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Novel ambient light induced trimerization of a simple copper(II) monomeric Schiff base complex

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Room temperature, light promoted trimerization of a monomeric complex [Cu(HL)(L)](NO$_3$).H$_2$O (HL = *N*,*N*-dimethyl-*N*′-propylsalicylideneimine) dissolved in CH$_2$Cl$_2$, was observed with the concomitant generation of new ligand moiety (ClCH$_2$L).

The molecular based inorganic materials that can exhibit a photo-switchable phenomenon are of great interest because of their wide range of potential applications. Despite the development of several photo-responsive inorganic materials[1] such as azo-benzene transition metal complexes,[1a] Fe-spin crossover complexes,[1b] Prussian blue analogues,[1c] sodium nitroprusside,[1d] one dimensional organometallic sandwich compounds[1e] and a copper amine complex with a long-lived metastable state,[1f] the number of photo-tunable inorganic molecular materials is, unfortunately, still quite small. In this paper we report an unprecedented room temperature, light-assisted, reaction of a monomeric unit to form a spiral trinuclear species, along with the formation of a new ligand moiety.

Two equivalents of a methanolic solution of Schiff base HL[2] and one equivalent of Cu(II)(NO$_3$)$_2$·3H$_2$O, in aqueous solution, react in the presence of NaOH to yield a distorted square-pyramidal, mononuclear complex **1**, [Cu(HL)(L)](NO$_3$)·H$_2$O,† containing one –(CH$_2$)$_3$–NMe$_2$H pendant arm, as evidenced by the X-ray structure‡ of a single crystal of the anhydrous† form of **1**. The crystal was obtained from a dichloromethane solution kept in the dark. A view of the cation of **1** is depicted in Fig. 1. When a dichloromethane solution of **1** was exposed to the ambient light (fluorescent), the formation of **2** [Cu(ClCH$_2$L)$_2$][Cu$_3$(ClCH$_2$L)$_6$]Cl$_8$·4H$_2$O† takes place, rapidly, and a color change from olive green to purple was observed. This new species consists of a spiral trinuclear copper(II) entity [Cu$_3$(ClCH$_2$L)$_6$]$^{6+}$, co-crystallized with a monomeric unit [Cu(ClCH$_2$L)$_2$]$^{2+}$, both lying at inversion centers. The trimer was formed by the generation of a bridging phenoxy ligand analogous to the earlier work by Karlin *et al*.[3] A new ligand moiety (ClCH$_2$L) was generated as revealed by the single crystal structure study. Fig. 2a and 2b show the trinuclear and mononuclear cationic units of **2** and the spiral arrangement for the trinuclear core, respectively. The light induced reaction is completed within five minutes, as observed by the time resolved spectra of this reaction shown in Fig. 3. Dichloromethane solution of the monomeric species **1** in the absence of light shows only one broad d–d transition band at λ_{max} = 660 nm (ε ~ 400 cm^{-1} M^{-1}), which on exposure to the light exhibits the immediate appearance of a second d–d transition peak, at λ_{max} = 535 nm. The time-resolved spectra show that the development of the second peak ceased after ~5 minutes. It is noteworthy that the spectra of the dichloromethane solution of an isolated solid sample of **2** also show two well-resolved d–d transition peaks at 660 nm and 535 nm (ε ~

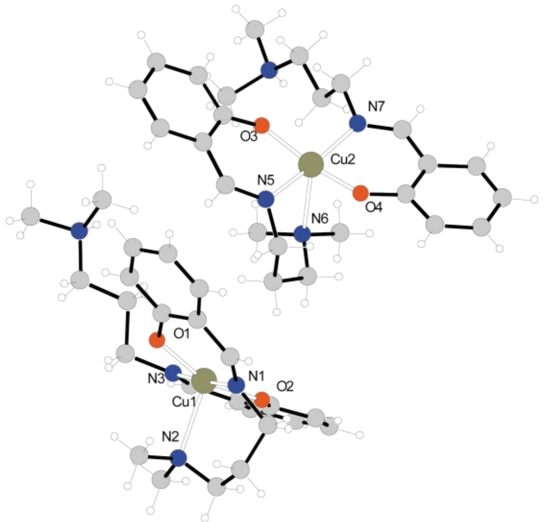

Fig. 1 Perspective view of two crystallographically independent cationic units in **1**. Gray, red, blue and green-brown are the colors for carbon, oxygen, nitrogen and copper respectively. Hydrogen atoms are presented by small white circles.

