Dinuclear Copper Complexes of *N*-(2-Hydroxybenzylidene or 5-Bromo-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine: Coordination Variation and Structural Diversity

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Dinuclear Cu(II) complexes of *N*-(2-hydroxybenzylidene or 5-bromo-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine with coordination variation and molecular and lattice structural variations are explored.

We have recently synthesised a series of 4,6-*O*-ethylidene-D-glucopyranosylamine based imine containing (saccharide-C1–N=C-) molecules[1] and established their interactions with Ni^{2+}, Zn^{2+}, VO_2^+, MoO_2^{2+} and UO_2^{2+} ions.[2] In continuation of our work of exploring the chelating ability of such ligands, herein we report the dinuclear complexes of Cu(II) using such saccharide derivatives. Our main interest in copper is due to the fact that it is the third most abundant and essential element in biological systems following iron and zinc. Structures of Cu(II) complexes derived from glucose containing *β*-oxo-enamine ligands to result in the imine centers at C2 or C5 or C6 position but not at C1 were reported.[3,4] However, the present study carries the first structurally characterised dinuclear Cu(II) complexes of saccharide-C1–N=C- molecules. Depending upon the crystallisation conditions, the products differed in their coordination behaviour leading to the formation of different types of dinuclear Cu(II) complexes with structural diversity as explored in this study.

Cu(II) complexes (**1** and **2**) were synthesised using *N*-(2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (H_3L1) and *N*-(5-bromo-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (H_3L2). In **1** and **2**, FAB mass as well as microanalyses revealed the presence of dinuclear complexes with metal to ligand ratio of 1 : 1. The complex formation was further supported by FTIR and UV-Visible spectra.[5,6] Slow diffusion of methanol into the concentrated solution of **1** and **2** in DMSO resulted in X-ray quality crystals **3** and **4** respectively.[7,8] Slow evaporation of pyridine from the solution of **1** resulted in pyridine bound compound as X-ray quality crystals **5**, and diffusion of pyridine into DMSO solution of **2** layered with methanol resulted in another pyridine bound compound as X-ray quality crystals **6**.[9,10] Dinuclear Cu(II) centers were observed in the structures of **3**–**6**, where C2–OH of the saccharide moiety bridges as $C2–O^-$ to form Cu_2O_2 rhomb (Figure 1), where the copper centers are separated by 2.899–2.992 Å revealing the absence of any bond between these centers. In all the structures, ligand binds as dianion with tridentate (binding through phenolate ion, imine nitrogen and saccharide-$C2–O^-$) plus one bridging mode to result in one five membered and another six membered chelates. The saccharide moiety maintained its pyranose form with 4- and 6-positions being protected by the ethylidene moiety and C1 being modified via imine bond formation. Further it possesses a $^4C_1$ conformation with double chair in the *β*-anomeric form. The aromatic ring and

