



Formation of an unusual copper(II) complex from the degradation of a novel tricopper(II) carbohydrazone complex

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ABSTRACT

An unusual copper(II) complex $[\text{Cu}(\text{L}^{1a})_2\text{Cl}_2] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\text{Cl}^-$ (**1a**) was isolated from a solution of a novel tricopper(II) complex $[\text{Cu}_3(\text{HL}^1)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (**1**) in methanol, where L^{1a} is 3-(2-pyridyl)triazolo [1,5-a]-pyridine, and characterized with single crystal X-ray diffraction study. The tricopper(II) complex of potential ligand 1,5-bis(di-2-pyridyl ketone) carbohydrazone (H_2L^1) was synthesized and physico-chemically characterized, while the formation of the complex **1a** was followed by time-dependant monitoring of the UV–visible spectra, which reveals degradation of ligand backbone as intensity loss of bands corresponding to $\text{O} \rightarrow \text{Cu}(\text{II})$ charge transfer.

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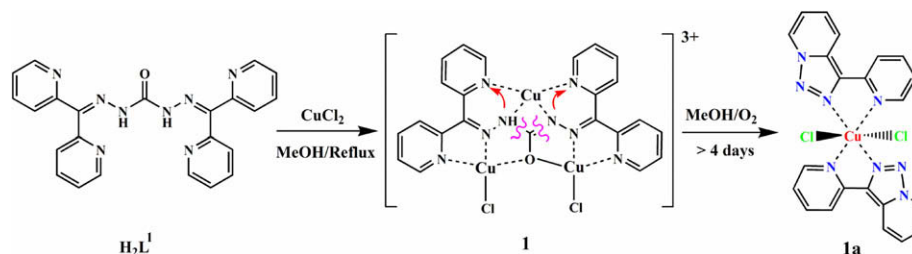
Copper complexes have been a subject of increasing interest because of their interesting applications in the fields ranging from material chemistry to biochemistry. Complexes containing two or more metal ions are of contemporary interest because of their relevance to biological systems, as evidenced by many multicopper complexes in biology [1] and the various applications such as DNA binding [2] and antimicrobial activity [3], to name a few. Recently, we have reported EPR and magnetic features of anticancer drug analogue multinuclear Cu(II) complexes of thiocarbohydrazones and dicopper(II) complexes of carbohydrazones [4]. We, also, have reported the first self-assembled metallocsupramolecular square grid of a carbohydrazone ligand [5]. The bridging oxygen atom makes it capable of generating self-assembled molecular squares for carbohydrazones [5] as in the case of sulfur bridging of thiocarbohydrazones [6,7]. There are reports of mono and disubstituted carbohydrazones and few of their copper(II) complexes [8,9]. Complexes of oxovanadium(IV) [10], La(III) and Pr(III) [11] of some carbohydrazones have also been reported. However, only one such report contains extensive investigation of structure using EPR and X-ray crystallography and having investigated magnetic properties [8]. The introduction of 2-pyridyl pendant groups on either side of carbohydrazone provide potential coordination positions for the ligand in addition to its conventional binding sites

or could offer proton acceptor sites in the resultant assembly. The chemistry of exchange coupled complexes of carbohydrazones are yet to be explored, which might be due to susceptibility of the resultant species to degradation of the carbonyl group. In this context, we report a novel trinuclear Cu(II) complex $[\text{Cu}_3(\text{HL}^1)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (**1**) of the flexible ligand H_2L^1 [12], which undergoes degradation of $-\text{CO}-$ group of the HL^1 anion ligand, upon standing in methanol, to yield a mononuclear Cu(II) complex $[\text{Cu}(\text{L}^{1a})_2\text{Cl}_2] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\text{Cl}^-$ (**1a**). Scheme 1 shows the structure of H_2L^1 , **1** and **1a** and a tentative mechanism for the degradation.

