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Tri- and Tetranuclear Copper(II) Complexes Consisting of Mononuclear Cu(II) Chiral Building Blocks with a Sugar-Derived Schiff's Base Ligand

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A new sugar-derived Schiff's base ligand *N*-(3-*tert*-butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-β-D-glucopyranosylamine (H_3L^1) has been developed which afforded the coordinatively labile, alcoholophilic trinuclear Cu(II) complex $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (**1**). Complex **1** has been further used in the synthesis of a series of alcohol-bound complexes with a common formula of $[Cu_3(L^1)_2(ROH)_2]$ (R = Me (**2**), Et (**3**), ^{n}Pr (**4**), ^{n}Bu (**5**), ^{n}Oct (**6**)). X-ray structural analyses of complexes **2**–**6** revealed the collinearity of trinuclear copper(II) centers with Cu–Cu–Cu angles in the range of 166–172°. The terminal and central coppers are bound with NO_3 and O_4 atoms, respectively, and exhibit square-planar geometry. The trinuclear structures of **2**–**6** can be viewed as the two $\{Cu(L^1)\}^-$ fragments capture a copper(II) ion in the central position, which is further stabilized by a hydrogen-bonding interaction between the alcohol ligands and the sugar C-3 alkoxo group. Complex **2** exhibits a strong antiferromagnetic interaction between the Cu(II) ions ($J = -238$ cm^{-1}). Diffusion of methanol into a solution of complex **1** in a chloroform/THF mixed solvent afforded the linear trinuclear complex $[Cu_3(L^1)_2(CH_3OH)_2(THF)_2]$ (**7**). The basic structure of **7** is identical to complex **2**; however, THF binding about the terminal coppers ($Cu–O_{THF} = 2.394(7)$ and 2.466(7) Å) has introduced the square-pyramidal geometry, indicating that the planar trinuclear complexes **2**–**6** are coordinatively unsaturated and the terminal metal sites are responsible for further ligations. In the venture of proton-transfer reactions, a successful proton transfer onto the saccharide C-3 alkoxo group has been achieved using 4,6-*O*-ethylidene-D-glucopyranose, resulting in the self-assembled tetranuclear complex, $[Cu_4(HL^1)_4]$ (**8**), consisting of the mononuclear Cu(II) chiral building blocks, $\{Cu(HL^1)\}$.

Introduction

Carbohydrates are one of the major sources of energy for living beings, and they also act as building blocks for formation of polysaccharides, nucleic acids, and antibiotics. Coexistence of metal ions and saccharides in the biological system has already been established, e.g., Ca(II) in C-type lectins,[1] Mn(II) and Ca(II) in concanavalin A,[2] Mg(II) in β-phosphoglucomutase[3] and ribulose-1,5-bisphosphate carboxylase,[4] Fe(II) in phosphoglucose isomerase,[5] etc.[6] Hence, metal−saccharide interactions are important from a biological viewpoint as well as an inorganic chemistry viewpoint due to the fact that saccharides can act as chiral polyfunctional bioligands. Due to this interesting feature, metal saccharide interactions were recognized long ago; however, most of the literature has dealt with solution study.[7] Lack of

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structurally characterized metal saccharide complexes provoke us to explore the chemistry of saccharides with biorelevant metal ions.

Most of the structurally characterized metal saccharide complexes have been synthesized using well-planned sugar-modified ligands. Few methods have been used for tailoring the sugar-modified ligand, and generally, most of the hydroxyl groups have been blocked through acetal formation, leaving either only one alkoxy group[8] or vicinal diols[9] free for metal complexation reactions. In the second category the C1 position has been modified via glycosylamine formation where metal ion binding is mainly governed by the amine portion of the ligand.[10] Formation of Schiff's bases by condensing the amino sugar with aromatic aldehydes has been known since 1922,[11] but the first report on its metal complexation appeared after about 60 years.[12] This report deals with complexes of Co(II), Cu(II), and Zn(II); however, no structural studies were reported. Recently few structurally characterized metal complexes of saccharide-derived Schiff's base ligand have been reported,[13−15] and in all cases formation of multinuclear Cu(II) complexes has been noted.[13,14]

Multinuclear complexes are important for catalysis as well as magnetic aspects, and in this direction we have already reported the synthesis and characterization of homo- (Zn(II)) and heterotrimetallic (Cu(II)/Zn(II)) complexes.[16] The versatile nature of this copper chemistry peaked our interest for further investigation, and in this direction a new glycosylamine-based Schiff's base ligand, *N*-(3-*tert*-butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (H_3L^1; where H_3 represents the three exchangeable hydrogens), has been developed, which yielded a coordinatively labile trinuclear Cu(II) complex, $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (**1**). The coordinatively labile behavior of complex **1** has been utilized in the synthesis of a series of alcohol-bound, linear trinuclear copper(II) complexes with a common formula of $[Cu_3(L^1)_2(ROH)_2]$ (R = Me (**2**), Et (**3**), ^{n}Pr (**4**), ^{n}Bu (**5**), ^{n}Oct (**6**)). The trinuclear structures of **2**−**6** are recognized as two mononuclear $\{Cu(L^1)\}$ fragments capture a copper(II) ion through the sugar C-2 and C-3 alkoxo groups. Deprotonation of weakly acidic glucose alkoxy groups ($pK_a > 12$),[17] during the copper ion binding, tempted us to explore the proton-transfer reactions onto the sugar alkoxo groups of the trinuclear complex **1**. Some attempts of these reactions could lead to the generation of mononuclear $\{Cu(HL^1)\}$ fragment, and successfully tetranuclear complex $[Cu_4(HL^1)_4]$ (**8**) was isolated. In this paper we report the synthesis and characterization of tri- and tetranuclear Cu(II) complexes utilizing mononuclear Cu(II) chiral building block with the sugar-derived Schiff's base ligand H_3L^1. Preliminary results have been already communicated.[18]

Experimental Section

Materials. 4,6-*O*-Ethylidene-D-glucopyranose[19] and 4,6-*O*-ethylidene-*β*-D-glucopyranosylamine[20] were prepared according to the reported procedure. 3-*tert*-Butyl-2-hydroxybenzaldehyde was purchased from Aldrich, and all other reagents were locally available commercial grade and used as received.

Measurements. Electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer and IR spectra on a Jasco FT/IR-410 spectrometer in KBr matrix. ^{1}H and ^{13}C NMR spectra were measured in DMSO-d_6 on a Varian Gemini 2000 instrument at 300 and 126 MHz, respectively. In both the cases, chemical shift were calibrated to DMSO as an internal reference. ESI-TOF mass spectra were recorded on an Applied Biosystems Mariner high-resolution mass spectrometer with positive ionization mode. FAB mass spectra were measured on a JEOL DX300-JMA3100 spectrometer using NBA matrix. Variable-temperature magnetic susceptibility data were measured over a range of 4.5−300 K by a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) susceptometer.

Preparation of *N*-(3-*tert*-Butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (H_3L^1). To a suspension of 4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (1.03 g, 5.01 mmol) in methanol (15 mL) was added 3-*tert*-butyl-2-hydroxybenzaldehyde (0.94 mL, 5.49 mmol), and the reaction mixture was refluxed for 6 h to result in a clear orange solution. The reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (3−4 mL), and excess hexane was added to the solution while stirring to afford the light yellow solid product ($H_3L^1 \cdot 0.5H_2O$), which was isolated through filtration and dried under vacuum. Yield: 1.57 g (84%, with respect to glycosylamine). Anal. Calcd for $H_3L^1 \cdot 0.5H_2O$ ($C_{19}H_{28}NO_{6.5}$): C, 60.95; H, 7.54; N, 3.74. Found C, 60.63; H, 7.23; N, 3.71. IR (KBr; cm^{-1}): ν_{OH} 3419, $\nu_{C=N}$ 1633, ν_{C-O} 1162, 1140, 1122, 1105, 1069. UV−Vis ($CHCl_3$) λ_{max}, nm (ϵ; M^{-1} cm^{-1}): 264 (1.55×10^4), 330 (4.82×10^3). ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): 13.87 (1H, s, Ar OH), 8.58 (1H, s, HC=N), 7.34 (2H, m, Ar H), 6.85 (1H, t, J = 7.80 Hz, Ar H), 5.56 (1H, d, J = 6.00 Hz, Sac C-2-OH), 5.36 (1H, d, J = 5.40 Hz, Sac C-3-OH), 4.75 (1H, q, J = 4.9 Hz, ethylidene CH), 4.55 (1H, d, J = 8.4 Hz, Sac C-1-H), 4.06 (1H, m, Sac C-5-H), 3.57−3.37

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(3H, m, Sac C-3 and C-6-H), 3.28 (1H, t, $J = 9.15$, Sac C-4-H), 3.13 (1H, m, Sac C-3-H), 1.36 (9H, s, ^{t}Bu), 1.25 (3H, d, $J = 5.1$ Hz, ethylidene CH_3). ^{13}C NMR (in DMSO-d_6, 126 MHz, ppm): 167.0 (C═N); Ar, 160.2, 136.7, 131.3, 130.2, 118.6, 118.4; Sac, 98.9, 95.5, 80.4, 74.9, 73.5, 68.1, 67.5; 34.6 (Ar−*C*$(CH_3)_3$), 29.4 (^{t}Bu), 20.5 (ethylidene CH_3). ESI-MS *m*/*z* 366.21 ($M + H^+$, 100%). Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of its concentrated methanolic solution at room temperature.

