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Synthesis, Structure and Magnetic Properties of a Tetranuclear Copper(II) Complex on the Basis of a 2-Substituted Glucopyranoside Schiff Base Ligand

Anja Burkhardt,[a] Axel Buchholz,[a] Helmar Görls,[a] and Winfried Plass*[a]

Dedicated to Professor Ernst-Gottfried Jäger on the occasion of his 70th birthday

Keywords: Carbohydrates / Schiff base ligands / Copper(II) complexes / Magnetic properties

Condensation of a derivatized 2-aminoglucose fragment with salicylaldehyde affords the new sugar-based Schiff base ligand benzyl 4,6-*O*-benzylidene-2-deoxy-2-salicylideneamino-α-D-glucopyranoside (H_2L). The reaction of the dibasic ligand H_2L with $[Cu(CH_3COO)_2]\cdot H_2O$ leads to the formation of the tetranuclear copper(II) complex $[\{Cu(L)\}_4]$ (**3**) by a self-assembly process. The X-ray structural analysis of complex **3** which crystallizes together with two molecules of chloroform and one molecule of ethanol in the space group $P2_12_12_1$ revealed for all copper atoms a NO_3 coordination environment with a square-planar geometry. The tetranuclear molecule **3** consists of four chiral building blocks {Cu(L)} with the rare 2,3-coordination of the *trans*-configured donor atoms of the sugar backbone. The observed coordination mode of the building blocks exemplifies how chitosan-derived polysaccharide ligands can act as a chiral support for transition-metal complexes. The C-3 alcoholate oxygen atoms of the carbohydrate unit is bridging adjacent {Cu(L)} moieties resulting in an eight-membered Cu_4O_4 ring with a boat-like conformation. Temperature-dependent magnetic measurements of **3** indicate moderate antiferromagnetic interactions between the four copper(II) ions with a coupling constant of $J = -130\ cm^{-1}$.

Introduction

Carbohydrates are the most abundant biogenic class of compounds involved in a wide range of functions in living organisms. In case of cellulose, sugars act as scaffolding material in plants. Monosaccharide fragments are participating in glycolipids and glycoproteins and play an important role in various biological processes e.g. as building blocks for nucleotides and of the ADP/ATP energy-storage system.[1] Many sugar-metabolizing enzymes have been revealed to function with alkaline earth and transition metal ions in the active sites.[2–10]

Although the importance of sugar–metal interaction is known for many years, the field of sugar–metal complexes is still largely unexplored. Only for the past two decades, sugars received a growing interest as ligand components in bioorganic chemistry due to their enantiomerically pure natural abundance and their polyfunctionality. The vicinal functional groups feature many donor atoms forming stable chelate complexes.[11–15] Furthermore, carbohydrates combine interesting properties like stable chiral scaffold and supramolecular arrangement. Well-known modification strategies for introducing additional donor groups into the sugar backbone are *N*-glycosylation with polyamines[16–22] and nucleophilic substitution of bromoethyl-*O*-glycosides.[23–28] A further method is the condensation of amino saccharides and carbonyl components resulting in tridentate Schiff base ligands.[29–31]

The corresponding transition-metal complexes show a large tendency for coordinative saturation via coligation or self-assembly to polynuclear compounds by oxo-bridging. Many naturally available copper-containing enzymes like catechol oxidase[32] or ascorbate oxidase[33] exhibit a polynuclear active site. Thus, polynuclear sugar-modified copper(II) complexes are interesting concerning their biorelevance as structural and/or functional models for various metalloenzymes. However, the rare examples described in literature are linear trinuclear and cyclic di- or tetranuclear copper(II) complexes which are based on either C-1 or C-6 amino functionalized carbohydrate fragments.[34–38]

Amino precursors have to be synthesized by *N*-glycosylation or a laborious six-step synthesis with participation of various protecting groups. 2-Aminoglucose is the monomer unit of chitosan which could be obtained from acidic deacetylation of chitin (see Scheme 1). The β-(1-4)-linked polysaccharide is the structural element in the exoskeleton of crustaceans. The vision of creating polymeric catalysts provoked us to more detailed studies of the coordination

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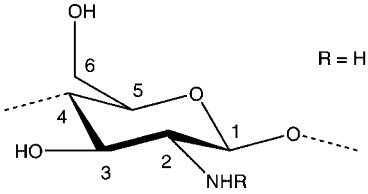
[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena,
Carl-Zeiss-Promenade 10, 07745 Jena, Germany
Fax: +49-3641-948132
E-mail: Sekr.Plass@uni-jena.de

chemistry of Schiff base ligands derived from the monomeric chitosan fragment 2-aminoglucose.