When H_2L^1 was treated¹ with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, with ligand to metal ratio 1:2, instead of an expected bimetallic complex, the compound **1** was formed with three Cu(II) centers and a monodeprotonated ligand. Nevertheless, complex **1** was found to be distinctive as there is

¹ All reagents were used as received from Aldrich or Merck. The ligand H_2L^1 was prepared according to reported procedure [12]. $[\text{Cu}_3(\text{HL}^1)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (**1**): A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.344 g, 2 mmol) in 10 ml of methanol was added to a solution of H_2L^1 (0.427 g, 1 mmol) in 40 ml boiling methanol and refluxed for 20 min and the green colored solution allowed to stand at room temperature. Dark colored product separated out was filtered, washed with methanol followed by ether and dried over P_4O_{10} *in vacuo*. Yield: 0.379 g (68.9%). Elemental Anal. Found (Calc.): C, 33.68 (33.47); H, 2.91 (2.56); N, 13.59 (13.58)%. Molar conductivity (Λ_{M} , 10^{-3} M DMF): $214 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR & Far IR (KBr & polyethylene): ν 3415 br, 3222 sh, 3052 m, 1562 m, 1516 s, 1480 s, 1423 s, 1366 s, 1303 vs, 1274 s, 1246 s, 1172 m, 1124 vs, 1018 m, 973 m, 790 s, 750 s, 674 m, 626 m, 518 w, 413 s, 384 m, 304 s, 281 s cm^{-1} .

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Scheme 1. Reaction scheme showing tentative structures of the compounds H_2L^1 , **1** and **1a**.

a report for a similar ligand 1,5-bis(2-benzoylpyridine) carbohydrazone with $CuCl_2$ resulted a degradation of $-CO-$ group and cyclization to form a copper complex of 3-phenyltriazolo[1,5-a]-pyridine [9]. However we could synthesize the chloride complex of H_2L^1 , compound **1**, as we used di-2-pyridyl derivative instead of 2-benzoyl pyridine and it is found to undergo degradation only in solutions at lower concentration on exposure to air. It has also been observed that di-2-pyridyl ketone azine undergoes decomposition in the presence of copper(II) ions in aqueous/methanolic solution to form $[Cu(L^{1a})_2(X)_2]$ where $X = H_2O, NO_3^-$ [13,14].

The electronic spectrum of **1** taken in methanol solution shows bands, λ_{max} , with extinction coefficients (ϵ) 44,250 (22,190), 37,590 (22,580), 33,220 sh (18,710), 28,250 (10,330), 22,030 cm^{-1} (15,160 $M^{-1} cm^{-1}$). The bands at $\sim 44,000$ and $\sim 34,000 cm^{-1}$ are assigned as intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the complex, which suffered marginal shift from that of their corresponding free ligand at 43,860 (26,030), 37,040 (27,110), and 30,120 cm^{-1} (27,500 $M^{-1} cm^{-1}$). The intense band at $\sim 22,000 cm^{-1}$ is attributed to $O \rightarrow Cu$ charge transfer transition and band near 28,000 cm^{-1} is attributed to $N \rightarrow Cu$ charge transfer transitions [4]. Due to broad nature of the bands, possible d-d transitions could not be resolved. The MALDI MS spectrum of Cu(II) carbohydrazone complex **1** taken in CH_2Cl_2 as DCTB mix on positive ion mode reveals labile nature in solution or under ionization conditions of MALDI. Though molecular ions could not be observed, sensible fragments were observed. The base peak centered at m/z 485 is assigned as $[Cu(HL^1)]^+$ (calc. 484) and another major peak at m/z 423 is assigned as that of the free ligand. A new coordinated species, would be formed under MALDI ionization condition, is seen as a weaker peak at 907 corresponding to $[Cu(HL^1)(H_2L^1)]^+$ (calc. 906).

The EPR spectrum of **1** in DMF at 77 K recorded is broad but not isotropic in nature with a single g value at 2.078, and is consistent with antiferromagnetic interaction between Cu(II) centers. The powder EPR spectrum was very broad in nature. The EPR spectrum of a somewhat similar dicopper(II) carbohydrazone complex [8] is also in agreement with a powder spectrum broad single g value at 2.073. The temperature dependence of molar magnetic susceptibility χ_m in the powder form of **1** is carried out in the temperature range 5–325 K and found to exhibit a dominant antiferromagnetic interaction. At room temperature the effective magnetic moment μ_{eff} , 2.19 μ_B , is appreciably lower than that expected for three uncoupled Cu(II) ions and show a regular decrease on cooling and reaches to a minimum of 0.31 μ_B at 5 K, consistent with strong coupling interactions between Cu(II) electrons through their connecting moiety. The nature of the curve and smaller μ_{eff} values at lower temperatures indicate the effective spin of the system at lower temperatures is less than $1/2$ by possible intermolecular interactions along with different intramolecular exchange interactions. Inter-trimer antiferromagnetic interactions, possibly through chloride ions, leading to dimeric trinuclear nature may also be behind this decrease in effective magnetic moments on cooling. The rapid increase in χ_m at low temperature is due to monomer impurity.

