Crystal-to-crystal transformation from tri- to mononuclear Cu(II) complex with a sugar-derived ligand *via* proton transfer reaction and rearrangement of hydrogen bonding networks†

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Treatment of a glycosylamine derived Cu(II) complex with ethylamine resulted in crystal-to-crystal transformation from trinuclear complex $[Cu_3(L^1)_2(EtNH_2)_2(MeOH)_2]\cdot 2MeOH\cdot CHCl_3$ (2·2MeOH·CHCl$_3$) to a dimeric structure of mononuclear complex $[Cu(HL^1)(EtNH_2)]$ (3) through proton transfer reaction and rearrangement of hydrogen bonding networks.

Recently we reported the synthesis of novel coordinatively unsaturated linear Cu(II) complex $[Cu_3(L^1)_2]\cdot MeOH\cdot H_2O$ (**1**; H_3L^1 = *N*-(3-*tert*-butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-β-D-glucopyranosylamine), which activates the C–Cl bond of solvent chloroform in presence of methylamine.[1] Generally it is difficult to activate the C–Cl bond due to high bond energy and lower leaving group ability.[2] In our case activation of such a bond has taken place at lower than room temperature (~4 °C) in presence of methylamine, however no such activity has been observed in the treatment of **1** with primary alcohols. The primary alcohols have taken part in the terminal copper ion binding to form the linear trinuclear Cu(II) complexes, $[Cu_3(L^1)_2(ROH)_2]$ (R = Me, Et, *n*-Pr, *n*-Bu).[1] Such variation in reactivity of the amine over alcohols tempted us to explore the cause of the difference and in this venture, replacement of methylamine by ethylamine has interestingly led to novel crystal-to-crystal transformation from the trinuclear Cu(II) complex $[Cu_3(L^1)_2(EtNH_2)_2(MeOH)_2]\cdot 2MeOH\cdot CHCl_3$ (**2**·2MeOH·CHCl$_3$) to a dimeric form of the mononuclear complex $[Cu(HL^1)(EtNH_2)]$ (**3**) through proton transfer reaction and switch of hydrogen bonding networks.

Vapour diffusion of ethylamine (2 M solution in MeOH) into a chloroform solution of complex **1** at 4 °C afforded X-ray quality crystalline blocks of **2**·2MeOH·CHCl$_3$. The ORTEP plot of complex **2** (Fig. 1)‡ clearly exhibits the conservation of linear trimetal centers (Cu1–Cu2–Cu3 = 178.46(2)°), with square pyramidal geometry about the terminal ones and square planar around the central one. The binding mode of ligand L^1 is the same as that in our previously reported alcohol bound complexes,[1] however in this case fourth basal positions around the terminal copper centers are occupied by the ethylamine and methanol binds from the apical side. Metal bound methanols are *cis* oriented with respect to the molecular plane with elongated Cu–O distances of 2.360(4) and 2.390(3) Å. The two lattice methanol molecules are strongly held by hydrogen bonding interactions with metal bound methanol and the C3-alkoxo oxygen of the sugar moiety (see ESI; Fig. S1).†

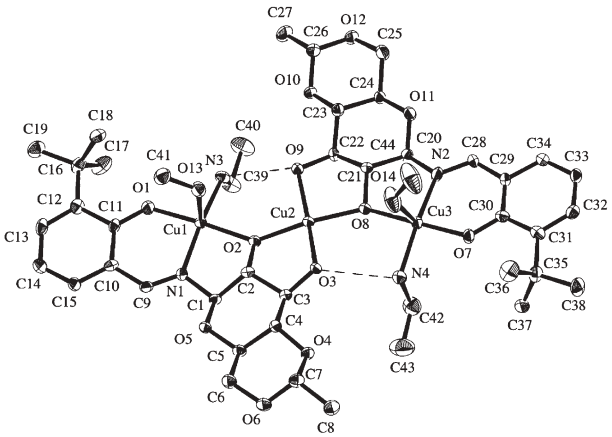

Fig. 1 ORTEP view of **2**·2MeOH·CHCl$_3$ with atom labeling; lattice solvent molecules have been omitted for clarity and the thin dotted line represents the hydrogen bonding interactions. Selected bond lengths (Å) and angles (°): Cu1–O1 1.919(4), Cu1–O2 1.994(3), Cu1–O13 2.390(3), Cu1–N1 1.949(5), Cu1–N3 1.989(4), Cu2–O2 1.958(4), Cu2–O3 1.931(3), Cu2–O8 1.956(4), Cu2–O9 1.933(3), Cu3–O7 1.910(4), Cu3–O8 1.997(4), Cu3–O14 2.360(4), Cu3–N2 1.944(5), Cu3–N4 1.965(5), Cu1–Cu2 3.7356(9), Cu2–Cu3 3.7515(9), O2–Cu1–O1 176.81(17), O8–Cu2–O2 167.19(15), O8–Cu3–O7 175.94(17), N1–Cu1–N3 166.21(18), O3–Cu2–O2 88.00(16), O8–Cu2–O9 88.87(16), Cu1–Cu2–Cu3 178.46(2).