Scheme 1. 2-Aminoglucose backbone as found in chitosan.

Results and Discussion

Synthesis and Characterization

Starting from benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**)[39,40] the Schiff base ligand H_2L (**2**) was prepared by condensation with salicylaldehyde in methanol as depicted in Scheme 2. The synthesized Schiff base ligand **2** was characterized by IR, NMR and ESI-MS studies as well as elemental analysis. The IR band at 1637 cm^{-1} is attributed to the valence vibration of the imino group. In the NMR spectra the corresponding resonances of the imino group are present at $\delta = 167.8$ ppm (^{13}C NMR) and at $\delta = 9.91$ ppm (^{1}H NMR). The proton on C-1 of the D-glucose moiety leads to a doublet in the ^{1}H NMR spectrum with $^{3}J_{12} = 3.7$ Hz indicative for the exclusive presence of the α-anomer of the saccharide unit associated with the *cis* position of the protons attached to C-1 and C-2. Due to its hydrophobic phenyl groups the sugar ligand **2** is soluble in less polar solvents.

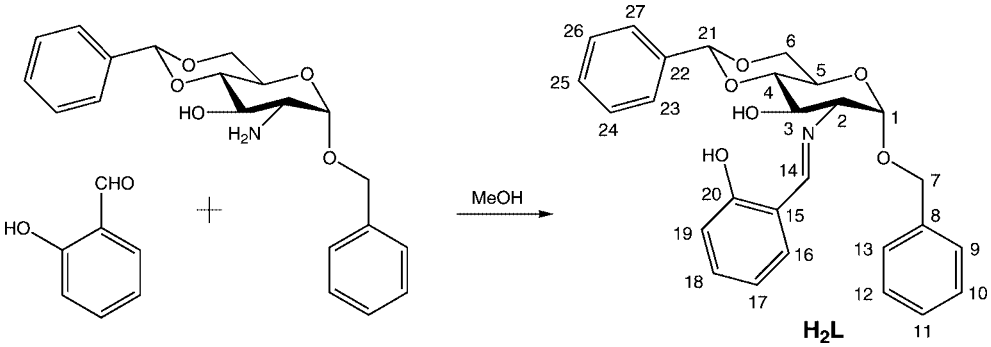
For complexation an aqueous solution of $[Cu(CH_3COO)_2]\cdot H_2O$ was added to a chloroform solution of **2** in a 1:1 molar ratio at room temperature. Ethanol was added under vigorous stirring for homogenization of the generated two-phase system. Slow evaporation of the dark green solution affords crystals of $[\{Cu(L)\}_4]\cdot 2CHCl_3\cdot EtOH$ (**3**·$2CHCl_3\cdot EtOH$) as green prisms after 4 d. Due to its volatility, chloroform is removed first from the reaction mixture leading to an increasing polarity of the remaining solution. Owing to the poor solubility of **3** in polar solvents the formed copper(II) complex can be isolated in very high yields.

In accordance with the molecular ion peaks at 2092 ($[\{Cu(L)\}_4+H]^+$) and 2113 ($[\{Cu(L)\}_4+Na]^+$) obtained from ESI-MS measurements, complex **3** also appears to exist as undissociated tetranuclear species in solution. UV/Vis studies of the green copper(II) complex **3** performed in chloroform solution exhibit two charge–transfer bands at 277 and 370 nm and a third band at 628 nm attributed to a d–d transition. No weight loss can be found up to the decomposition temperature by TGA measurement indicating that all solvent molecules are removed during the air-drying process consistent with the formula $[\{Cu(L)\}_4]$ for complex **3**. This is further corroborated by the results obtained from elemental analysis.