Preparation of $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (1). To a solution of $H_3L^1 \cdot 0.5H_2O$ (1.46 g, 3.91 mmol) in methanol (30 mL) was added $Cu(OAc)_2 \cdot H_2O$ (1.21 g, 6.08 mmol), and the reaction mixture was stirred for 24 h at room temperature to result in a green solid product $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (**1**). The product was filtered, washed with cold methanol, and dried under vacuum. Yield: 1.48 g (78%, with respect to H_3L^1). Anal. Calcd for $C_{39}H_{54}N_2O_{14}Cu_3$: C, 48.52; H, 5.64; N, 2.90. Found: C, 48.35; H, 5.58; N, 2.81. IR (KBr; cm^{-1}): ν_{OH} 3438, $\nu_{C=N}$ 1634, ν_{C-O} 1144, 1109, 1087. UV−vis ($CHCl_3$) λ_{max}, nm (ϵ; M^{-1} cm^{-1}): 280 (3.56×10^4), 377 (1.36×10^4), 638 (5.62×10^2).

Preparation of $[Cu_3(L^1)_2(CH_3OH)_2] \cdot 0.5CHCl_3$ (2·0.5CHCl$_3$). Complex **1** (50 mg, 0.052 mmol) was dissolved in chloroform/acetonitrile (4 mL; 1:1 mixed solvent), and methanol vapor was allowed to diffuse into the solution at 4 °C to afford single crystals of **2**·0.5$CHCl_3$ suitable for X-ray analysis. Yield: 46 mg (85%). Anal. Calcd for **2**·0.5$CHCl_3$ ($C_{40.5}H_{56.5}N_2O_{14}Cl_{1.5}Cu_3$): C, 46.81; H, 5.48; N, 2.70. Found: C, 47.11; H, 5.39; N, 2.99. IR (KBr; cm^{-1}): ν_{OH} 3449, $\nu_{C=N}$ 1634, ν_{C-O} 1145, 1110, 1088.

Preparation of $[Cu_3(L^1)_2(C_2H_5OH)_2] \cdot 0.25CHCl_3$ (3·0.25CHCl$_3$). To a solution of complex **1** (50 mg, 0.052 mmol) in chloroform/acetonitrile (4 mL; 1:1 mixed solvent), ethanol (0.25 mL) was added, and the mixture was allowed to slowly evaporate at room temperature to afford single crystals of **3**·0.25$CHCl_3$. Yield: 41 mg (76%). Anal. Calcd for **3**·0.25$CHCl_3$ ($C_{42.25}H_{60.25}N_2O_{14}Cl_{0.75}Cu_3$): C, 48.92; H, 5.85; N, 2.70. Found: C, 49.13; H, 5.57; N, 2.82. IR (KBr; cm^{-1}): ν_{OH} 3439, $\nu_{C=N}$ 1635, ν_{C-O} 1145, 1111, 1088.

Preparation of $[Cu_3(L^1)_2(C_3H_7OH)_2]$ (4). This compound was prepared by adopting the procedure given for **3** but using *n*-propanol (0.5 mL). Yield: 40 mg (74%). Anal. Calcd for **4** ($C_{44}H_{64}N_2O_{14}Cu_3$): C, 51.03; H, 6.23; N, 2.70. Found: C, 50.54; H, 6.26; N, 2.78. IR (KBr; cm^{-1}): ν_{OH} 3434, $\nu_{C=N}$ 1636, ν_{C-O} 1145, 1112, 1087.

Preparation of $[Cu_3(L^1)_2(C_4H_9OH)_2] \cdot 0.25CHCl_3$ (5·0.25CHCl$_3$). This compound was prepared by a procedure similar to that adopted for **3** but using *n*-butanol (1 mL). Yield: 45 mg (79%). Anal. Calcd for **5**·0.25$CHCl_3$ ($C_{46.25}H_{68.25}N_2O_{14}Cl_{0.75}Cu_3$): C, 50.80; H, 6.29; N, 2.56. Found: C, 51.02; H, 6.18; N, 2.67. IR (KBr; cm^{-1}): ν_{OH} 3433, $\nu_{C=N}$ 1635, ν_{C-O} 1145, 1111, 1088.

Preparation of $[Cu_3(L^1)_2(C_8H_{17}OH)_2]$ (6). This compound was prepared by adopting the procedure given for **3** but using complex **1** (78 mg, 0.081 mmol) in a mixed solvent chloroform/acetonitrile (4 mL; 1:1) and *n*-octanol (0.75 mL). Yield: 52 mg (55%). Anal. Calcd for **6** ($C_{54}H_{84}N_2O_{14}Cu_3$): C, 55.16; H, 7.20; N, 2.38. Found: C, 55.09; H, 7.35; N, 2.46. IR (KBr; cm^{-1}): ν_{OH} 3433, $\nu_{C=N}$ 1637, ν_{C-O} 1145, 1111, 1088.

Preparation of $[Cu_3(L^1)_2(CH_3OH)_2(THF)_2] \cdot 2THF \cdot 0.5CHCl_3$ (7·2THF·0.5CHCl$_3$). This compound was prepared by adopting the procedure given for **2** but replacing the acetonitrile by an equal amount of THF. Yield: 40 mg (58%). Anal. Calcd for **7**·2THF·0.5$CHCl_3$ ($C_{56.5}H_{88.5}N_2O_{18}Cl_{1.5}Cu_3$): C, 51.11; H, 6.72; N, 2.11. Found: C, 50.79; H, 6.57; N, 2.51. IR (KBr; cm^{-1}): ν_{OH} 3448, $\nu_{C=N}$ 1634, ν_{C-O} 1145, 1111, 1088.

Preparation of $[Cu_4(HL^1)_4] \cdot 2CH_3CN \cdot 0.25CHCl_3$ (8·2CH$_3$CN·0.25CHCl$_3$). To a solution of complex **1** (0.47 g, 0.49 mmol) in chloroform (25 mL) was added a solution (50 mL) of 4,6-*O*-ethylidene-D-glucopyranose (0.21 g, 1.02 mmol) in acetonitrile, and the resultant mixture was allowed to slowly evaporate at room temperature. Green crystals of **8**·2CH_3CN·0.25$CHCl_3$ were separated out along with solid 4,6-*O*-ethylidene-D-glucopyranose, which were isolated through filtration. The mixture of solids was extracted with $CHCl_3$, and acetonitrile was added to the solution. Slow evaporation of complex solution yielded crystals of pure tetranuclear Cu(II) complex. Yield: 44 mg (10% with respect to complex **1**). Anal. Calcd for **8**·2CH_3CN·0.25$CHCl_3$ ($C_{80.25}H_{106.25}N_6O_{24}Cl_{0.75}Cu_4$): C, 52.97; H, 5.88; N, 4.62. Found: C, 53.13; H, 5.85; N, 4.89. IR (KBr; cm^{-1}): ν_{OH} 3428, $\nu_{C=N}$ 1635, ν_{C-O} 1145, 1111, 1088. UV−vis (in $CHCl_3$) λ_{max}, nm (ϵ; M^{-1} cm^{-1}): 280 (6.14×10^4), 380 (2.41×10^4), 677 (7.22×10^2).