Storage of mother liquor containing the crystals of **2**·2MeOH·CHCl$_3$ under the amine atmosphere at room temperature led to the slow conversion of block shaped dark green crystals into thin bluish green ones. The crystals exhibited changes in colour and morphology and crystallographic analysis of the latter revealed the structure of mononuclear complex $[Cu(HL^1)(EtNH_2)]$ (**3**), which might have been formed by releasing one copper per trinuclear complex. Even if the isolated **2**·2MeOH·CHCl$_3$ was dissolved in chloroform and treated with ethylamine vapour, first crystals of the trinuclear complex reappeared and then they slowly converted to the mononuclear ones. This is one of the few examples of crystal-to-crystal transformation[3] and the first instance in metal-saccharide chemistry.

X-ray diffraction studies with complex **3** revealed the presence of two mononuclear Cu(II) complexes in the asymmetric unit (Fig. 2).§ Both the mononuclear units were strongly held by mutual intermolecular O–H···O type (shown by dotted line)

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† Electronic supplementary information (ESI) available: Details of synthesis and structural data for **2**·2MeOH·CHCl$_3$ and **3**, and ORTEP plot of complex **2**·2MeOH·CHCl$_3$ showing hydrogen bonding. See DOI: 10.1039/b513788h

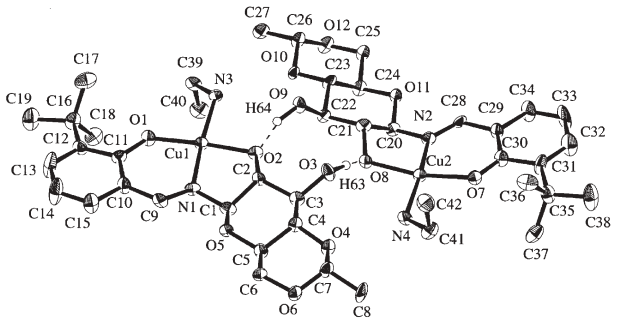

Fig. 2 ORTEP view of the dimeric structure of **3** with atom labelling; the thin dotted line represents the hydrogen bonding interactions. Selected bond lengths (Å) and angles (°): Cu1–O1 1.896(10), Cu1–O2 1.968(9), Cu1–N1 1.957(10), Cu1–N3 2.002(10), Cu2–O7 1.963(9), Cu2–O8 1.967(9), Cu2–N2 1.942(11), Cu2–N4 2.007(10), O2–O9 2.550(11), O3–O8 2.648(13), O1–Cu1–O2 175.9(3), N1–Cu1–N3 172.8(4), O7–Cu2–O8 167.2(3), N2–Cu2–N4 169.5(4).

hydrogen bonding interactions. The saccharide derived ligand became monoprotonated resulting in the alkoxy group at the C3 position and acted only as dianionic rather than tri-. This C3–OH is involved in hydrogen bonding interactions with the C2–O$^-$ of the second complex resulting in a ten-membered hydrogen bonded ring (O2–O9 = 2.550(11) Å and O3–O8 = 2.648(13) Å). The copper center exhibits square planar geometry with N_2O_2 ligating atoms. Structurally characterised copper complexes of saccharide derived ligands are mostly multinuclear[4–8] and reports on mononuclear complexes are limited.[9,10] Complex **3** is regarded as a novel chiral building block with the mononuclear Cu(II) center just trapped *via* the crystal-to-crystal transformation.

Superposition of the planar structures of **2** and **3** (Fig. 3) interestingly demonstrated the conservation of the spatial arrangement for the two terminal {CuL^1} fragments. Both the structures were stabilized by hydrogen bonding interactions where the N–H···O type of interaction for the former was switched to the O–H···O type in the latter to avoid further drastic structural changes. The presence of the Cu(II)-templated space in complex **3** suggested that it can be used as a metalloligand for the synthesis of CuMCu homo- and heterometallic systems where an additional oxophilic metal ion can be incorporated in the central position. In fact, the trinuclear Cu(II) complex has been regenerated in quantitative yield by reacting complex **3** with $Cu(OAc)_2{\cdot}H_2O$.

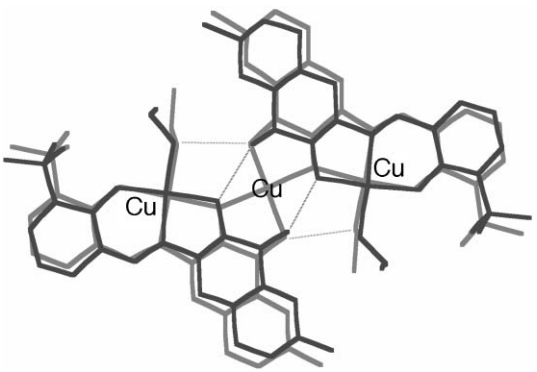

Fig. 3 Overlap view of mono- (top) and trinuclear (below) Cu(II) complexes, revealing the preorganisation of metalloligand **3** to accommodate the third metal ion. Thin lines represent the hydrogen bonding interactions.