To the best of our knowledge complex **3** is the first tetranuclear transition-metal complex derived from the monomeric chitosan unit 2-aminoglucose. Copper(II) structures on the basis of C-1-salicylidene-functionalized Schiff base ligands of 1-amino-D-sorbitol[35] and 1-amino-4,6-*O*-ethylidene-β-D-glucopyranose[38] have recently been reported. Furthermore, **3** is the first transition-metal complex characterized by X-ray crystallography featuring a *trans*-configured coordination of donor atoms at C-2 and C-3 of the sugar moiety. From literature 2-aminoglucose-derived *cis*-dioxomolybdenum(VI) complexes are known with the metal center coordinated by the imino nitrogen atom and the alcoholate oxygen atom at the anomeric carbon atom C-1.[41]

Structure Description

Figure 1 shows the molecular structure of the complex $[\{Cu(L)\}_4]$ (**3**) which was found in crystals of **3**·$2CHCl_3\cdot EtOH$. The observed space group $P2_12_12_1$ is consistent with the appearance of only one diastereomer formed by self-assembly of the four neutral mononuclear chiral building blocks {Cu(L)}. Selected distances and angles are given in Table 1. Each copper(II) center is coordinated in a square-planar environment by a phenolate oxygen atom of the salicylidene residue, a nitrogen atom of the C-2 imino group and a C-3 alcoholate oxygen atom of the sugar backbone. The fourth position is occupied by an additional C-3 alcoholate group from an adjacent sugar unit.



Scheme 2. Reaction scheme for the synthesis of ligand H_2L (**2**).

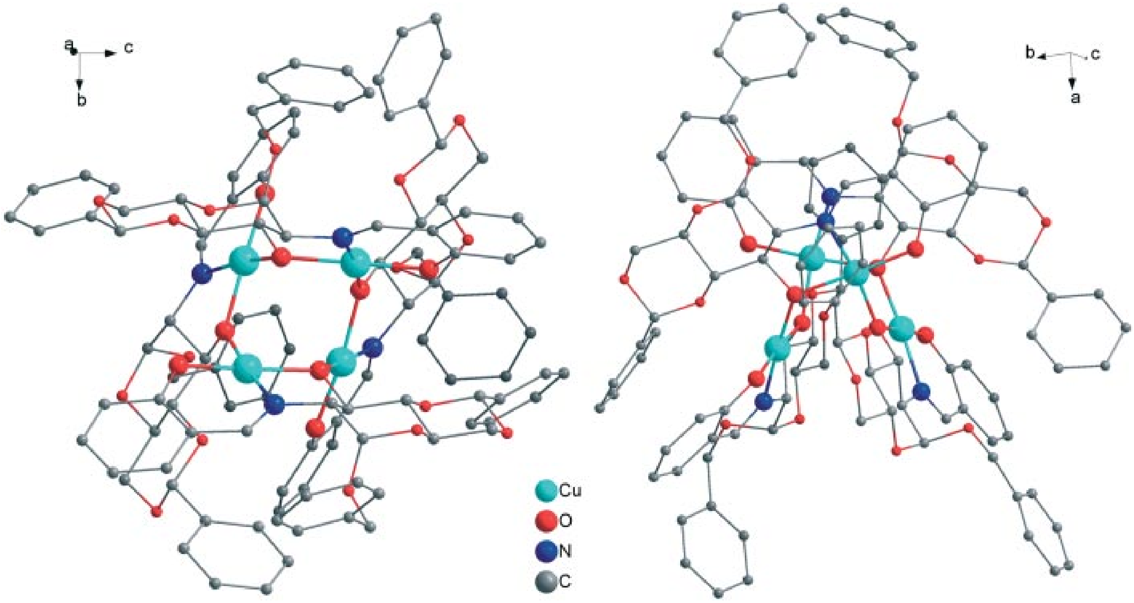


Figure 1. Molecular structure of [{Cu(L)}$_4$] (**3**) in crystals of **3**·2CHCl$_3$·EtOH. Solvent molecules and hydrogen atoms are omitted for clarity. (left) View approximately along the pseudo S_4 axis of the central Cu$_4$ tetrahedron. (right) Side view, indicating the boat-like conformation of the Cu$_4$O$_4$ metallocycle.

All 2-aminoglucose moieties adopt the more stable $^4C_1$ chair conformation. The copper(II) centers are included well in each NO$_3$ coordination plane with deviations less than 0.05 Å from the corresponding mean planes. The N–Cu–O and O–Cu–O angles are varying from 83.9 to 94.5° and from 170.5 to 177.1°, which is consistent with a slightly distorted square-planar geometry at the copper atoms.

