Trinuclear coordinatively labile Cu(II) complex of 4,6-*O*-ethylidene-β-D-glucopyranosylamine derived Schiff base ligand and its reactivity towards primary alcohols and amines†

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A novel neutral trinuclear Cu(II) complex of a Schiff base ligand derived from D-glucose has been synthesised and structurally characterised, which exhibits excellent alcohol binding affinity and activates the C–Cl bond of chloroform in the presence of primary amine.

Copper is one of the most important transition metal ions in biological systems, it plays an important role in transport and activation of molecular oxygen.[1–3] Due to its versatile nature, a lot of work has been published on copper with a variety of ligands, however, it is surprising to note that its chemistry with carbohydrates, which is one of the chiral polyfunctional biomolecules, has not been well documented. Only a countable number of structurally characterised glucose derived Cu(II) complexes are recorded in the literature.[4–8] Hence, the lack of copper complexes with saccharides has aroused our interest to explore its chemistry[9] and in this direction, we are reporting here for the first time a structurally characterised trinuclear complex of *N*-(3-*tert*-butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-β-D-glucopyranosylamine (H_3L^1) and some of its reactivity towards alcohols and amines.

The ligand (H_3L^1) was synthesised in 84% yield by condensing 3-*tert*-butyl-2-hydroxybenzaldehyde with 4,6-*O*-ethylidene-β-D-glucopyranosylamine in methanol (Scheme 1). Its reaction with $Cu(OAc)_2{\cdot}H_2O$ (metal : ligand = 3 : 2) in methanol afforded the trinuclear complex, $[Cu_3(L^1)_2]{\cdot}MeOH{\cdot}H_2O$ (**1**) in 78% yield. Methanol vapour diffusion into the complex solution in $CHCl_3$/MeCN (1 : 1 mixed solvent) resulted in the formation of single crystals of $[Cu_3(L^1)_2(MeOH)_2]$ (**2a**) suitable for X-ray crystallography (Fig. 1).‡ All the previously reported copper complexes with similar ligands are dinuclear where each ligand acts as a dianion and the saccharide C2 hydroxo group bridges the copper centres resulting in a Cu_2O_2 four membered rhombus.[7,8] The presence of a tertiary butyl group in the present case might have restricted the formation of such a ring and thus resulted in a coordinatively labile novel trinuclear complex suitable for ligand exchange studies. The unique feature of complex **2a** is that all the saccharide hydroxyl groups are deprotonated and engaged in metal ion binding. The saccharide C2 hydroxo group bridges the terminal and central copper ions, while the C3 hydroxo group is bound to the central copper resulting in a square planar geometry around it. Each ligand acts as a trianionic species and occupies five coordination sites around the metal centres to result in a neutral trinuclear core. The terminal Cu(II) centres are expected to be coordinatively unsaturated in complex **1** where phenolate, imine nitrogen and saccharide C2 hydroxo group fulfil only three sites. The fourth basal site is occupied by methanol in **2a**, resulting in a square planar geometry. Although acetonitrile is supposed to be a good coordinating solvent for Cu(II), it is surprising to note that even in the presence of excess acetonitrile, it is the trace amount of methanol that occupies the fourth position. This selectivity of the complex towards the alcohols may be attributed to the involvement of alkoxy hydrogen in strong intramolecular hydrogen bonding interaction with the saccharide C3 hydroxo group. Similarly the complex was crystallised using ethanol, *n*-propanol and *n*-butanol to result in X-ray suitable single crystals of $[Cu_3(L^1)_2(ROH)_2]$ (R = Et (**2b**), *n*-Pr (**2c**), *n*-Bu (**2d**)), where the fourth basal coordination sites about the terminal copper is occupied by the respective alcohol molecules.[10] In all cases copper centres are in a square planar geometry with an almost linear arrangement (Cu(1)–Cu(2)–Cu(3), 166–172°). Linear trinuclear copper complexes are rare in the literature and hence these complexes are important from a magnetic point of view.[11,12]

When the complex was crystallised by diffusing the methanol vapour into $CHCl_3$/THF (1 : 1 mixed solvent) solution, THF