X-ray Crystallography. Crystals of ligand H_3L^1 and complexes **2**−**8** were coated with Paraton N oil and mounted on the tip of glass fiber at low temperature. Crystal data and experimental conditions are summarized in Tables 1 and 2. All data were collected at −120 °C on a Rigaku AFC8R/Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using a rotating-anode X-ray generator. A total of 1440−2160 oscillation images, covering a whole sphere of $2\theta < 52$ °, were corrected with exposure rates of 96° (**5**), 128° (H_3L^1, **2**−**4**, **6**, **7**), and 192° s^{-1} (**8**) by ω scan method ($-70 < \omega < 110$° or $-62 < \omega < 118$°) with $\Delta\omega = 0.25$°. The crystal-to-detector (70×70 mm) distance was set to 60 mm. The data were processed using Crystal Clear 1.3.5 (Rigaku/MSC)[21] and corrected for Lorentz polarization and absorption effects. The structures of complexes were solved by direct methods (**2**−**5**, **7**, **8** by SIR97[22] and **6** by SIR92[23]) and refined on *F* with full-matrix least-squares techniques with Crystal Structure 3.6.[24] All non-hydrogen atoms of **2** were refined with anisotropic thermal parameters, and the positions of C−H hydrogen atoms were calculated and refined with riding models. The positions of O−H hydrogen atoms of methanol molecules were determined by difference Fourier syntheses and refined isotropically. In the refinements of **3**−**8**, part of the non-hydrogen atoms (Cu, O, and N atoms for **4**, **5**, **7**, **8**; Cu atoms for **3**, **6**) were refined with anisotropic temperature factors, and other non-hydrogen atoms were refined isotropically. All C−H hydrogen atoms of **3**−**8** were placed at ideal positions and refined with riding models. The position of O−H hydrogen atoms for the metal-bound alcohols in **3**, **5**, **6**, and **8** were determined from difference Fourier maps and fixed in the refinements, and those for **4** and **7** were not determined. In complex **4** the solvent chloroform was disordered and refined using two site rigid-group models with 0.5 occupancy. One of the terminal carbons of the ^{n}Pr group was disordered in two sites with each 0.5 occupancy. In complexes **7** and **8** the solvent molecules were refined isotropically. The structure of H_3L^1 was solved by direct methods (SIR97) and refined on F^2 by least-squares techniques with SHELXL-97.[25] The non-hydrogen atoms were refined with anisotropic thermal parameters, and the C−H hydrogen atoms were placed at calculated positions and refined with riding

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Table 1. Crystallographic and Experimental Data for H_3L^1, **2**, **3**, and **4**·$CHCl_3$

compound	H_3L^1	**2**	**3**	**4**·$CHCl_3$
formula	$C_{19}H_{27}NO_6$	$C_{40}H_{56}Cu_3N_2O_{14}$	$C_{42}H_60Cu_3N_2O_{14}$	$C_{45}H_{65}Cu_3N_2O_{14}Cl_3$
fw	365.43	979.53	1007.58	1155.01
cryst syst	monoclinic	orthorhombic	triclinic	triclinic
space group	$P2_1$	$P2_12_12_1$	$P1$	$P1$
a/Å	10.428 (2)	6.4406(2)	8.0205(4)	7.9542(2)
b/Å	6.4356(9)	14.9072(5)	11.3239(7)	11.3439(5)
c/Å	14.875(3)	42.412(1)	13.2253(2)	15.2227(5)
α/deg			72.59(1)	78.269(8)
β/deg	105.027(2)		76.16(1)	75.176(7)
γ/deg			81.71(1)	80.948(9)
V/Å^3	964.1(3)	4072.0(2)	1109.41(9)	1292.04(8)
Z	2	4	1	1
T/°C	−120	−120	−120	−120
d_{calcd}/g cm^{-1}	1.259	1.598	1.508	1.484
$2\theta_{max}$/deg	52	52	52	52
no. of obsd data	2524	13250 ($I > 2.00\sigma(I)$)	2638 ($I > 2.00\sigma(I)$)	3917 ($I > 2.00\sigma(I)$)
solution	direct methods SIR97	direct methods SIR97	direct methods SIR97	direct methods SIR97
no. of param	250	593	322	425
data/param	10.10	22.34	8.19	9.22
R[a]	0.034	0.040	0.068	0.071
R_w	0.086[b]	0.050[c]	0.074[c]	0.091[c]
GOF	1.04[d]	0.41[e]	0.97[e]	1.38[e]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [d] GOF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$ (N_o = no. data, N_v = no. variables). [e] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ (N_o = no. data, N_v = no. variables).

Table 2. Crystallographic and Experimental Data for **5**, **6**, **7**·2THF, and **8**·$2CH_3CN$·$2CHCl_3$·H_2O

compound	**5**	**6**	**7**·2THF	**8**·$2CH_3CN$·$2CHCl_3$·H_2O
formula	$C_{46}H_{68}Cu_3N_2O_{14}$	$C_{54}H_{84}Cu_3N_2O_{14}$	$C_{56}H_{88}Cu_3N_2O_{18}$	$C_{82}H_{110}Cu_4N_6O_{25}Cl_6$
fw	1063.69	1175.90	1267.95	2046.70
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P1$	$P1$	$P1$	$P2_1$
a/Å	8.313(1)	12.782(8)	8.1487(1)	12.768(1)
b/Å	11.754(2)	14.869(9)	12.2359(1)	16.658(1)
c/Å	13.342(2)	17.617(10)	16.9972(3)	22.081(2)
α/deg	107.902(4)	110.769(4)	72.113(8)	
β/deg	101.114(5)	98.502(2)	78.973(9)	100.419(2)
γ/deg	93.751(4)	109.585(7)	65.529(6)	
V/Å^3	1206.3(3)	2811(3)	1463.92(3)	4618.6(8)
Z	1	2	1	2
T/°C	−120	−120	−120	−120
d_{calcd}/g cm^{-1}	1.464	1.389	1.438	1.472
$2\theta_{max}$/deg	52	52	52	52
no. of obsd data	4155 ($I > 2.00\sigma(I)$)	5959 ($I > 2.00\sigma(I)$)	5309 ($I > 2.00\sigma(I)$)	7290 ($I > 2.00\sigma(I)$)
solution	direct methods SIR97	direct methods SIR92	direct methods SIR97	direct methods SIR97
no. of param	424	781	509	780
data/param	9.80	7.63	10.43	9.35
R[a]	0.057	0.062	0.047	0.060
R_w[b]	0.066	0.075	0.056	0.073
GOF[c]	0.91	1.22	0.79	1.14

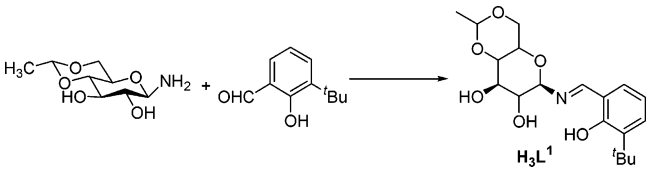
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [c] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ (N_o = no. data, N_v = no. variables).

models. The positions of O−H hydrogen atoms were determined from difference Fourier maps and refined isotropically. All calculations were carried out on a Pentium PC with Crystal Structure package 3.6[24] and a Silicon Graphics O2 station with the teXsan crystallographic software package.[26]

Results and Discussion

***N*-(3-*tert*-Butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-β-D-glucopyranosylamine (H_3L^1).** The ligand H_3L^1 was prepared by condensing 4,6-*O*-ethylidene-β-D-glucopyranosylamine with 3-*tert*-butyl-2-hydroxybenzaldehyde in methanol (Scheme 1), and product formation was supported by IR, NMR, ESI-MS, and microanalysis studies. The ^{1}H NMR spectra in DMSO-d_6 exhibited a doublet for the C-1-H proton of D-glucose unit with $^3J_{HH}$ of 8.4 Hz, revealing the β-anomeric form of the saccharide moiety[10b] in which H atoms of the C-1 and C-2 positions are in a trans arrangement. Slow evaporation of its concentrated methanolic solution afforded yellowish single crystals, and the structure was confirmed by X-ray crystallography (Figure 1 and Table 3). Both six-membered rings consisting of the saccharide and its ethylidene protection at the 4 and 6 positions adopted a

Scheme 1



(26) *TEXSAN: Crystal Structure Analysis Package*; Rigaku and Molecular Structure Corp.: Tokyo, Japan, 1999.