The tetranuclear complex **3** is formed by a self-assembly process of four chiral building blocks {Cu(L)}, with the C-3 alcoholate oxygen atoms being the bridging links between adjacent {Cu(L)} moieties. The resulting eight-membered Cu$_4$O$_4$ ring depicted in Figure 2 is folded in a boat-like conformation. The metal centers occupy the vertices of a distorted tetrahedron which is bisected by the distorted tetragonal plane [torsion angle τ(O13–O23–O33–O43) = 51.8°] composed of the linker alcoholate oxygen atoms O*i*3 (*i* is the running number assigned to the {Cu(L)} moieties) with its normal vector almost collinear to the pseudo C_2 axis of the [{Cu(L)}$_4$] molecule. This results in a non-coplanar orientation of the coordination planes of the four {Cu(L)} moieties given by Cu*i*, N*i*, O*i*3, O*i*6 and O*j*3 (*i* and *j* are the running numbers of the {Cu(L)} moieties). The angles between adjacent planes are ranging from 68.4 to 88.9°, whereas the angles between opposite planes are 43.0 (Cu1 and Cu3) and 45.7° (Cu2 and Cu4).

In accordance with the Cu*i*–O*i*3 distances ranging from 1.917 to 1.957 Å the C-3 alcoholate groups are deprotonated affording a dianionic ligand unit and finally complex **3** as a neutral species. All bond lengths and angles of complex **3** are in the expected range (see Table 1). Unlike the square-planar coordination found for the metal centers in **3**, the only two other sugar-based tetranuclear copper(II) complexes described in literature[35,38] exhibit a square-pyramidal coordination environment at the copper(II) ions. In the latter cases, the apical position is occupied by an additional alcoholate group from the sugar backbone. The absence of an auxiliary accessible donor function in H$_2$L (**2**) may be the reason for the observed coordination number four in complex **3**. Unsaturated copper(II) centers are interesting with respect to catalysis due to a possible substrate binding at the unoccupied fifth position.

Table 1. Selected distances [Å] and angles [°] for [{Cu(L)}$_4$] (**3**) in crystals of **3**·2CHCl$_3$·EtOH.

Distances			
Cu1–N1	1.926(3)	Cu2–N2	1.982(3)
Cu1–O13	1.957(3)	Cu2–O23	1.917(3)
Cu1–O16	1.900(3)	Cu2–O26	1.908(3)
Cu1–O43	1.938(3)	Cu2–O13	1.939(3)
Cu3–N3	1.953(3)	Cu4–N4	1.956(3)
Cu3–O23	1.933(3)	Cu4–O33	1.928(3)
Cu3–O33	1.925(3)	Cu4–O43	1.947(3)
Cu3–O36	1.890(3)	Cu4–O46	1.917(3)
Cu1···Cu2	3.395(4)	Cu2···Cu3	3.407(6)
Cu1···Cu3	3.610(5)	Cu2···Cu4	3.881(5)
Cu1···Cu4	3.435(5)	Cu3···Cu4	3.454(5)
Angles			
N1–Cu1–O13	84.56(12)	N2–Cu2–O23	83.91(12)
N1–Cu1–O16	93.49(12)	N2–Cu2–O26	92.05(13)
N1–Cu1–O43	170.50(13)	N2–Cu2–O13	173.43(13)
O13–Cu1–O16	171.96(13)	O23–Cu2–O26	175.53(12)
O13–Cu1–O43	88.49(11)	O23–Cu2–O13	89.92(11)
O16–Cu1–O43	94.26(12)	O26–Cu2–O13	94.05(12)
N3–Cu3–O33	85.32(12)	N4–Cu4–O43	84.11(13)
N3–Cu3–O36	93.68(13)	N4–Cu4–O46	91.61(13)
N3–Cu3–O23	171.75(13)	N4–Cu4–O33	176.11(13)
O33–Cu3–O36	177.16(13)	O43–Cu4–O46	174.41(11)
O33–Cu3–O23	86.59(12)	O43–Cu4–O33	92.49(12)
O36–Cu3–O23	94.48(12)	O46–Cu4–O33	91.65(12)
Cu1–O13–Cu2	121.21(13)	Cu2–O23–Cu3	124.47(13)
Cu1–O43–Cu4	124.30(14)	Cu3–O33–Cu4	127.34(14)

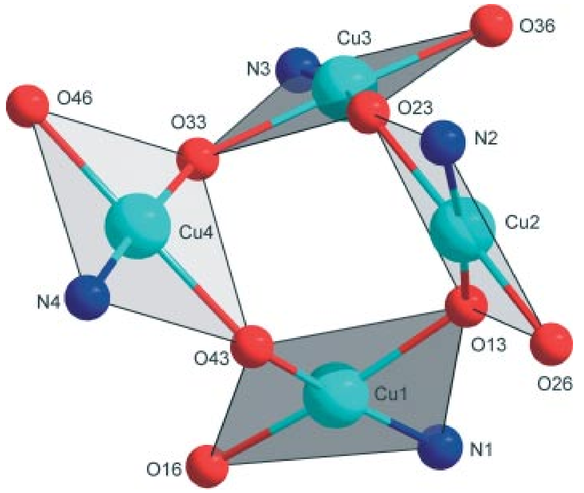


Figure 2. Representation of the central Cu_4O_4 core of complex **3**.