† Electronic supplementary information (ESI) available: Details of synthesis, characterisation, structural data and ORTEP plots of **4** and **5**. See http://www.rsc.org/suppdata/cc/b4/b413923b/

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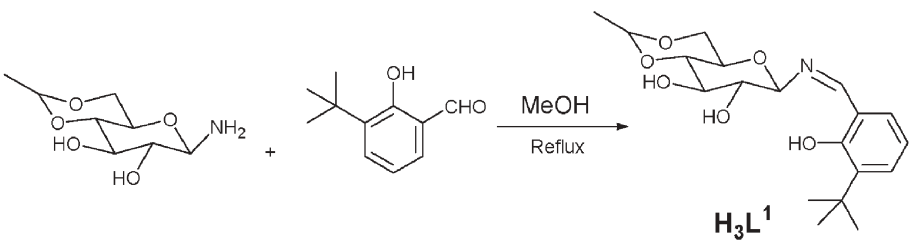

Scheme 1

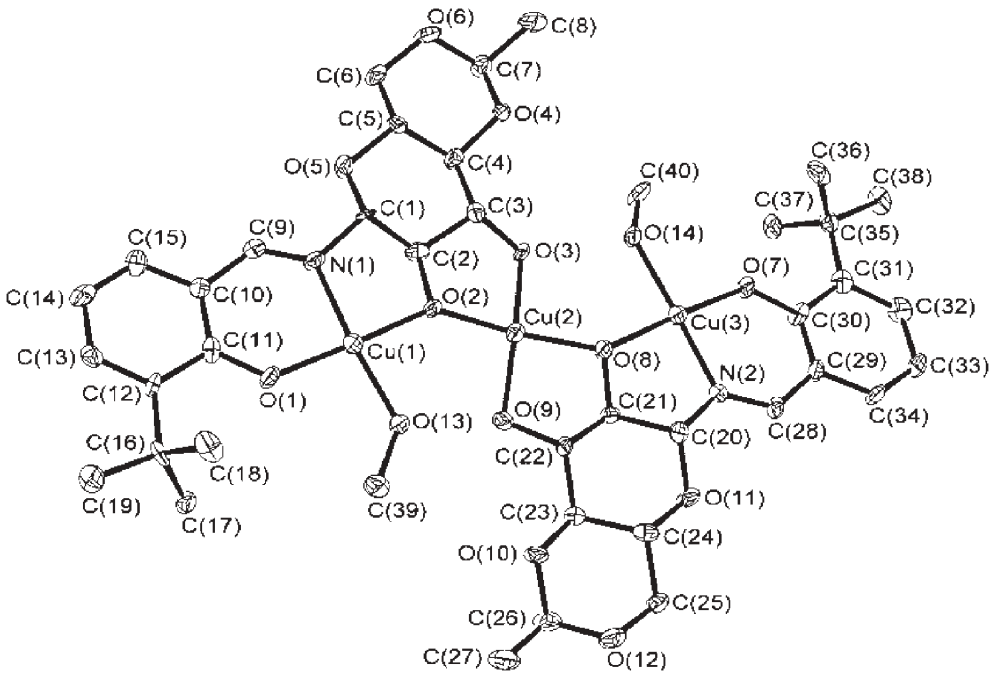

Fig. 1 ORTEP view of **2a** with atom labelling. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.900(3), Cu(1)–O(2) 1.953(3), Cu(1)–O(13) 1.932(4), Cu(1)–N(1) 1.941(4), Cu(2)–O(2) 1.941(3), Cu(2)–O(3) 1.913(3), Cu(2)–O(8) 1.934(3), Cu(2)–O(9) 1.911(3), Cu(3)–O(7) 1.887(3), Cu(3)–O(8) 1.941(3), Cu(3)–O(14) 1.941(3), Cu(3)–N(2) 1.940(4), Cu(1)–Cu(2) 3.683(1), Cu(2)–Cu(3) 3.668(1), O(2)–Cu(1)–O(1) 176.0(1), O(8)–Cu(2)–O(2) 165.9(1), O(8)–Cu(3)–O(7) 174.5(1), N(1)–Cu(1)–O(13) 171.6(2), O(3)–Cu(2)–O(2) 88.8(1), Cu(1)–Cu(2)–Cu(3) 172.41(3).