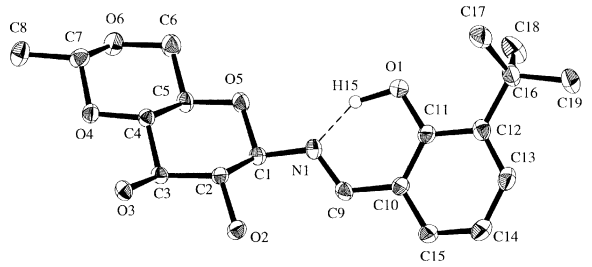


Figure 1. ORTEP plot of ligand H_3L^1.

Table 3. Selected Bond Distances (Å) and Angles (deg) for H_3L^{1a}

O1−C11	1.363(2)	O2−C2	1.421(2)
O3−C3	1.434(2)	O4−C4	1.437(2)
O4−C7	1.442(2)	O5−C1	1.431(2)
O5−C5	1.426(2)	O6−C6	1.445(2)
O6−C7	1.416(2)	N1−C1	1.450(2)
N1−C9	1.277(2)	C9−C10	1.461(2)
C1−O5−C5	112.2(2)	C1−N1−C9	120.1(2)
O5−C1−N1	104.7(2)	N1−C9−C10	122.2(2)
C9−C10−C11	121.2(2)	C9−C10−C15	118.9(2)
O1−C11−C10	119.8(2)	O1−C11−C12	119.2(2)
C1−N1−C9−C10	−177.3(2)	C9−N1−C1−O5	−167.4(2)
N1−C1−C2−O2	−67.2(2)	N1−C9−C10−C11	−9.2(3)

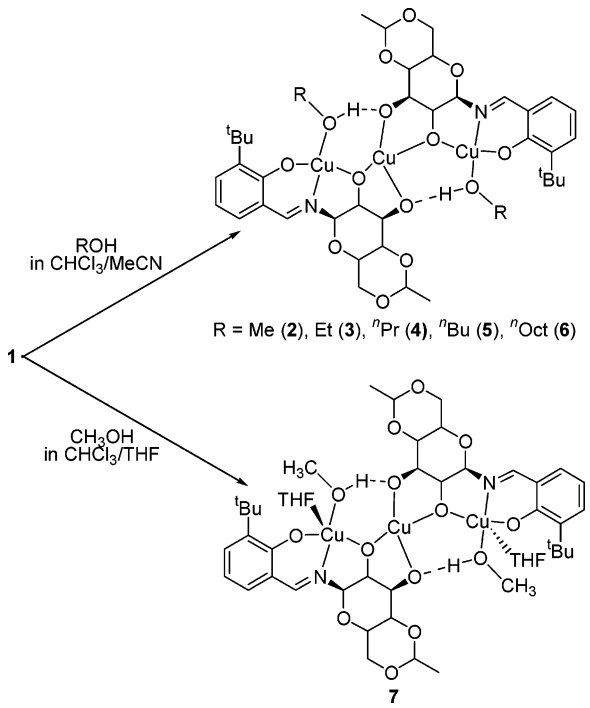
[a] Estimated standard deviations are given in parentheses.

fused chair conformation similar to other reported structures derived from different aldehydes (salicylaldehyde (H_3L^2),[27a] 5-bromosalicylaldehyde (H_3L^3),[27b] and 3-methoxysalicylaldehyde (H_3L^4)[27b]). The main difference for this structure compared to earlier reported structures of H_3L^n ($n = 2-4$) is the orientation of phenolic group with respect to the saccharide C-2 alkoxy group. A similar orientation of the analogous ligand H_3L^2 has been observed while Zn(II) binding;[15c] however, the ^{1}H NMR data of H_3L^1 does not match with this complex. The five saccharide skeleton protons of H_3L^1 appeared in the range of 3−3.6 ppm, similar to earlier reported ligands H_3L^n ($n = 2-4$),[27] whereas only three protons were observed in this region for a zinc-bound ligand and two were upfield shifted. Hence, a dual conformation of H_3L^1 in solution and the solid state may be expected, and a comparison of torsion angles (O5−C1−N1−C9 = −167.40(17)° for H_3L^1 and −11.1(2)°, 40.2(3)°, −3.6(6)° for H_3L^n ($n = 2-4$), respectively) supported the C1−N1 single-bond rotation in H_3L^1 during crystallization. The saccharide adopts a $^4C_1$ chair conformation with a β-anomeric form, which was also established by NMR studies, revealing the conservation of this form in both solution and the solid state.

Preparations of Trinuclear Cu(II) Complexes 1−7 with H_3L^1 ligand. Reaction of H_3L^1 with copper acetate in methanol yielded the green solid complex formulated as $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (**1**). Notably, complex **1** has fair solubility in less polar organic solvents such as $CHCl_3$ and THF. Vapor diffusion of methanol into a solution containing complex **1** in a $CHCl_3/CH_3CN$ mixed solvent resulted in formation of dark green crystals of $[Cu_3(L^1)_2(CH_3OH)_2]$ (**2**). Involvement of methanol into the coordination sphere

(27) (a) Sah, A. K.; Rao, C. P.; Saarenketo, P. K.; Rissanen, K. *Carbohydr. Res.* **2002**, *337*, 79. (b) Sah, A. K.; Rao, C. P.; Saarenketo, P. K.; Kolehmainen, E.; Rissanen, K. *Carbohydr. Res.* **2001**, *335*, 33.

Scheme 2

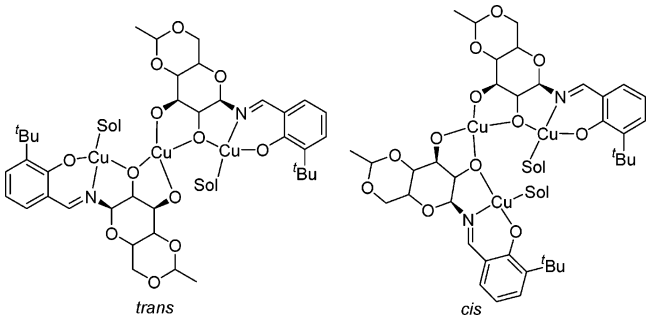


provoked us to explore the alcoholophilic character of complex **1** and further extension of these studies to develop the liquid-crystalline material using the long-chain aliphatic alcohols. Along this line, ethanol, *n*-propanol, *n*-butanol, and *n*-octanol have been successfully incorporated in the coordination sphere to result in crystals of $[Cu_3(L^1)_2(ROH)_2]$ (R = Et (**3**), ^{n}Pr (**4**), ^{n}Bu (**5**), ^{n}Oct (**6**)). All crystallizations were carried out using the solution of complex **1** in a $CHCl_3/CH_3CN$ mixed solvent and the respective alcohols as shown in Scheme 2. Complexes **2**−**6** are sparingly soluble in organic solvents such as chloroform. Complex **6** was subjected to variable-temperature microscopic studies to explore the liquid-crystalline properties. The complex was stable to 180 °C; however, it converted to an isotropic liquid and finally decomposed above 200 °C, revealing its inability to exhibit liquid-crystalline behavior.

All the IR spectra of complexes **1**−**6** were recorded in solid KBr matrix, exhibiting a medium broad ν_{O-H} peak in the range of 3433−3449 cm^{-1} and three sharp ν_{C-O} peaks at around 1145, 1111, and 1088 cm^{-1}, as observed in the IR spectrum of the ligand H_3L^1. The peak positions for $\nu_{C=N}$ were almost invariant in the case of the ligand as well as the complexes as it appeared at 1633 cm^{-1} for ligand and in the range of 1634−1636 cm^{-1} for complexes **1**−**6**. The identical nature of the IR spectra for the entire complex supported the presence of an identical core structure in **1**−**6** (the same was established by X-ray crystallography).

The UV−vis studies of the ligand H_3L^1 in $CHCl_3$ exhibited two bands at 264 and 330 nm, whereas three bands were observed for complex **1** in the same solvent at 280, 377, and 638 nm. The bands at 377 and 638 nm for complex **1** may be attributed to the ligand to metal charge-transfer and d−d transition, respectively. The low solubility of the other crystalline complexes (**2**−**6**) restricted their quantitative UV−

Chart 1



vis studies. To understand the alcoholophilic behavior of complex **1**, a chloroform solution of the complex was titrated with methanol and the change in the d−d transition band (638 nm) was monitored by UV−vis studies. Initial successive addition of methanol resulted in an increase of the absorbance value until it reaches the maxima followed by saturation. The increment of absorbance may be attributed to participation of methanol in the metal ion binding, and the maximum absorbance value reflects the saturation of the coordination sphere.