Magnetic Properties

Magnetic susceptibility measurements of powder samples of **3** were carried out in the temperature range of 2–300 K at an applied magnetic field of 500 Oe. The magnetic data are represented as χ_M vs. T and $\chi_M T$ vs. T plots in Figure 3. The molar paramagnetic susceptibility χ_M is corrected for the diamagnetic contributions using Pascal's constants. χ_M goes through a maximum at about 150 K and is increasing again below 25 K due to the presence of paramagnetic impurities. The observed low-temperature value of $\chi_M T$ is in accordance with an $S = 0$ ground state of **3**. The high-temperature value of 1.41 $cm^3\,K\,mol^{-1}$ at 300 K is slightly below the expected spin-only value for four independent copper(II) ions. The temperature dependence of $\chi_M T$ clearly indicates antiferromagnetic exchange interactions within the tetranuclear core of complex **3**.

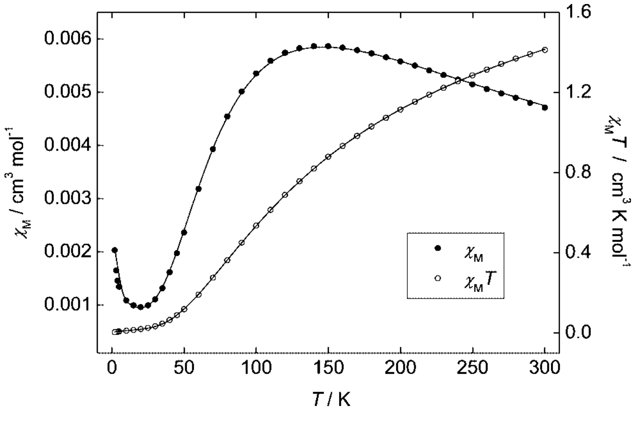


Figure 3. Plots of χ_M vs. T (●), $\chi_M T$ vs. T (○) for **3**. The solid lines represent the best fit to the experimental data (see text).

On the basis of the Cu···Cu distances ranging from 3.39 to 3.88 Å and the unfavorable relative orientations of the copper coordination planes, direct interactions between the metal centers are not very likely. Therefore, the prominent interaction is most likely superexchange through the alcoholate bridges. In the majority of cases the central Cu_4O_4 unit of tetranuclear copper(II) complexes exhibits a cubane-like structure treated as a dimer of Cu_2O_2 fragments. In complex **3** the Cu_4O_4 metallocyclic core unit adopts the unusual boat-like conformation found for only two other magnetically studied examples.[35,42]

Because of the similarity of the Cu*i*–O*i*3 distances ranging from 1.917 to 1.957 Å and the Cu*i*–O*i*3–Cu*j* bridging angles ranging from 121.2 to 127.3°, only one coupling constant J is employed. This assumption is confirmed by the obtained quality of the best fit (solid lines in Figure 3) on the basis of the Heisenberg spin Hamiltonian given in Equation (1)[43] to the experimental data, which results in a coefficient of determination of $r^2 = 0.99999$. The fit parameters $g = 2.15$, $J = -130\ cm^{-1}$, $\rho = 0.0024$ and $\chi_{TIP} = 6.9 \cdot 10^{-4}\ cm^3\,mol^{-1}$ were obtained by least-square methods utilizing Equation (2) (χ_{TIP} = temperature-independent paramagnetism). To account for small amounts of paramagnetic impurity in the sample indicated by the χ_M vs. T plot, the additional constant ρ (fraction of paramagnetic impurity) was included in Equation (2). The contributions of ρ become significant at temperatures below 20 K.

$$H = -J\,(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) \tag{1}$$

$$\chi_M \cdot T = \frac{2Ng^2\beta^2}{k}\left[(1-\rho)\left(\frac{e^{\frac{J}{kT}} + 2e^{\frac{2J}{kT}} + 5e^{\frac{3J}{kT}}}{1 + 3e^{\frac{J}{kT}} + 7e^{\frac{2J}{kT}} + 5e^{\frac{3J}{kT}}}\right) + \frac{\rho}{2}\right] + \chi_{TIP} \cdot T \tag{2}$$