The EPR spectrum and temperature dependency of magnetic susceptibility are given in the Appendix A.

The thermal properties of the compound **1** was tested by TG and DTA using a sample mass of 1.751 mg in air atmosphere at a heating rate of 10 $^\circ C/min$ from 30 to 920 $^\circ C$ (Appendix A). The TG curve shows a loss of two water molecules (4.4%) within the temperature range 30–68.5 $^\circ C$ and then the loss of a chlorine molecule (9%) mainly in the range 140–213.5 $^\circ C$ and it is followed by the removal of two more chloride ions (9.9%) till 460 $^\circ C$. This is continued by a prolonged decomposition, which extends up to 650 $^\circ C$, and leading to a weight loss of 63.15% in the temperature range 460–847 $^\circ C$ to form complete CuO residue. The DTA curve shows mainly three peaks at around 59, 211 and 581 $^\circ C$. The exothermic peak area at 581 $^\circ C$ is calculated and the enthalpy change (ΔH) is found to be $-3.754 kJ/g$, indicating this large energy is released during decomposition in air.

The complex **1** is found to undergo color loss in common organic solvents like methanol, ethanol and DMF in lower concentrations on exposure to air for 4–5 days, attributed to possible dissociation, though they are very stable in their solid form. Crystals of the new compound $[Cu(L^{1a})_2Cl_2] \cdot CH_3OH \cdot H_2O \cdot H_3O^+ Cl^-$ (**1a**), with agreeing elemental analysis: Found (Calc.): C, 43.77 (43.75); H, 3.64 (3.99); N, 17.65 (17.75)%, were isolated in good yield (80%) by slow evaporation during its formation from a solution of **1** in methanol in air after a month. These crystals were characterized by X-ray crystallography and found that the compound **1** has suffered degradation of H_2L^1 by removal of $-CO-$ group from the ligand backbone and cyclization to form a mononuclear copper complex of L^{1a} , where two axial positions are occupied by Cl^- ions. Somewhat similar kind of ligand N', N'' -bis[(1E)-1-(2-pyridyl)ethylidene] ethanedihydrazide having two N,N,O coordination pockets on reaction with $Fe(ClO_4)_3 \cdot 6H_2O$ have been reported to undergo an oxidative degradation of the side chain ($-CO-CO-$) and a reduction of Fe^{III} to Fe^{II} to form a complex, which is supported by crystallographic evidence [15]. Since the color loss of complex **1** may be attributed to the changes on coordination environment or even a change in oxidation state, the follow up of UV-visible spectra of **1** in methanol solution at different time intervals were carried out. It was seen that the absorption at 22,030 cm^{-1} , attributed to $O \rightarrow Cu(II)$ charge transfer transition, gradually loses its intensity. However the band at 28,250 cm^{-1} assigned to $Cl \rightarrow Cu(II)$ charge transfer transition retains its identity. Therefore it is inferred as a consequence of the formation of complex **1a**, in that the $>C=O$ group leaves the coordination sphere of copper in complex **1** in methanol solution in the presence of air. The UV-visible spectra follow up is given in Fig. 1.

The powder and frozen DMF solution EPR spectra in the X-band (attached in the Appendix A) of compound **1a** suggest the presence of a Cu(II) $3d^9$ species with typical axial nature. The powder spectrum exhibits a $g_{||}$ value of 2.257 and g_{\perp} value of 2.073. The frozen DMF spectrum also exhibits similar values as evidenced by $g_{||} = 2.237$ (with $A_{||} = 196 G$) and $g_{\perp} = 2.063$. $g_{||} > g_{\perp} > 2.0023$ and G value of 3.60 at 298 K in powder state and 3.87 at 77 K in DMF