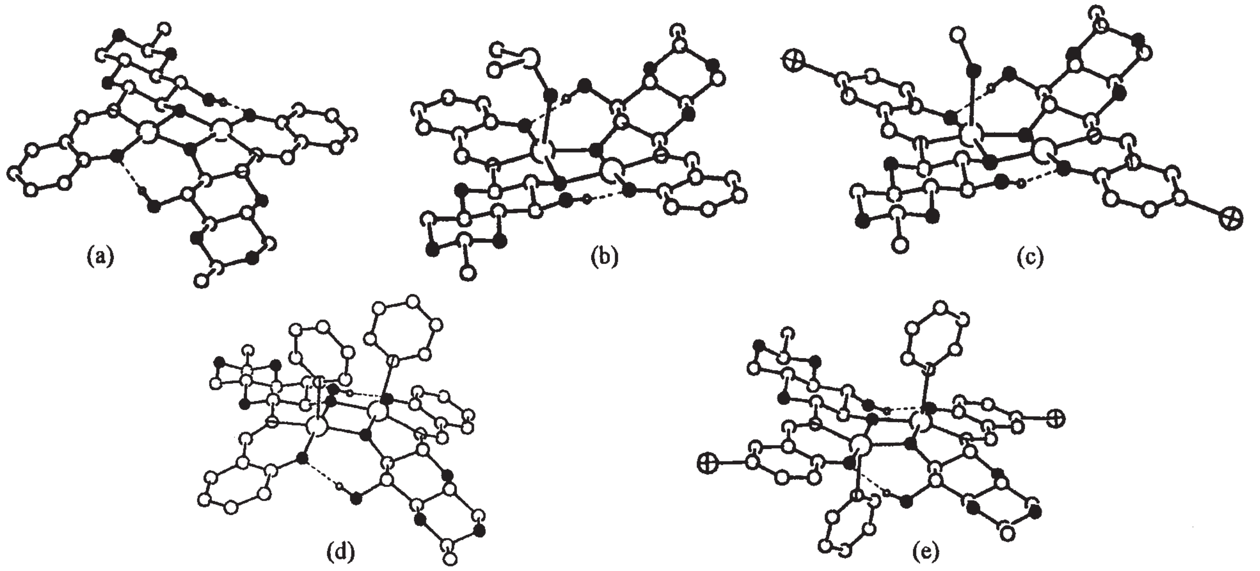

Figure 1. PLUTO plots of the dinuclear copper centers from the crystal structures: (a) and (b), **3**; (c), **4**; (d), **5** and (e), **6**, where filled circles denote oxygens, circles bisected with one line denote nitrogen and circles with cross denote bromines. Dotted lines represent hydrogen bonds.

the saccharide moieties were oriented *trans*- with respect to the C=N bond. In case of **3**, **4** and **6**, two dinuclear units were present in the asymmetric unit. Out of the two dinuclear units present in **3**, the geometry about only one of the Cu(II) centers' is square pyramidal where the fifth position is being occupied by a DMSO (Figure 1b) and all the other three centers showed only square planar geometry. On the other hand, both the dinuclear units present in **4** and **6** exhibited identical cores. In case of **4**, one copper is square planar and the other is square pyramidal in each dimeric unit, where the fifth position is being occupied by MeOH (Figure 1c). In case of **5** and **6**, the geometry around each copper center is square pyramidal where the fifth coordination is occupied by pyridine, with the orientation of bound pyridines being *syn*- in **5** (Figure 1d) and *anti*- in **6** (Figure 1e) with respect to the Cu_2O_2 rhomb. Formation of these two conformers is attributable to the over all shape of the dimeric complex unit. While it is in bowl shape in case of **5**, the same unit is almost planar in case of **6** as understood from the stereo views. In case of **6**, the orientation of C3-OH exerts some steric hindrance for the entry of pyridine. Thus various coordination types and structural types are observed in the crystal structures (Figure 1). In **3**–**6**, ligating atoms present in the plane were having normal bond lengths whereas in case of square pyramidal Cu(II), the distances with the axial, Cu-N/O were found in the range of 2.252–2.428 Å and are well within the literature reports for similar geometry.[3,4,11]

In all the cases, the observed intra-complex hydrogen-bond interactions ($\mathrm{C3{-}O{-}H\cdots O_{phenolate}}$) would presumably bring additional stability in the corresponding dinuclear complexes with Cu_2O_2 core. In addition, intermolecular H-bond interactions were noticed, in **3** (four C–H···O), **4** (four O–H···O and six C–H···O) and **5** (one O–H···O and one C–H···O), and the corresponding distance data for donor-acceptor and hydrogen-acceptor shows fairly linear correlation (Figure 2). Such interactions resulted in layer type structures in all the lattices.

At room temperature **4** and **6** are EPR silent. Variable temperature magnetic data measured in the range 275 to 5 K exhibited antiferromagnetic behaviour in **4** and **6**. In this temperature range, the magnetic moment per dimer changes from 2.13 to 1.38 BM in **4** and from 2.13 to 0.33 BM in **6**.

Presence of bound DMSO and MeOH in **3** and **4**, and bound pyridine as *syn*- and *anti*- in **5** and **6**, indicated coordination variation around the Cu(II) centers and also structural diversity both at the molecular and lattice levels. Hence these compounds are potentially important in bioinorganic chemistry as models of 'Type III' copper centers in proteins and enzymes. Some reactivity studies are currently underway in our laboratory.