For dinuclear copper complexes with a planar Cu_2O_2 core magneto-structural correlations between the Cu–O(R)–Cu bridging angle (α) and the singlet-triplet splitting (J) have been reported depending on the nature of the bridging unit (R = H, alkyl, aryl).[44] On the basis of the Cu*i*–O*i*3–Cu*j* bridging angles observed for complex **3**, ranging from 121 to 127°, the relationship found for alcoholate-bridged copper(II) complexes ($J = 82.1\alpha - 7857$) would estimate a very strong antiferromagnetic interaction of about 2000 cm^{-1}, which is a rather poor prediction. Although this difference may be related to the variation of the number of bridges, this cannot account for the overall effect. More important is the fact that for planar Cu_2O_2 arrangements the bridging angle is a sufficient parameter to describe the interaction of the magnetic orbitals based on their given coplanar orientation, whereas this is not the case for complexes with single alcoholate bridges. Therefore, additional parameters are essential in order to describe the relative orientation of the magnetic orbitals for systems with single alcoholate bridges, as found in the case of complex **3**. An important structural feature in this context is the torsion angle between adjacent copper coordination planes.[45] For complex **3** the relevant torsion angles range from 68 to 89°. This missing coplanarity of the adjacent Cu coordination planes is associated with poor overlap of the magnetic orbitals.[46] Hence, this can explain the comparatively low value of J observed for complex **3**.

Conclusions

The reaction of the sugar-derived Schiff base ligand H_2L (**2**), obtained from the condensation of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**) and salicylaldehyde, with $[Cu(CH_3COO)_2]\cdot H_2O$ affords the tetranuclear complex $[\{Cu(L)\}_4]$ (**3**) by a self-assembly process of the chiral building blocks {Cu(L)}. The structure determination by X-ray crystallography revealed the exclusive presence of square-planar coordination environments for the copper(II) ions, which to the best of our knowledge is as yet unprecedented in literature for oligonuclear complexes with sugar-derived Schiff base ligands. The square-planar coordination of the copper centers is given by a phenolate oxygen atom of the salicylidene residue, a nitrogen atom of the C-2 imino group and a C-3 alcoholate oxygen atom of the sugar backbone as well as the bridging C-3 alcoholate oxygen atom of the adjacent {Cu(L)} building block. The four adjacent {Cu(L)} moieties are linked by the C-3 alcoholate oxygen atoms resulting in an eight-membered Cu_4O_4 metallocycle adopting a boat-like conformation. This is uncommon for such a tetranuclear oxygen atom bridged core unit, for which usually a cubane-like structure is observed. Magnetic studies of complex **3** show moderate antiferromagnetic interactions between the copper(II) centers with a coupling constant of $J = -130\ \mathrm{cm}^{-1}$. Regarding to the obtuse Cu*i*–O*i*3–Cu*j* bridging angles of more than 120° much larger exchange interactions would be predicted on the basis of magneto-structural correlations derived from binuclear complexes. This is mainly because of the missing coplanarity of the adjacent Cu coordination planes and hence the magnetic orbitals. As first example for 2-amino sugar-derived transition-metal complexes exhibiting a 2,3-coordination of the *trans*-configured donor atoms of the sugar backbone, **3** provides useful insight to the opportunity of constructing polysaccharide-based coordination compounds, in particular chitosan-derived polymer complexes.

Experimental Section

Material: The precursor ligand benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**) was obtained by a three-step synthesis starting from *N*-acetyl-α-D-glucopyranosamine following reported procedures.[39,40] All other chemicals were purchased from commercial suppliers and used without further purification.

Physical Measurements: Melting points are given uncorrected and were determined with a VEB Analytik Dresden HMK 72/41555. Thermogravimetric analysis (TGA) for powdered samples was performed with a Netzsch STA409PC Luxx apparatus under constant flow of nitrogen ranging from room temperature up to 1000 °C with a heating rate of 1 °C/min. Infrared and Raman spectra were recorded with a Bruker IFS55/EQUINOX spectrometer. ^{1}H and ^{13}C NMR experiments were carried out with a Bruker AVANCE DRX 400 spectrometer. The exact interpretation was accomplished by additional two-dimensional experiments. For the labeling scheme see Scheme 2. UV/Vis spectra were recorded with a Varian CARY 5000 UV/Vis-NIR spectrometer. Mass spectra were measured with a Bruker MAT SSQ 710 spectrometer. Elemental analyses were determined with a Leco CHNS/932 elemental analyzer and a VARIO EL III. Magnetic susceptibilities were obtained from powdered samples using a Quantum-Design MPMSR-5S SQUID magnetometer equipped with a 5-Tesla magnet in the range from 300 to 2 K. The diamagnetic correction of the sample was estimated from Pascal's constants.