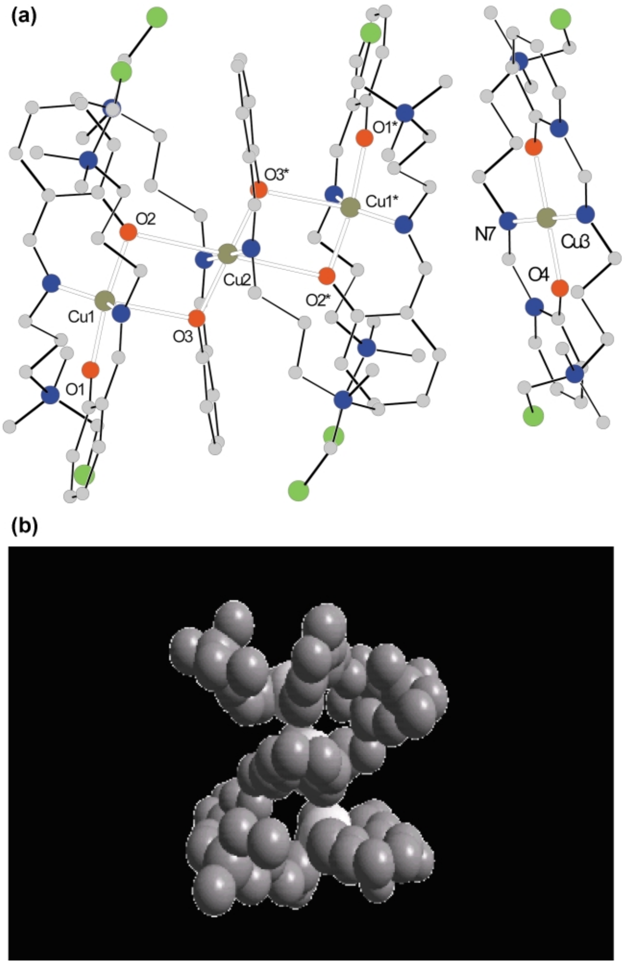

Fig. 2 a) The trimeric and the monomeric cationic units in **2**. Gray, red, blue, light green and green-brown are the colors for carbon, oxygen, nitrogen, chlorine and copper respectively. Hydrogen atoms are omitted for clarity. b) The spiral arrangement for the trinuclear unit.

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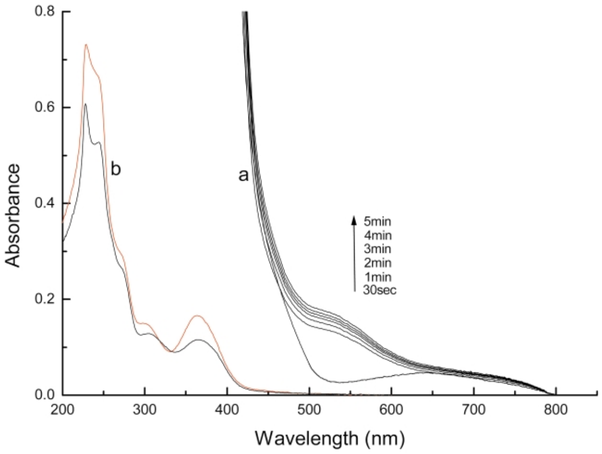

Fig. 3 UV-VIS absorption spectra. a) Time-resolved formation of the second d–d transition peak at 535 nm when a dichloromethane solution of **1** was exposed to ambient light for the formation of **2**. b) UV-VIS absorption of the monomer **1** (in red) and after the conversion of **1** to **2** on exposure to light (in black).

820 cm^{-1} M^{-1}). Referring to the generally proposed criteria[4] it appears that the second d–d band at 535 nm is not consistent with the hexacoordinate copper center nor the pentacoordinated copper centers of the trinuclear unit which are expected to be at wavelengths longer than 600 nm. Indeed, the pentacoordinated copper absorbs at 660 nm as observed for **1** recorded in darkness. The absorption at the relatively lower wavelength suggests that the peak generated is due to a lower coordinated copper center, which is, in the present case, the newly generated square planar monomeric unit, co-crystallized along with the trimeric in **2**. For **1** and **2**, the spectra over the other regions show similar absorption, except that the extent of absorption decreases during the course of formation of **2**. After ~5 minutes the peak height shows no further changes and shows similar intensity as that recorded for a dichloromethane solution of **2**. The new ligand moiety was generated by the light-induced reaction of **1** with the chlorinated molecule, CH_2Cl_2. Oxidative addition of C–Cl bonds some metal centers, such as Pt(II), *via* a radical mechanism have been proposed in the past.[5] However, we were unable to document free radical involvement and experienced no addition at the metal center.