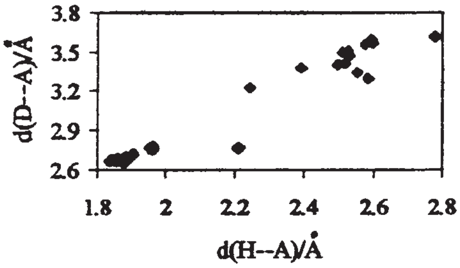

Figure 2. Plot of d(H···A) vs d(D···A) present in lattices of **3**, **4**, **5** and **6**, where 'D' refers to the donor, 'A' refers to the acceptor.

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References and Notes

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5 Analytical Data for **1**: Yield: 97%; mp > 250 °C. Anal. Calcd for $C_{30}H_{34}N_2O_{12}Cu_2$: C, 48.58; H, 4.62; N, 3.78%. Found: C, 48.05; H, 4.63; N, 3.98%. FAB-MS *m/z* 741 (65% for $Cu_2(HL1)_2$). IR (cm^{-1}): ν_{OH}, 3229; $\nu_{C=N}$, 1636; $\nu_{Ar-C=C}$, 1602, 1540; $\nu_{sacch\text{-}C\text{-}O}$, 1148, 1110, 1089. UV-vis, λ_{max}/nm, (ε/$Lmol^{-1}cm^{-1}$): 274(55513), 362(21271) and 642(183).

6 Analytical Data for **2**: Yield: 88%; mp > 250 °C. Anal. Calcd for $C_{30}H_{32}N_2Br_2O_{12}Cu_2 \cdot 3H_2O$: C, 37.79; H, 4.02; N, 2.94%. Found: C, 37.85; H, 3.95; N, 2.68%. FAB-MS *m/z* 899 (70% for $Cu_2(HL2)_2$). IR (cm^{-1}): ν_{OH}, 3339; $\nu_{C=N}$, 1642; $\nu_{Ar-C=C}$, 1607, 1549; $\nu_{sacch\text{-}C\text{-}O}$, 1148, 1090. UV-vis, λ_{max}/nm, (ε/$Lmol^{-1}cm^{-1}$): 267(63340), 371(21640) and 651(200).

7 Crystal data for **3**. Empirical formula: $C_{62}H_{76}Cu_4N_4O_{26}S$; fw.: 1579.49; Crystal system: Orthorhombic, $P2_12_12_1$; Unit cell Dimension (Å): 13.184(1), 13.683(1), 35.411(2); $V = 6388.0(8)$ $Å^3$; $Z = 8$; $D_{calc} = 1.642\ Mg/m^3$; Unique reflections: 10241 [R(int) = 0.0556]; Final R [I > 2σ (I)]: 0.0449 and R_w: 0.0761.

8 Crystal data for **4**. Empirical Formula: $C_{32}H_{40}Br_2Cu_2N_2O_{14}$; fw.: 963.56; Crystal system: Triclinic, $P1$; Unit cell Dimension (Å and °): 10.488(1), 12.677(1), 14.761(1) 110.07(1), 102.19(1) 91.21(1); $V = 1792.4(3)$ $Å^3$; $Z = 2$; $D_{calc} = 1.785\ Mg/m^3$; Unique reflections: 9701 [R(int) = 0.0337]; Final R [I > 2σ (I)]: 0.0294 and R_w: 0.0697.

9 Crystal data for **5**. Empirical Formula: $C_{50}H_{54}Cu_2N_6O_{12}$; fw.: 1058.07; Crystal system: Orthorhombic, $P2_12_12_1$; Unit cell Dimension (Å): 13.304(1), 13.548(1), 26.292(1); $V = 4738.9(5)$ $Å^3$; $Z = 4$; $D_{calc} = 1.483\ Mg/m^3$; Unique reflections: 8318 [R(int) = 0.0793]; Final R [I > 2σ (I)]: 0.0535 and R_w: 0.0976.

10 Crystal data for **6**. Empirical Formula: $C_{40}H_{42}Br_2Cu_2N_4O_{12}$; fw.: 1057.68; Crystal system: Triclinic, $P1$; Unit cell Dimension (Å and °): 13.230(1), 13.242(1), 13.426(1) 104.83(1), 105.40(1) 104.06(1); $V = 2066.6(3)$ $Å^3$; $Z = 2$; $D_{calc} = 1.700\ Mg/m^3$; Unique reflections: 11552 [R(int) = 0.0546]; Final R [I > 2σ (I)]: 0.0621 and R_w: 0.1488.

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