Crystallographic Study: Crystallization of complex **3** from a mixture of chloroform, ethanol and water afforded green prismatic crystals of $[\{Cu(L)\}_4]\cdot 2CHCl_3\cdot EtOH$ (**3**$\cdot 2CHCl_3\cdot EtOH$) suitable for X-ray measurements. Single crystals were selected while still covered with mother liquor under a polarizing microscope and fixed on fine glass fibers. X-ray measurements were carried out with a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystallographic data is summarized in Table 2. The structure was solved by direct methods with SHELXS-97[47] and was full-matrix least-squares refined against F^2 using SHELXL-97.[47] The refinement afforded a Flack parameter of 0.004(8). Anisotropic thermal parameters were used for all non-hydrogen atoms except the ethanol solvent molecules. Hydrogen atoms were calculated and treated as riding atoms with fixed thermal parameters. CCDC-602321 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data-request/cif.

Table 2. Crystallographic data and structure refinement parameters for **3**$\cdot 2CHCl_3\cdot EtOH$.

Empirical formula	$C_{112}H_{108}Cl_6Cu_4N_4O_{25}$
Formula mass [g/mol]	2376.88
Crystal size [mm]	0.5 × 0.5 × 0.5
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	15.137(3)
b [Å]	26.021(5)
c [Å]	26.987(5)
V [Å^3]	10629(4)
T [K]	183(2)
Z	4
$\rho_{\mathrm{calcd.}}$ [g/cm^{-1}]	1.485
μ [mm^{-1}]	1.017
θ range [°]	1.09–27.48
Unique data	24107
Observed data [$I > 2\sigma(I)$]	17801
Parameters	1362
Goodness-of-fit on F^2	1.077
R_1 for observed data	0.0464
wR_2 for all data	0.1270

Synthesis of Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-salicylideneamino-α-D-glucopyranoside (H_2L) (2): Salicylaldehyde (0.65 mL; 6.10 mmol) was added to a suspension of **1** (2.00 g, 4.33 mmol) in 60 mL methanol at room temperature. A clear yellow solution was obtained within 2 min. After stirring additional 10 min a yellow solid precipitated. The mixture was subsequently stirred for another 20 min before the precipitate was collected by filtration. The product was washed with a small amount of methanol and then dried in air. Yield: 2.40 g (93%). $C_{27}H_{27}NO_6$ (461.52): calcd. C 70.27, H 5.90, N 3.04; found C 69.12, H 6.00, N 2.70. M.p. 94–96 °C. IR (KBr): $\tilde{\nu}$ = 3447 (ν O–H), 3064, 3032 (ν C–H arom.), 2909 (ν_{as} CH_2), 2870 (ν_s CH_2), 1637 (ν CH=N), 1580, 1498 (ν C=C), 1454 (δ CH_2), 1374, 1351, 1316, 1282, 1211, 1151 (ν C–O), 1050 (ν C–O), 1024 (ν C–O), 984, 754, 733, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.45 (dd, $^{3}J_{2,1}$ = 3.7, $^{3}J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.63 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.81 (dd, $^2J_{6a,6e}$ = $^3J_{6a,5}$ = 10.4 Hz, 1 H, 6a-H), 4.09 (ddd, $^3J_{5,6a}$ = 9.9, $^3J_{5,6e}$ = 4.9 Hz, 1 H, 5-H), 4.29–4.36 (m, 2 H, 3-H and 6e-H), 4.61 and 4.81 (2d, $^2J_{7a,7b}$ = 12.2 Hz, each 1 H, 7a-H and 7b-H), 4.92 (d, $^3J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.59 (s, 1 H, 21-H), 6.89 (dt, J_d = 1.1, J_t = 7.5 Hz, 1 H, Ph), 7.01 (d, J_d = 8.2 Hz, 1 H, Ph), 7.26–7.41 (m, 10 H, Ph), 7.50–7.53 (m, 2 H, Ph), 9.91 (s, 1 H, 14-H), 13.50 (s, 1 H, 20-OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 62.9 (C5), 69.0 (C3, C6), 69.8 (C7), 72.6 (C2), 81.9 (C4), 98.5 (C1), 102.2 (C21), 117.3, 118.5, 118.6, 126.36, 127.9, 128.0, 128.4, 128.5, 129.3, 131.8, 132.8, 136.9, 137.1 (all Ph), 161.6 (C20), 167.8 (C14) ppm. ESI-MS: *m/z* (%) = 484 $[(H_2L)+Na]^+$ (100).