bound crystals of $[Cu_3(L^1)_2(MeOH)_2(THF)_2]\cdot 2THF$ (3) were isolated (Fig. 2).§ In this case two molecules of THF are bound to the terminal copper centres. The basal position about the terminal copper is occupied by the methanol molecule and THF occupy the axial positions, resulting in a square pyramidal geometry around the terminal copper centres and square planar

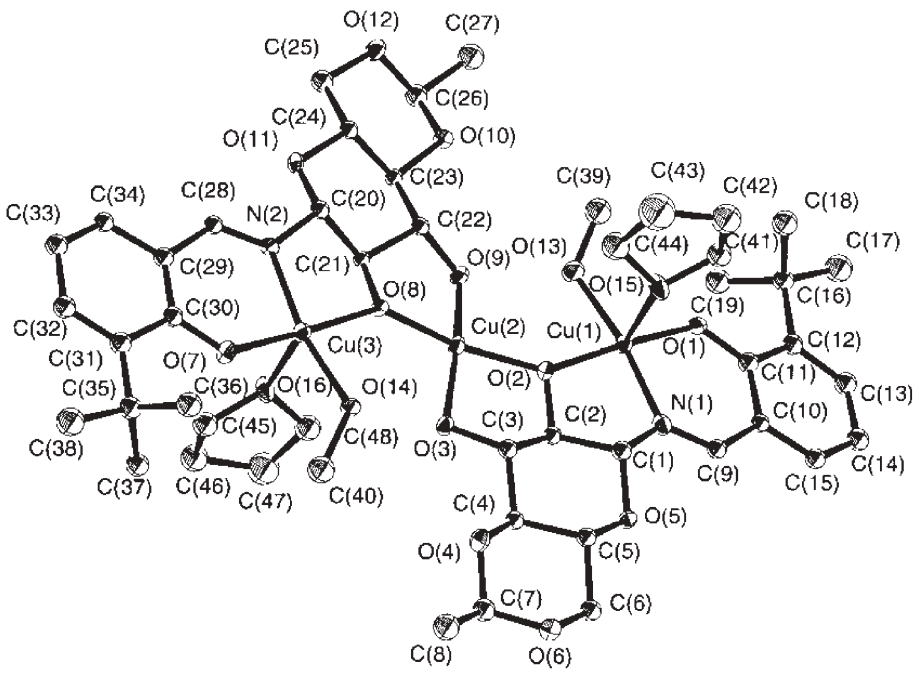

Fig. 2 ORTEP view of **3** with atom labelling, lattice THF molecules are removed for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.900(7), Cu(1)–O(2) 1.956(7), Cu(1)–O(13) 1.979(9), Cu(1)–N(1) 1.96(1), Cu(1)–O(15) 2.394(7), Cu(2)–O(2) 1.923(8), Cu(2)–O(3) 1.907(6), Cu(2)–O(8) 1.932(6), Cu(2)–O(9) 1.924(7), Cu(3)–O(7) 1.888(7), Cu(3)–O(8) 1.944(6), Cu(3)–O(14) 1.944(8), Cu(3)–O(16) 2.466(7), Cu(3)–N(2) 1.959(9), Cu(1)–Cu(2) 3.673(3), Cu(2)–Cu(3) 3.648(3), O(2)–Cu(1)–O(1) 173.5(3), O(8)–Cu(2)–O(2) 163.0(3), O(8)–Cu(3)–O(7) 177.1(3), N(1)–Cu(1)–O(13) 171.1(4), O(3)–Cu(2)–O(2) 88.5(3), Cu(1)–Cu(2)–Cu(3) 170.28(7).

about the central one. Both the THF molecules are *trans* to each other with respect to the molecular plane. All the equatorial bond lengths are in the range of 1.89–1.98 Å for both the complexes and axial Cu–O distances are 2.394(7) and 2.466(7) Å which are within the range for similar geometry.[13,14]