The asymmetric unit of **2** contains half a molecule in which the central, and monomeric copper(II) centers are on inversion centers. The spiral structure is comprised of three copper(II) ions and six alkylated ligands. Each ligand coordinates through two imine nitrogens, phenoxo and μ-phenoxo oxygens while the tertiary nitrogen terminal is alkylated, and remains dangling. The trinuclear copper center is arrayed in a linear fashion in which the central copper ion is in a distorted octahedral geometry. It is flanked by two terminal copper ions whose environments are intermediate between square-pyramidal and trigonal-bipyramidal ($\tau^6 = 0.33$). The distorted geometries of the Cu(II) sites result from ligand constraints and the Jahn–Teller effect, the latter being responsible for the elongated axial bonds. The three copper(II) ions are held together by μ-phenoxo bridges, through O2, O3, O3* and O2* (*mark signify symmetry generated atoms) located in an equatorial-axial/axial-equatorial fashion. The crystal structure of **2** is an interesting example in which the environment at the metal ions consists of three different geometries: octahedral, a square pyramidal-trigonal bipyramidal intermediate, and square planar. For bond distances and angles see ESI.‡ Other than the importance of the photo triggered reactions and their various potentialities, the reaction leading to the formation of the **2**, containing mono- and trimeric units, has the additional importance of being relevance to the active center present in the methane monooxygenase (pMMO) from *Methylococcus capsulatus* (Bath). That molecule contains one mononuclear copper center and five trinuclear aggregates with an O/N ligand environment of heretofore unknown structure.[7]

In conclusion, the mononuclear complex $[Cu(HL)(L^-)](NO_3)\cdot H_2O$ undergoes conversion to a trinuclear spiral complex when illuminated. The trinuclear unit formation is controlled by the concomitant generation of a new chlorinated ligand. The formation of a four coordinated monomeric unit within the asymmetric unit of **2** may suggest the formation of this species as an intermediate during the course of the trimerization process of the mononuclear entity **1**. As result of the photochemical process, the ligand becomes chlorinated by C–Cl bond cleavage in the reaction involving the solvent.

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Notes and references

† Satisfactory spectroscopic and analytical data are obtained for the compounds.

‡ Crystal data: for **1** $[Cu(HL)(L)](NO_3)$: $C_{24}H_{35}N_5O_5Cu$ $M_W = 537.6$, Orthorhombic, space group *Pbca*, $a = 10.586(3)$, $b = 25.272(6)$, $c = 39.355(7)$ Å, $V = 10529.81$ Å^3, Two independent monomers occur in the asymmetric unit, $Z = 16$ (note: there are two independent monomers × 8 equivalent positions = 16 Cu monomers in the cell, unless both lie on special positions), $\rho_{calcd.} = 1.36$ gcc^{-1}, $\mu = 0.872$ mm^{-1}, θ range of data collection $\theta = 2.1–20°$, final $R = 0.0603$, $wR_2 = 0.1369$, GOF = 1.027. The structure was solved by Sir 92[8] analyses and refined by the full-matrix least square based on F^2 using SHELX 97.[9] All calculations were performed using the WinGX system (ver 1.64).[10]

For **2** $[Cu(ClCH_2L)_2][Cu_3(ClCH_2L)_3]Cl_8.4H_2O$: C_{104} H_{172} $Cl_{16}Cu_4N_{16}$ O_{18} $M_W = 2755.94$, Triclinic, space group $P\bar{1}$, $a = 13.206(6)$, $b = 15.113(6)$, $c = 16.999(8)$ Å, $\alpha = 107.37(2)$, $\beta = 92.56(2)$, $\gamma = 99.28(2)$; $V = 3180(2)$ Å^3, $Z = 1$, $\rho_{calcd.} = 1.44$ gcc^{-1}, $\mu = 1.06$ mm^{-1}, θ range of data collection $\theta = 2.1–25°$, final $R = 0.066$, $wR_2 = 0.142$, GOF = 1.003. For structural solution details of **1** and **2** see supplementary materials.

CCDC 219122 and 219123 contains the supplementary crystallographic data for **1** and **2** respectively. See http://www.rsc.org/suppdata/cc/b3/b310764g/ for crystallographic data in .cif or other electronic format.

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