The ESI-TOF mass spectrum of H_3L^1 in methanol exhibited two sets of peaks at *m*/*z* 366.208 and 388.189 for (H_3L^1 + H^+) and (H_3L^1 + Na^+), respectively; however, the same method was unsuitable for determination of molecular ion peaks of complexes **1**−**6**. The FAB mass spectra with complexes **1** and **2** exhibited identical molecular ion peak maxima at around 918 and 980, attributable to $[Cu_3(L^1)_2 + 3H]^+$ and $[Cu_3(L^1)_2(CH_3OH)_2]^+$, respectively. The spectroscopic similarity between **1** and **2** and the crystal structure of **2** strongly suggested that complex **1** contains the *trans*-oriented, linear trinuclear Cu(II) structure as observed in **2** (Chart 1). However, considering the large difference of their solubility, the possibility of a *cis*-oriented trinuclear arrangement cannot be ruled out.

Diffusion of methanol vapor into the complex **1** solution in a $CHCl_3$/THF mixed solvent afforded crystals of $[Cu_3(L^1)_2(CH_3OH)_2(THF)_2]\cdot 2THF$ (**7**·2THF). The IR spectrum of complex **7** was almost identical with those of **2**−**6,** supporting conservation of the metal-binding core. In general, structurally characterized linear trinuclear copper complexes are limited,[28] and only one report is available on a saccharide-containing complex.[29] Other reports on saccharide-derived trinuclear complexes deal with noncollinear metal centers.[30] To the best of our knowledge, these are the first cases of trinuclear Cu(II) complexes containing glycosylamine-derived Schiff's base ligands; all other reports with similar Schiff's base lead to only the dinuclear complexes.[14]

Structural Description of Complexes 2−7. The binding mode of the ligand and geometries around the copper centers were identical in all complexes **2**−**6**. Due to the similarity in the structural feature, an ORTEP plot of representative complex **2** with numbering scheme is shown in Figure 2, and those of other complexes **3**−**6** are deposited as Supporting Information. A comparison of bond lengths and bond angles for these complexes are summarized in Table 4. The structure of complex **2** consists of linearly ordered three Cu(II) ions bridged by two L^1 ligands (Cu1···Cu2 = 3.683(1) Å, Cu2···Cu3 = 3.668(1) Å, Cu1−Cu2−Cu3 = 172.41(3)°).

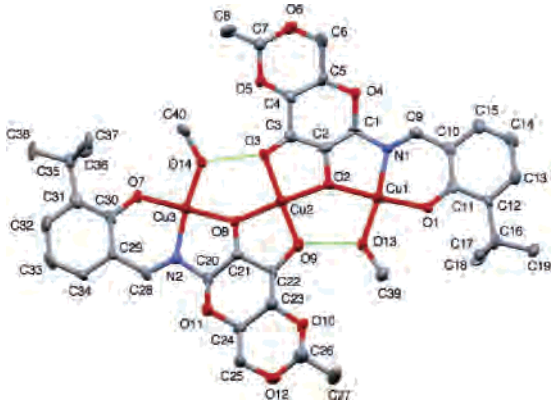


Figure 2. ORTEP plot of complex **2**, $[Cu_3(L^1)_2(CH_3OH)_2]$. Thin green line indicates the intramolecular hydrogen-bonding interactions.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**, **3**, **4**·$CHCl_3$, **5**, and **6**[a]

connecting atoms	**2**	**3**	**4**·$CHCl_3$	**5**	**6**
Cu1−O1	1.900(3)	1.873(9)	1.884(9)	1.867(9)	1.89(1)
Cu1−O2	1.953(3)	1.942(9)	1.942(9)	1.949(9)	2.00(1)
Cu1−O13	1.932(4)	1.95(1)	1.94(1)	1.944(8)	1.95(1)
Cu1−N1	1.941(4)	1.92(2)	1.91(1)	1.937(9)	1.96(2)
Cu2−O2	1.941(3)	1.96(1)	1.93(1)	1.913(9)	1.90(1)
Cu2−O3	1.913(3)	1.91(1)	1.916(9)	1.922(7)	1.90(1)
Cu2−O8	1.934(3)	1.94(1)	1.93(1)	1.958(8)	1.91(1)
Cu2−O9	1.911(3)	1.92(1)	1.907(8)	1.912(8)	1.93(1)
Cu3−O7	1.887(3)	1.87(1)	1.888(9)	1.878(9)	1.86(1)
Cu3−O8	1.941(3)	1.93(1)	1.931(9)	1.925(9)	1.97(1)
Cu3−O14	1.941(3)	1.93(1)	1.94(1)	1.940(8)	1.97(1)
Cu3−N2	1.940(4)	1.95(1)	1.95(1)	1.968(9)	1.97(2)
O3−O14	2.450(5)	2.44(1)	2.46(2)	2.47(1)	2.45(2)
O9−O13	2.488(5)	2.48(1)	2.46(1)	2.45(1)	2.52(2)
O1−O13	2.826(5)	2.79(2)	2.80(2)	2.78(1)	2.81(2)
O7−O14	2.823(5)	2.78(2)	2.81(2)	2.78(1)	2.81(2)
Cu1−Cu2	3.683(1)	3.684(3)	3.667(3)	3.647(3)	3.695(4)
Cu2−Cu3	3.668(1)	3.658(3)	3.650(3)	3.675(3)	3.662(4)
O2−Cu1−O1	176.0(1)	175.9(4)	177.4(4)	177.3(3)	174.2(3)
O13−Cu1−O1	95.0(1)	94.0(4)	94.1(4)	93.8(3)	94.1(5)
N1−Cu1−O1	92.1(2)	93.2(5)	93.9(4)	93.1(4)	92.8(5)
O13−Cu1−O2	87.0(1)	88.3(4)	87.1(4)	87.8(3)	87.7(5)
N1−Cu1−O2	85.7(2)	84.8(5)	85.2(4)	85.3(4)	86.0(5)
N1−Cu1−O13	171.6(2)	170.5(4)	168.8(5)	173.1(4)	171.4(4)
O3−Cu2−O2	88.8(1)	88.5(4)	88.5(4)	88.8(3)	88.8(5)
O8−Cu2−O2	165.9(1)	157.7(4)	159.3(4)	163.0(2)	157.8(3)
O9−Cu2−O2	93.8(1)	92.6(4)	92.4(4)	93.8(3)	92.9(5)
O8−Cu2−O3	92.0(1)	93.3(4)	94.3(4)	92.2(3)	94.0(4)
O9−Cu2−O3	166.5(1)	169.7(4)	169.9(4)	167.7(2)	169.6(3)
O9−Cu2−O8	88.7(1)	89.6(4)	88.4(4)	88.8(3)	88.3(5)
O8−Cu3−O7	174.5(1)	177.2(4)	177.1(4)	177.7(3)	177.8(5)
O14−Cu3−O7	95.0(1)	93.7(5)	94.1(4)	93.4(3)	94.7(5)
N2−Cu3−O7	92.6(2)	93.8(5)	93.2(4)	93.2(4)	92.2(5)
O14−Cu3−O8	87.4(1)	86.7(4)	87.3(4)	88.3(3)	87.4(5)
N2−Cu3−O8	85.7(2)	85.8(5)	85.3(4)	85.3(3)	85.7(5)
N2−Cu3−O14	168.6(2)	172.3(4)	172.6(4)	171.7(3)	173.0(5)
Cu1−O2−Cu2	142.0(2)	141.2(7)	142.5(5)	141.5(4)	143.2(6)
Cu2−O8−Cu3	142.4(2)	142.4(6)	142.0(5)	142.4(4)	141.0(6)
Cu1−Cu2−Cu3	172.41(3)	166.0(1)	166.3(1)	171.03(6)	165.94(8)

[a] Estimated standard deviations are given in parentheses.

(28) van Albada, G. A.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Eur. J. Inorg. Chem.* **1998**, 547.
(29) Klüfers, P.; Kunte, T. *Eur. J. Inorg. Chem.* **2002**, 1285.
(30) (a) Wegner, R.; Gottschaldt, M.; Görls, H.; Jäger, E.-G.; Klemm, D. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 595. (b) Wegner, R.; Gottschaldt, M.; Görls, H.; Jäger, E.-G.; Klemm, D. *Chem. Eur. J.* **2001**, *7*, 2143.

