].

To evaluate the catalytic performance of the synthesized CuO nanoparticles, the absorption spectra of the illuminated MB samples at various time intervals were monitored. The degradation process of MB was initiated by addition of H_2O_2 solution to the MB solution and immediately turning on the ultraviolet irradiation (see the supporting information for details). For comparison, the MB degradation experiment was also done without CuO nanoparticles, but in presence of H_2O_2 and illumination with UV light. Fig. 3a shows the time-dependent absorption electronic spectra of MB as a function of the illumination time at 365 nm in presence of H_2O_2/CuO nanoparticles (sample no. **2**). Similar spectra for samples no. **1**, **3** and **4**, and for the blank sample are given in Fig. S4[†]. In other words, control experiment indicated that the degradation of MB hardly proceeds in absence of CuO nanoparticles.

The degradation efficiency $[R = 100 \times ((A_t-A_0)/A_0)]$ of methylene blue (MB) was determined, where A_0 and A_t are the initial absorbance and that obtained after the illumination time (t). The addition of CuO nanoparticles to the MB+H₂O₂+UV system degraded about 99% (**1**), 90% (**2**), 83% (**3**) and 42% (**4**) of MB exposed to the UV light (365 nm), while 29% of MB is degraded in the absence of CuO nanoparticles, within about 150 min. The obtained results are comparable to the previously published data used CuO nanostructures as a catalyst **[26].** The photo-catalytic degradation of MB was found to be first order reaction $[\ln(C_t/C_0)=kt]$. Its $\ln(C_t/C_0)$ plot versus time, shows a linear relationship with the illumination time (Fig. 3b), where slope is the rate constant (k). The calculated rate constants for the photo-catalytic reactions are 2.26×10^{-2} (**1**), 1.47×10^{-2} (**2**), 1.22×10^{-2} min⁻¹ (**3**) and 4.92×10^{-3} min⁻¹ (**4**) while it is only about 2.05×10^{-3} min⁻¹ (MB+UV+H₂O₂) for blank sample. The $t_{1/2}$ value was found to be 31 (**1**), 47 (**2**), 57 (**3**) and 141 min (**4**) compared with 5.6 hours for (MB+UV+H₂O₂) blank sample .It is worthy to mention

that almost no degradation of MB was observed in dark, which reveals that the mechanism of the reaction is photo-degradation rather than adsorption **[27]**.

In summary, synthesis and structural study of new trigonal-bipyramidal Cu(II) complexes of FLU drug have been developed. FLU is a neutral bidentate ligand coordinated to Cu(II) *via* the pyridine-type N of benzimidazole ring and C=O of the carbamate group. Thermal decomposition of the studied complexes proved to be a simple and nontoxic method for preparation of tenorite nanoparticles. The prepared CuO nanoparticles exhibited good photo-catalytic activity in the degradation process of an industrial pollutant methylene-blue by means of Fenton-like reagent.

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Scheme 1: Synthesis of Flubendazole-Copper(II) complexes 1-4.



Fig. 1: Local minimum structures of complexes a) 1, b) 2, c) 3, and d) 4 obtained at the DFT/B3LYP level of theory.



Fig. 2: FE-SEM images of CuO nanoparticles obtained from thermal decomposition of a) 1, b) 2, c) 3 and d) 4.



Fig. 3: a) Time-dependent UV-vis. absorption spectra for the photocatalytic degradation of MB with CuO (2) [10 mL dye (14 mg L⁻¹), 0.1 mL H₂O₂ (35%), 10 mg CuO, λ = 365 nm], **b)** Linear plots of ln(Ct/CO) vs. time for the decolorization of MB under different conditions.