Successive isolation of ethylamine bound tri- and mononuclear Cu(II) complexes with metal to ligand ratio 3 : 2 and 1 : 1, respectively, supported the occurrence of proton transfer reaction from solvent to the sugar C3 alkoxo groups, which might involve the key step of C–Cl bond activation as chloroform is well known to form the dichlorocarbene releasing H^+ and Cl^- in presence of strong base during Reimer–Tiemann reactions. In our reaction, the generation of chloride anions was already confirmed by isolating $[Cu(NH_2CH_3)_5]Cl_2$.[1] It should be noted that such activation might have resulted in the formation of dichlorocarbene, however the fate of such a carbene is not yet known due to its fleeting existence.[11] Carbenes are widely used in organic synthesis[12] and hence a proper understanding of our reactions might be useful in organic synthesis. The drastic change in the rate of C–Cl bond activation in the presence of methyl-[1] and ethylamine supports the view that the amine plays a crucial role in the process and hence experiments on the effect of various amines on the chloroform solution of complex **1** are underway.

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Notes and references

‡ Crystal data for **2**·2MeOH·$CHCl_3$: $C_{47}H_{79}Cu_3N_4O_{16}Cl_3$, M = 1253.16, triclinic, a = 8.0925(5), b = 12.2513(11), c = 14.9817(11) Å, α = 91.958(4), β = 98.528(3), γ = 96.609(4)°, U = 1457.2(2) Å^3, T = −120 °C, space group $P\bar{1}$ (no. 1), Z = 1, D_c = 1.428 g cm^{-3}, μ(Mo-Kα) = 12.874 cm^{-1}, 13283 reflections measured, 5141 unique, $R(I > 2.00\sigma(I))$ = 0.045, R_w(all reflections) = 0.107. CCDC 286668. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513788h

§ Crystal data for **3**: $C_{21}H_{32}CuN_2O_6$, M = 472.04, triclinic, a = 6.612(4), b = 12.230(6), c = 14.089(7) Å, α = 77.465(10), β = 82.337(14), γ = 88.386(16)°, U = 1102.3(10) Å^3, T = −120 °C, space group $P\bar{1}$ (no. 1), Z = 2, D_c = 1.422 g cm^{-3}, μ(Mo-Kα) = 10.298 cm^{-1}, 9568 reflections measured, 4120 unique, $R(I > 2.00\sigma(I))$ = 0.074, R_w(all reflections) = 0.203. CCDC 286669. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513788h

1 A. K. Sah, M. Kato and T. Tanase, *Chem. Commun.*, 2005, 675.
2 H. V. R. Dias, R. G. Browning, S. A. Polach, H. V. K. Diyabalanage and C. J. Lovely, *J. Am. Chem. Soc.*, 2003, **125**, 9270.
3 D. Armentano, G. D. Munno, T. F. Mastropietro, M. Julve and F. Lloret, *J. Am. Chem. Soc.*, 2005, **127**, 10778.
4 M. Stolmàr, C. Floriani, G. Gervasio and D. Viterbo, *J. Chem. Soc., Dalton Trans.*, 1997, 1119.
5 A. Fragoso, M. L. Kahn, A. Castiñeiras, J.-P. Sutter, O. Kahn and R. Cao, *Chem. Commun.*, 2000, 1547.
6 (*a*) R. Wegner, M. Gottschaldt, H. Görls, E.-G. Jäger and D. Klemm, *Angew. Chem., Int. Ed.*, 2000, **39**, 595; (*b*) R. Wegner, M. Gottschaldt, H. Görls, E.-G. Jäger and D. Klemm, *Chem.–Eur. J.*, 2001, **7**, 2143; (*c*) M. Gottschaldt, R. Wegner, H. Görls, P. Klüfers, E.-G. Jäger and D. Klemm, *Carbohydr. Res.*, 2004, **339**, 1941.
7 P. Klüfers and T. Kunte, *Eur. J. Inorg. Chem.*, 2002, 1285.
8 (*a*) A. K. Sah, C. P. Rao, P. K. Saarenketo, K. Rissanen, G. A. van Albada and J. Reedijk, *Chem. Lett.*, 2002, 348; (*b*) G. Rajsekhar, A. K. Sah, C. P. Rao, P. Guionneau, M. Bharathy and T. N. GuruRow, *Dalton Trans.*, 2003, 3126.
9 T. Tanase, H. Inukai, T. Onaka, M. Kato, S. Yano and S. J. Lippard, *Inorg. Chem.*, 2001, **40**, 3943.
10 W. Zhang, T. Jiang, S. Ren, Z. Zhang, H. Guan and J. Yu, *Carbohydr. Res.*, 2004, **339**, 2139.
11 J. K. Lee and K. N. Houk, *Science*, 1997, **276**, 942.
12 Y. Cheng and O. Meth-Cohn, *Chem. Rev.*, 2004, **104**, 2507 and references cited therein.