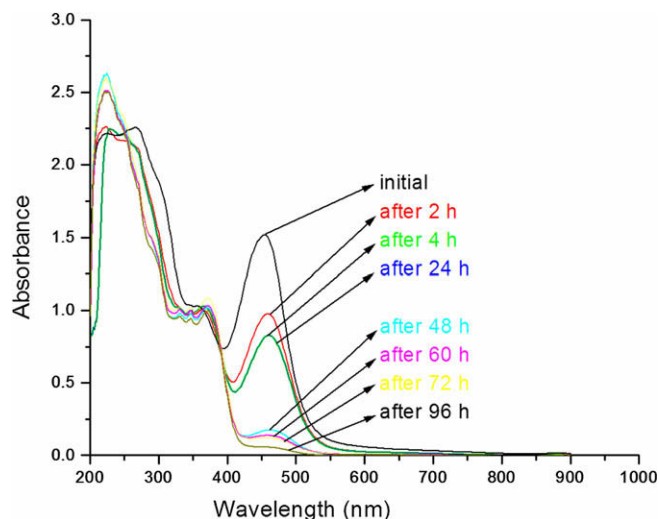


Fig. 1. The electronic spectra follow up of complex **1** in 10^{-4} M methanol.

are consistent with a $d_{x^2-y^2}$ ground state. The g_{\parallel} values obtained indicate a significant degree of covalency in the metal-ligand bonds and the G values indicate some exchange interaction. However there was no half-field signal. The α^2 value of 0.7256 indicates that 72% electron density is in the copper $d_{x^2-y^2}$ orbital.

The X-ray crystallographic study [16] has unequivocally confirmed the formation of the novel complex $[\text{Cu}(\text{L}^{1a})_2\text{Cl}_2] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\text{Cl}^-$ (**1a**). The molecular structure of **1a** with relevant atom numbering scheme is given in Fig. 2. The asymmetric unit consists of half of two independent molecules of $[\text{Cu}(\text{L}^{1a})_2\text{Cl}_2]$, one chloride ion, one hydronium ion, a water and a methanol molecule. Half part of each molecule was generated. However, hydrogen atoms of water or hydronium ion could not be located by using difference Fourier maps; and the assignment of hydronium ion was done by taking in consideration of various aspects like bond lengths, planarity of triazolo group, etc. For instance, a CSD search shows one report of a related Cu(II) complex with the same topology (octahedral coordination by four nitrogens and two chloride

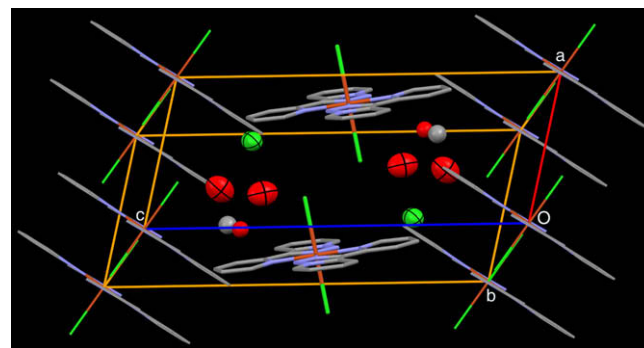


Fig. 3. The unit cell packing of the complex **1a**. Eight occupied corners (wireframe) contribute one molecule and two occupied face centers (stick) contribute the second molecule. The charges of the two free chloride ions (green, 70% ellipsoid) are balanced by two hydronium ions of four oxygen atoms shown (red, 70% ellipsoid). Methanol molecules are shown by ball model. Hydrogen atoms all are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ions) [17] and is having hydronium ion and perchlorate anion. The EPR spectra of **1a** also agrees a Cu(II) species and rules out the possibility of a Cu(III) species.

The crystal structure of the ligand L^{1a} has been reported elsewhere [18]. The Cu(II) centers in both molecules are in an octahedral coordination and the difference between the molecules is slight variations in bond parameters. The Cu(1A) is coordinated by triazolo nitrogen N(1A) and pyridyl nitrogen N(4A) of two neutral ligands L^{1a} , to form the basal plane and the apical positions are occupied by chloride ions to form the octahedral geometry. The bond parameters are given in Table 1 as Appendix A. The bond lengths in the ligand moieties of **1a** are comparable with its related Cu complex [18].

Each of the ligand moiety in both molecules is in a plane, with maximum mean plane deviation of $-0.035(3)$ Å for C(10A) and for molecule B this deviation is $-0.037(2)$ Å for C(4B). Also, the molecule $[\text{Cu}(\text{L}^{1a})_2\text{Cl}_2]$ except the apical chlorides are in an approximate plane with maximum deviations of $-0.098(2)$ Å for N(2A) and $0.098(2)$ Å for N(2A') for molecule A. In molecule B these maximum