All Cu(II) ions adopt a square-planar geometry, and the three coordination planes are coplanar with dihedral angles of 2.0(1)−3.9(1)°. The three copper ions are included well in each square plane with deviations less than 0.01 Å. Notably, linear trinuclear copper(II) complexes with all square-planar geometry are extremely rare, most of the earlier reports deal with trinuclear structures with mixed geometry about the copper centers,[28,29,31−34] and only one report is available with a solely octahedral geometry.[35] As for carbohydrate-bridged trinuclear Cu(II) complexes, the only previously characterized examples are $[Cu_3(\beta\text{-D-lyxopyranose}^{3-})_2(L)_2(H_2O)_2]$ (L = $2NH_3$ (**9**), en (**10**)),[29] in which two deprotonated lyxopyranose trianions bridge the square-planar central copper(II) and the square-pyramidal terminal copper(II) ions. The trianionic ligand L^1 results from deprotonation of the phenol and the saccharide C-2 and C-3 alkoxy groups of H_3L^1. The saccharide C-2 alkoxo group bridges the terminal and central copper centers, while the C-3 alkoxo group is bound only to the central copper and the phenolate oxygen, and the imino nitrogen atoms attach to the terminal one. The central square plane around the Cu2 atom is comprised of two chelations from the C-2 and C-3 alkoxo groups of the sugar units (O2−Cu2−O3 = 88.8(1)°, O8−Cu2−O9 = 88.7(1)°); the two five-membered $[CuO_2C_2]$ chelate rings are appreciably twisted with a dihedral angle of the mean planes of 14.4(1)°. The terminal Cu(II) ions are ligated by the ONO donors of L^1 ligand, leading to strain-free coordination with a combination of the $[CuONC_3]$ six-membered and the $[CuONC_2]$ five-membered chelate rings (O1−Cu1−N1 = 92.1(2)°, O2−Cu1−N1 = 85.7(2)°, O1−Cu1−O2 = 176.0(1)°; O7−Cu3−N2 = 92.6(2)°, O8−Cu3−N2 = 85.7(2)°, O7−Cu3−O8 = 174.5(1)°). The square-planar coordination geometry around the terminal copper atoms is completed by coordination of methanol to the fourth site trans to the imino nitrogen atom (N1−Cu1−O13 = 171.6(2)°, N2−Cu3−O14 = 168.6(2)°). The alcoholic protons of methanol ligands were determined by X-ray crystallographic analysis to be involved in a characteristic intramolecular hydrogen-bonding interaction with the C-3 sugar alkoxo units. The considerably short O···H−O inter-oxygen distances, O3···O14 = 2.450(5) Å and O9···O13 = 2.488(5) Å, suggested that the strong hydrogen bonds establish a robust planar structure with trinuclear copper centers. The structure of complex **2** can be viewed as two $\{Cu(L^1)\}$ anionic fragments capture a copper(II) ion through the sugar C-2 and C-3 alkoxo groups, and methanol coordination to the terminal Cu(II) centers locks it up through a hydrogen-bonding interaction. All these features resulted in a *pseudo*-C_2-symmetrical structure with planar trinuclear Cu(II) centers.

As for the bridging behavior of carbohydrates, it had been well elucidated that mannose and lyxose, possessing the 2,3-*cis*-configuration of alkoxy groups, have strong ability as bridging ligands with their β-furanose form,[36−38] and recently, they were also shown to bridge two metal ions with their β-pyranose form using a cis,cis sequence of the three donor atoms on the C-1, C-2, and C-3 positions; characterized examples are $[\{Mn(aldose_3\text{-}tren^{2-})\}_2Mn(H_2O)]^{3+}$ (aldose$_3$-tren = tris(*N*-aldopyranosyl-2-aminoethyl)-amine; aldose = D-mannose (**11**), L-rhamnose (**12**));[39] and $[Cu_3(\beta\text{-D-lyxopyranose}^{3-})_2(L)_2(H_2O)_2]$ (L = $2NH_3$ (**9**), en (**10**)).[29] In contrast, metal complexes containing D-glucopyranose bridging with a trans,trans arrangement of the three sequential donor atoms on the C-1, C-2, and C-3 positions have extremely been scarce despite D-glucose being the most abundant carbohydrate that can be used as a biogenic raw material. The only available example is reported in the structures of $[M_2Zn\{(D\text{-glucose})_2\text{-tacn}\}_2(XDK)]Cl_2$ (M = Zn (**13**), Cu (**14**); (D-glucose)$_2$-tacn = *N*,*N*′-bis(D-glucopyranosyl)-1,4,7-triazacyclononane, H_2XDK = *m*-xylylenediamine bis(Kemp's triacid imide)).[16] In complex **2** the D-glucopyranosyl moieties have a β-anomeric form with a stable $^4C_1$ chair conformation and connect two copper(II) ions with the μ-η^1:η^1-alkoxo group at the C-2 position while the C-1 *N*-glycosidic imino and the C-3 alkoxo groups are bound to the terminal and central metal ions, respectively. Hence, the glucopyranosyl unit utilizes three sequential donor atoms of the C-1, C-2, and C-3 positions that are arranged in a trans,trans configuration. The C-2 alkoxo bridge is symmetric with remarkably large Cu−O−Cu angles (Cu1−O2−Cu2 = 142.0(2)°, Cu2−O8−Cu3 = 142.4(2)°) due presumably to the rigid hydrogen bond between the methanol and the C-3 alkoxo group. The sums of bond angles around the C-2 alkoxo oxygen, 356.2° (O2) and 357.2° (O8), indicate their sp^2 character.

The planar trinuclear copper(II) structures of complexes **3**−**6** are essentially identical to that of **2** besides the orientation of the alkyl chains (Figures S1−S4). In complex **3** the two ethyl groups of the metal-bound alcohols are trans oriented with respect to the molecular plane; in other words, they are related by *pseudo*-centro symmetry with an inversion center at the central copper position. A mismatch between the C_2 and centro symmetry, for the respective arrangements of two sugar-derived ligands and two metal-bound ethanol molecules, resulted in a slight and asymmetric deformation

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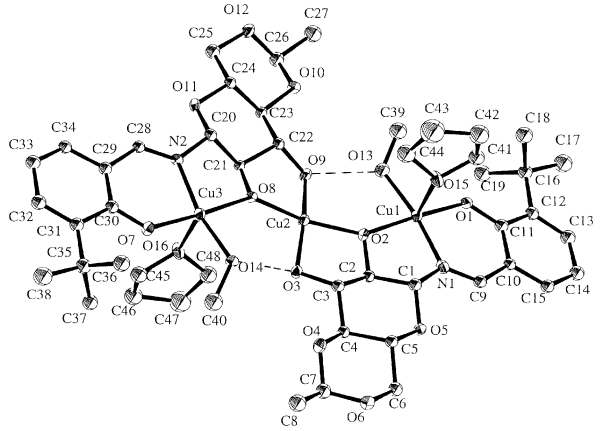

Figure 3. ORTEP plot of complex **7**, $[Cu_3(L^1)_2(CH_3OH)_2(THF)_2]$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **7**·2THF[a]

Cu1−O1	1.900(7)	Cu1−O2	1.956(7)
Cu1−O13	1.979(9)	Cu1−O15	2.394(7)
Cu1−N1	1.96(1)	Cu2−O2	1.923(8)
Cu2−O3	1.907(6)	Cu2−O8	1.932(6)
Cu2−O9	1.924(7)	Cu3−O7	1.888(7)
Cu3−O8	1.944(6)	Cu3−O14	1.944(8)
Cu3−O16	2.466(7)	Cu3−N2	1.959(9)
O9−O13	2.470(9)	O1−O13	2.82(1)
O3−O14	2.481(8)	O7−O14	2.81(1)
Cu1−Cu2	3.673(3)	Cu2−Cu3	3.648(3)
O2−Cu1−O1	173.5(3)	O13−Cu1−O1	93.0(3)
O15−Cu1−O1	97.2(3)	N1−Cu1−O1	92.7(3)
O13−Cu1−O2	87.9(3)	O15−Cu1−O2	89.2(3)
Cu1−O2−Cu2	142.4(4)	N1−Cu1−O2	85.6(3)
O15−Cu1−O13	95.1(3)	N1−Cu1−O13	171.1(4)
N1−Cu1−O15	91.0(3)	O3−Cu2−O2	88.5(3)
O8−Cu2−O2	163.0(3)	O9−Cu2−O2	93.6(3)
O8−Cu2−O3	92.9(3)	O9−Cu2−O3	167.4(3)
O9−Cu2−O8	88.7(3)	Cu2−O8−Cu3	140.5(3)
O8−Cu3−O7	177.1(3)	O14−Cu3−O7	94.3(3)
N2−Cu3−O7	92.3(3)	O16−Cu3−O7	94.3(3)
O14−Cu3−O8	87.8(3)	N2−Cu3−O16	98.2(3)
O16−Cu3−O8	87.5(3)	N2−Cu3−O8	85.2(3)
O16−Cu3−O14	93.4(3)	N2−Cu3−O14	166.1(4)
Cu1−Cu2−Cu3	170.28(7)		

[a] Estimated standard deviations are given in parentheses.

of the linear tricopper(II) core (Cu1···Cu2 = 3.684(3) Å, Cu2···Cu3 = 3.658(3) Å, Cu1−Cu2−Cu3 = 166.0(1)°). With longer primary alcohols in **4**−**6** relatively large thermal motions of alkyl chains indicated that they were likely to be flexible and arranged in asymmetrical fashions.