Such an affinity of complex **1** towards alcohols indicates that primary amines could also be introduced into the tricopper system, resulting in a cyclic hydrogen bonding network through the interaction of amino hydrogen donors with the phenolate as well as the sugar C3 hydroxo groups. An attempt along this line has been tried using aniline and *p*-toluidine, however no suitable crystals have been isolated. Diffusion of methylamine (40% in methanol) vapours into a chloroform solution of complex **1** has resulted in interesting results. From the reaction mixture, the crystals of brown colored Cu(II) complex, $[Cu(L^2)_2]$ (**4**, L^2H = 2-*tert*-butyl-6-[(methylimino)methyl]phenol),¶ and the blue colored crystals of $[Cu(NH_2Me)_5]Cl_2$ (**5**)‖ were obtained and characterised by X-ray crystallography (see ESI).† The formation of complex **5**, strongly demonstrated the C–Cl bond activation of the chloroform molecule. In order to avoid the presence of any acid chloride in the chloroform, a number of crystallisations were performed using freshly distilled $CHCl_3$ as well as NaOH treated $CHCl_3$ and in all cases similar complexes were isolated. The ESI-MS analysis of the mother liquor supported the formation of *N*-methyl-4,6-*O*-ethylidene-D-glucopyranosylamine revealing a single pot *trans* imination and *trans* amination reactions. Generally C–Cl bonds of alkyl chloride are difficult to activate due to intrinsically high bond energy and lower leaving group ability,[15] however, in our case, it has formed by methylamine under mild conditions. Details of the solution study and reactivity of the complex with other primary amines are in progress.

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Notes and references

‡ Crystal data for **2a**: $C_{40}H_{56}Cu_3N_2O_{14}$, M = 979.53, orthorhombic, a = 6.4406(2), b = 14.9072(5), c = 42.412(1) Å, U = 4072.0(2) Å^3, T = −120 °C, space group $P2_12_12_1$ (no. 19), Z = 4, D_c = 1.598 g cm^{-3}, μ(Mo-Kα) = 16.24 cm^{-1}, 22509 reflections measured, 13250 unique (R_{int} = 0.052), $R(I > 2.00\sigma(I))$ = 0.040, $R_w(I > 2.00\sigma(I))$ = 0.050.
§ Crystal data for **3**: $C_{56}H_{88}Cu_3N_2O_{18}$, M = 1267.95, triclinic, a = 8.1487(1), b = 12.2359(1), c = 16.9972(3) Å, α = 72.113(8), β = 78.973(9), γ = 65.529(6)°, U = 1463.92(3) Å^3, T = −120 °C, space group $P\bar{1}$ (no. 1), Z = 1, D_c = 1.438 g cm^{-3}, μ(Mo-Kα) = 11.52 cm^{-1}, 7377 reflections measured, 5309 unique (R_{int} = 0.014), $R(I > 2.00\sigma(I))$ = 0.047, $R_w(I > 2.00\sigma(I))$ = 0.056.
¶ Crystal data for **4**: $C_{24}H_{32}CuN_2O_2$, M = 444.07, monoclinic, a = 12.830(4), b = 10.858(3), c = 17.007(5) Å, β = 102.255(4)°, U = 2315.3(11) Å^3, T = −120 °C, space group $P2_1/c$ (no. 14), Z = 4, D_c = 1.274 g cm^{-3}, μ(Mo-Kα) = 9.64 cm^{-1}, 12529 reflections measured, 5096 unique (R_{int} = 0.057), $R(I > 2.00\sigma(I))$ = 0.090, $R_w(I > 2.00\sigma(I))$ = 0.106.
‖ Crystal data for **5**: $C_5H_{25}CuN_5Cl_2$, M = 289.74, orthorhombic, a = 14.0065(10), b = 11.6044(11), c = 8.5136(5) Å, U = 1383.8(2) Å^3, T = −120 °C, space group $Pnma$ (no. 62), Z = 4, D_c = 1.391 g cm^{-3}, μ(Mo-Kα) = 19.38 cm^{-1}, 7810 reflections measured, 1023 unique (R_{int} = 0.019), $R(I > 2.00\sigma(I))$ = 0.037, $R_w(I > 2.00\sigma(I))$ = 0.048.**
** CCDC 250717–250720. See http://www.rsc.org/suppdata/cc/b4/b413923b/ for crystallographic data in .cif or other electronic format.

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