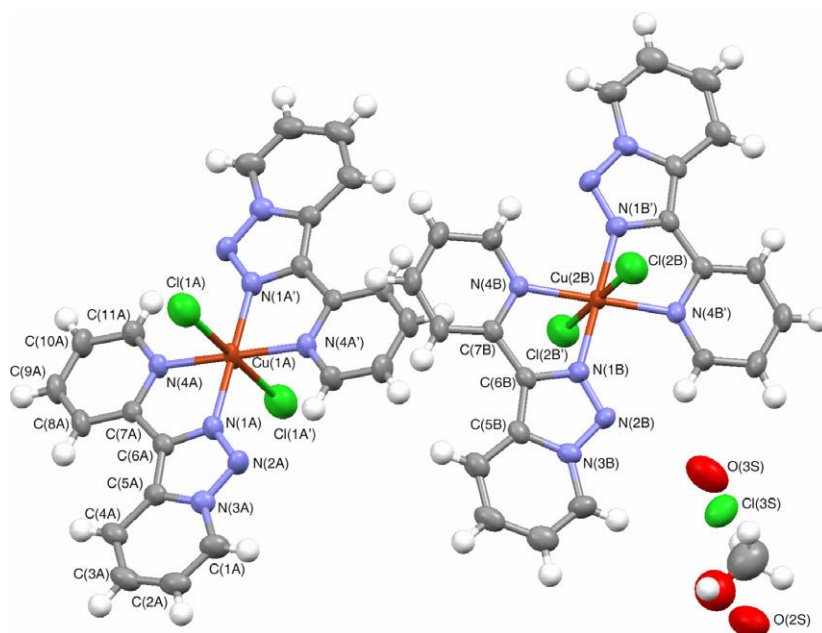


Fig. 2. The molecular structures of the two molecules of **1a** in the asymmetric unit.

deviations are $-0.097(2)$ Å for N(2B) and $0.097(2)$ Å for N(2B'). The bicyclic chelate ring N(1A)–C(6A)–C(7A)–N(4A)–Cu(1A)–N(1A')–C(6A')–C(7A')–N(4A') formed by the coordination is in a plane with a maximum mean plane deviations of $-0.035(2)$ Å for N(1A) and $0.035(2)$ Å for N(1A'), while its counterpart in molecule B shows maximum deviations of $-0.034(2)$ Å for N(1B) and $0.034(2)$ Å for N(1B'). This along with the angles around Cu(II) centers are indicative of the deviation from a perfect octahedron is least.

The Cu(1A)–N(1A) and Cu(1B)–N(1B) bond lengths are less than that seen in related Cu(II) complexes, where Cu–N_{triazolo} bond lengths are $2.0135(17)$ [13] $2.018(3)$ Å [18], $2.007(4)$ Å [19] and $2.110(5)$ Å [14], and rules out the possibility of Cu(III). The unit cell packing of the molecules is given in Fig. 3.

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Appendix A. Supplementary material

CCDC 718083 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2009.07.010](https://doi.org/10.1016/j.inoche.2009.07.010).

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- [16] Crystal data for $C_{23}H_{25}Cl_3CuN_8O_3$ (**1a**): Mr = 622.34, Triclinic, $0.18 \times 0.24 \times 0.38$ mm³, space group P1; $a = 7.132(3)$ Å, $b = 10.542(4)$ Å, $c = 18.477(7)$ Å, $\alpha = 97.397(6)^\circ$, $\beta = 101.145(6)^\circ$, $\gamma = 109.751(6)^\circ$, $V = 1254.2(9)$ Å³, Mo K α radiation ($\lambda = 0.71073$ Å), $\mu = 1.235$ mm⁻¹, $T = 273$ K, $Z = 2$, $F(000) = 628$, $D_c = 1.648$ g/cm³, θ range 1.15–27.44, 5735 collected reflections, 5735 unique reflections [$R(\text{int}) = 0.0000$] were used for refinement. The final R values were $R1 = 0.0388$, $wR2 = 0.1436$ [$I > 2\sigma(I)$], $R1 = 0.0389$, $wR2 = 0.1438$ (all data) for 346 parameters. The largest difference peak and hole were 0.322 and -0.841 e Å⁻³. Data were collected using Bruker SMART APEX2 CCD diffractometer at the Department of Inorganic and Physical Chemistry, IISc, Bangalore, India. The trial structure was solved using SHELXS-97 (Sheldrick, 97) and refinement was carried out by full-matrix least squares on F² (SHELXL-97). The H atoms were calculated, and were allowed to ride on their respective parent atoms.
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