The ORTEP plot of complex **7** is presented in Figure 3, and selected bond lengths and angles are listed in Table 5. The coordinating atoms constituting the basal planes are similar to that in complex **2**; however, two THF molecules bind the terminal coppers to result in the square-pyramidal geometry. The geometry around the central one is square planar. The orientation of both metal-bound THF molecules are trans with respect to the molecular plane with Cu−O distances of 2.394(7) and 2.466(7) Å. The longer distances along the axial positions are well within the range for the copper complex with the similar geometry.[31a−c] The structure of **7** implied that planar complex **2** is coordinatively unsaturated and the axial sites of the terminal copper ions are able to accommodate further ligations.

Magnetic Properties. Structurally and magnetically investigated linear trinuclear Cu(II) complexes are limited,[32]

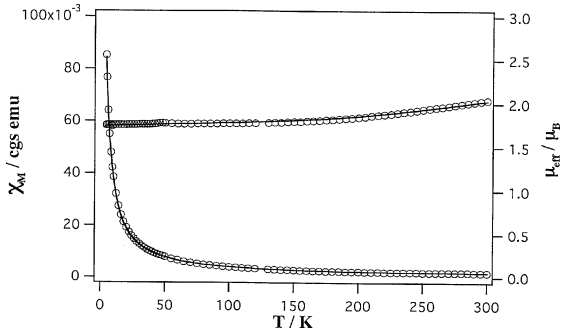

Figure 4. Temperature dependence of χ_M and magnetic moment for complex **2**; solid line is the theoretical calculated best-fitting curve.

and hence, we tried to explore the magnetochemistry of only complex **2** assuming that others will exhibit the same behavior due to identical metal-binding sites. Temperature-dependent magnetic susceptibility measurements were carried out in the range of 4.5−300 K (Figure 4). At room temperature (300 K) the magnetic moment was 2.04 μ_B/Cu_3, and it started decreasing gradually with temperature to 175 K (1.81 μ_B). Below 175 K the decrement of moment value was very low, and it decreased to 1.75 μ_B at 4.5 K, which agrees with the ground state of only one unpaired electron per three Cu(II) centers. The χ_M values were fitted with the following equation

$$\chi_M = (N\mu_B{}^2g^2/4kT)[10\exp(-J/kT) + \exp(-2J/kT) + 1]/[2\exp(-J/kT) + \exp(-2J/kT) + 1] + 3N\alpha$$

giving the best fitted values of g, J, and $N\alpha$ being 2.01, −238 cm^{-1}, and 60 × 10^{-6} emu mol^{-1}, respectively. During calculation equal interactions between the vicinal copper centers were considered, and the coupling between the terminal copper was neglected. The determined J value (−238 cm^{-1}) revealed strong antiferromagnetic interaction between the central and terminal Cu(II) ions of the trinuclear core.

Proton-Transfer Reactions. Deprotonation of C-2 and C-3 alkoxy groups of the saccharide moiety during the copper ion binding tempted us to explore the proton-transfer reaction on it to generate the mononuclear chiral building block of {Cu(HL^1)} as monosaccharides are weakly acidic with pK_a values above 12.[18] Different weak hydrogen donors such as acetic acid (pK_a = 4.76), H_2O_2 (pK_a = 11.6), and protected saccharides (pK_a > 12) have been used to achieve the goal. In the case of acetic acid, a ligand-exchange reaction took place and crystals of copper acetate were isolated. The existence of free ligand H_3L^1 in the mother liquor was supported by ESI-MS studies. H_2O_2 acted as an oxidizing agent rather than a proton source, and consequently, copper oxalate was isolated. Crystallization of complex in the presence of bpy as a co-ligand resulted in X-ray-quality crystals of mono and polymeric copper oxalate formulated as [Cu(bpy)(Ox)]·2.5H_2O and [Cu(bpy)(Ox)]·2H_2O, respectively. Similar structures are already reported,[40] and hence,

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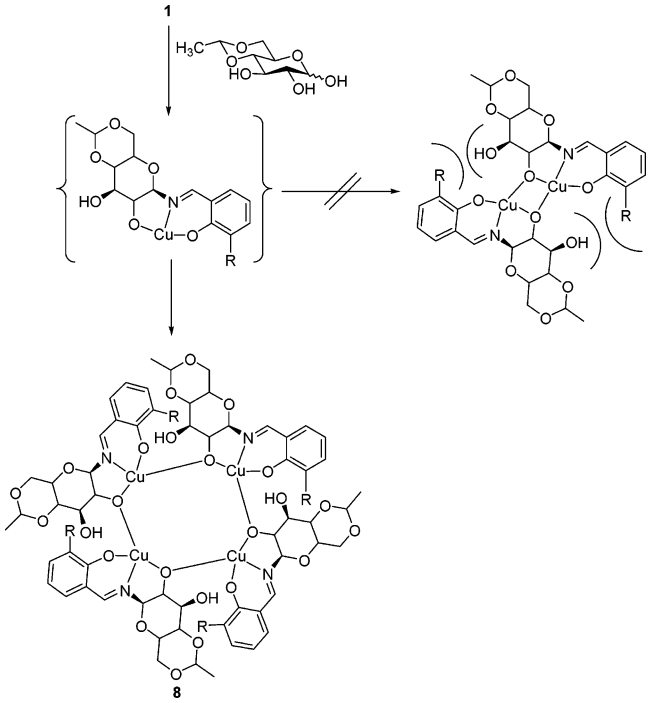
Scheme 3



their details have been excluded here. Sugar oxidation by peroxide has been known for quite some time, and most of the reports deal with formation of formic acid;[41] however, we isolated the oxalate complexes. Three different protected glucose derivatives, 4,6-*O*-ethylidene-D-glucopyranose, methyl-4,6-*O*-benzylidene-D-glucopyranoside, and 1,2;5,6-di-*O*-isopropylidene-D-glucofuranoside, have been used as proton sources, and in the former case a tetranuclear complex $[Cu_4(HL^1)_4]$ (**8**) (Scheme 3) has been isolated with a metal-to-ligand ratio of 1:1, revealing a successful proton-transfer reaction accompanied by trapping of the central copper ions with the sugar derivative. The structure of complex **8** is comprised of four neutral $\{Cu(HL^1)\}$ fragments which might have been generated by protonation of the sugar C-3 alkoxo groups in complex **1** (Figure 5; Table 6). Each copper(II) ion is ligated by a HL^1 ligand through the phenoxo and the C-2 alkoxo oxygen and imino nitrogen atoms as observed in **2**−**7**. The four copper fragments are further held together by the C-2 alkoxo bridge in a head-to-tail arrangement, resulting in the eight-membered Cu_4O_4 metallocycle folded in a boat conformation. The similar tetracopper structure was reported with a sugar-derived Schiff's base ligand from salicylaldehyde and 1-amino-1-deoxy-D-sorbitol.[13] The average interatomic distances between the two alkoxo-bridged copper atoms is 3.499 Å (Cu1···Cu2 = 3.497(2) Å, Cu1···Cu3 = 3.536(2) Å, Cu2···Cu4 = 3.484(2) Å, Cu3···Cu4 = 3.478(2) Å), which is shorter by ca. 0.18 Å than that of **2**. The diagonal Cu···Cu distances are 3.869(2) (Cu1···Cu4) and 4.056(2) Å (Cu2···Cu3). The Cu−O−Cu angles are appreciably smaller than those found in the trinuclear complexes **2**−**7** (Cu1−O2−Cu3 = 129.7(3)°, Cu1−O8−Cu2 = 128.3(3)°, Cu3−O14−Cu4 = 127.7(3)°, Cu2−O20−Cu4 = 125.5(3)°). This feature may be attributable to weaker interaction of the protonated C-3 alkoxy groups with the neighboring Cu center at its axial position. Considering the axial weak interaction (Cu1−O9 = 2.619(7) Å, Cu2−O21 = 2.616(7) Å, Cu3−O3 = 2.462(7) Å, and Cu4−O15 = 2.554(6) Å), the four copper ions have a distorted square-pyramidal geometry with the $[NO_3]$ basal planes tilted toward each other, dihedral angles being 72.5(2)−92.5(2)° and forming a small-size chiral cavity (Figure 6). The crystal structure of **8** demonstrated that reaction of **1** with 4,6-*O*-ethylidene-D-glucopyranose generated the $\{Cu(HL^1)\}$ frag-

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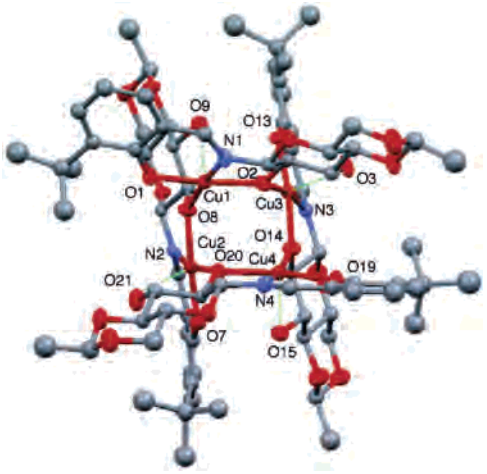

Figure 5. ORTEP plot of complex **8**, $[Cu_4(HL^1)_4]$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **8**·$2CH_3CN$·$2CHCl_3$·H_2O[a]

Cu1−O1	1.920(6)	Cu1−O2	1.977(6)
Cu1−O8	1.935(7)	Cu1−N1	1.943(8)
Cu1−O9	2.619(7)	Cu2−O21	2.616(7)
Cu2−O7	1.938(6)	Cu2−O8	1.951(6)
Cu2−O20	1.929(6)	Cu2−N2	1.945(8)
Cu3−O2	1.930(6)	Cu3−O13	1.939(6)
Cu3−O14	1.940(6)	Cu3−N3	1.952(7)
Cu4−O14	1.934(6)	Cu4−O19	1.918(5)
Cu4−O20	1.991(6)	Cu4−N4	1.925(8)
Cu3−O3	2.462(7)	Cu4−O15	2.554(6)
Cu1−Cu2	3.497(2)	Cu1−Cu3	3.536(2)
Cu1−Cu4	3.869(2)	Cu2−Cu3	4.056(2)
Cu2−Cu4	3.484(2)	Cu3−Cu4	3.478(2)
O1−Cu1−O2	173.2(2)	O1−Cu1−O8	92.9(2)
O1−Cu1−N1	90.1(2)	O2−Cu1−O8	93.9(2)
O2−Cu1−N1	83.2(2)	O8−Cu1−N1	174.9(3)
O9−Cu1−O2	84.9(2)	O9−Cu1−N1	106.3(2)
O9−Cu1−O1	96.2(2)	O9−Cu1−O8	77.5(2)
O7−Cu2−O8	175.0(2)	O7−Cu2−O20	97.0(2)
O7−Cu2−N2	91.8(3)	O8−Cu2−O20	85.5(2)
O8−Cu2−N2	84.8(3)	O20−Cu2−N2	165.1(2)
O21−Cu2−O7	80.9(2)	O21−Cu2−O20	75.8(2)
O21−Cu2−O8	104.0(2)	O21−Cu2−N2	117.6(2)
O2−Cu3−O13	93.4(2)	O2−Cu3−O14	86.9(2)
O2−Cu3−N3	167.9(3)	O13−Cu3−O14	171.7(2)
O13−Cu3−N3	93.3(3)	O14−Cu3−N3	85.0(3)
O3−Cu3−O13	88.4(2)	O3−Cu3−N3	111.4(2)
O3−Cu3−O14	99.9(2)	O3−Cu3−O2	78.7(2)
O14−Cu4−O19	91.2(2)	O14−Cu4−O20	95.0(2)
O14−Cu4−N4	166.9(3)	O19−Cu4−O20	172.9(2)
O19−Cu4−N4	91.3(3)	O20−Cu4−N4	83.5(2)
O15−Cu4−O14	76.8(2)	O15−Cu4−N4	116.0(2)
O15−Cu4−O20	86.5(2)	O15−Cu4−O19	91.5(2)
Cu1−O2−Cu3	129.7(3)	Cu2−O20−Cu4	125.5(3)
Cu1−O8−Cu2	128.3(3)	Cu3−O14−Cu4	127.7(3)

[a] Estimated standard deviations are given in parentheses.

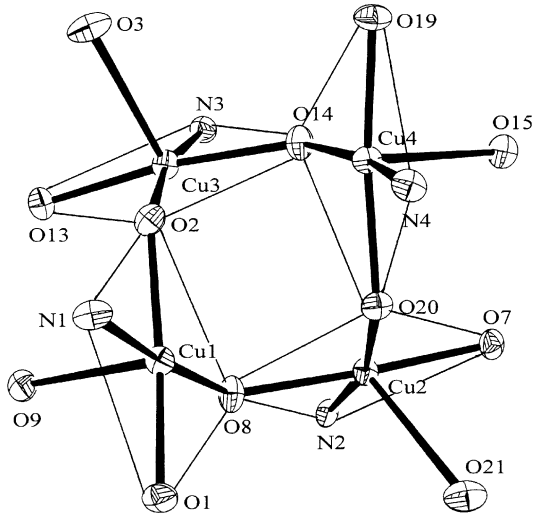

Figure 6. ORTEP plot of coordination core about copper centers in complex **8**.

ment, which may further self-assemble into the tetranuclear complex **8** as a thermodynamically stable species (Scheme 3). The steric bulkiness of the *tert*-butyl group in L^1 may prevent formation of a dimeric complex with a Cu_2O_2 rhombic structure (Scheme 3).

Conclusion

A new D-glucose-derived Schiff's base ligand *N*-(3-*tert*-butyl-2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine (H_3L^1) has been synthesized and structurally characterized. Reaction of H_3L^1 with $Cu(OAc)_2 \cdot H_2O$ afforded coordinatively labile trinuclear Cu(II) complex $[Cu_3(L^1)_2(CH_3OH)(H_2O)]$ (**1**), which was further transformed into a series of alcohol-bound complexes, $[Cu_3(L^1)_2(ROH)_2]$ (R = Me, Et, ^{n}Pr, ^{n}Bu, ^{n}Oct). The structures of all complexes have been revealed by X-ray crystallography to involve two $\{Cu(L^1)\}$ anionic fragments trapping a Cu(II) ion in the central position, resulting in a linear trinuclear Cu(II) structure with planar geometry around the metal ions. The trinuclear structures were stabilized by strong hydrogen-bonding interaction between the metal-bound alcohols and the C-3 akloxo groups of the sugar units. The distance between these two oxygen atoms is so short that prediction of anionic species (C-3-O^- or R−O^-) could not be concluded. Recently we introduced ethylamine at the fourth equatorial positions about the terminal copper centers,[42] which might support the possibility of C-3-O^- and not R−O^- in the present case. The THF adduct of complex **1** (complex **7**) suggested the terminal Cu(II) ion could be responsible for further ligation at each apical position. In the reaction of **1** with 4,6-*O*-ethylidene-D-glucopyranose, one proton has been successfully transferred at the saccharide C-3 alkoxo group of L^1, resulting in formation of tetranuclear complex $[Cu_4(HL^1)_4]$ (**8**) as a thermodynamically stable self-assembled compound from the $\{Cu(HL^1)\}$ units. The present results could provide useful information to create an efficient method for constructing chiral multinuclear complexes by utilizing the mononuclear $\{Cu(HL^1)\}$ chiral building blocks.

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Supporting Information Available: X-ray crystallographic file in CIF format for the complexes **2**−**8** and H_3L^1; ORTEP plots of complexes **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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