Synthesis of $[\{Cu(L)\}_4]$ (3): A solution of $[Cu(CH_3COO)_2]\cdot H_2O$ (174 mg, 0.87 mmol) in 5 mL water was added dropwise to a solution of **2** (400 mg, 0.87 mmol) in 15 mL chloroform at room temperature. Subsequently 30 mL ethanol were added under vigorous stirring. Complex **3** was obtained in form of green crystals of $[\{Cu(L)\}_4]\cdot 2CHCl_3\cdot EtOH$ suitable for X-ray measurements after 4 d. The crystals have been isolated, washed with a small amount of ethanol and dried in air affording a solvent-free material. Yield: 417 mg (92%). $C_{108}H_{100}Cu_4N_4O_{24}$ (2092.23): calcd. C 62.00, H 4.82, N 2.69; found C 61.95, H 4.79, N 2.57. Decomposition interval: 284–307 °C. IR (KBr): $\tilde{\nu}$ = 3447 (ν O–H), 3063, 3030 (ν C–H arom.), 2929 and 2910 (ν_{as} CH_2), 2884 and 2860 (ν_s CH_2), 1636 (ν CH=N), 1603 and 1533 (ν C=C), 1452 (δ CH_2), 1387, 1349, 1332, 1192, 1148 (ν C–O), 1119 (ν C–O), 1097 (ν C–O), 1065 (ν C–O), 1024 (ν C–O), 913, 756, 737, 699, 653 cm^{-1}. Raman (solid): $\tilde{\nu}$ = 3052 (ν C–H arom.), 2962, 2937 (ν_{as} CH_2), 2889, 2870, 2860 (ν_s CH_2), 1637 (ν C=N), 1603, 1535 (ν C=C), 1457, 1451 (δ CH_2), 1359, 1350, 1249, 1209, 1027 and 1003 (ν C–O), 808 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 277 ($4.21\cdot 10^4$), 370 ($2.17\cdot 10^4$), 632 nm ($4.97\cdot 10^2$ $l\,mol^{-1}\,cm^{-1}$). ESI-MS: *m/z* (%) = 2092 $[\{Cu(L)\}_4+H]^+$ (11); 2113 $[\{Cu(L)\}_4+Na]^+$ (100).

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[1] J. F. Kennedy, C. A. White, *Bioactive Carbohydrates in Chemistry, Biochemistry and Biology*, John Wiley & Sons, New York, **1983**.

[2] R. W. Gracy, E. A. Noltmann, *J. Biol. Chem.* **1968**, *243*, 4109–4116.

[3] K. D. Hardman, R. C. Agarwal, M. J. Freiser, *J. Mol. Biol.* **1982**, *157*, 69–86.

[4] R. L. Root, J. R. Durrwachter, C.-H. Wong, *J. Am. Chem. Soc.* **1985**, *107*, 2997–2999.

[5] G. K. Farber, A. Glasfeld, G. Tiraby, D. Ringe, G. A. Petsko, *Biochemistry* **1989**, *28*, 7289–7297.

[6] J. Jenkins, J. Janin, F. Rey, M. Chiadmi, H. Van Tilbeurgh, I. Lasters, M. D. Maeyer, D. V. Belle, S. J. Wodak, M. Lauwereys, P. Stanssens, N. T. Mrabet, J. Snauwaert, G. Matthyssens, A.-M. Lambeir, *Biochemistry* **1992**, *31*, 5449–5458.

[7] Y. Zhang, J.-Y. Liang, S. Huang, H. Ke, W. N. Lipscomb, *Biochemistry* **1993**, *32*, 1844–1857.

[8] A. Lavie, K. N. Allen, G. A. Petsko, D. Ringe, *Biochemistry* **1994**, *33*, 5469–5480.

[9] K. K.-S. Ng, W. I. Weis, *Biochemistry* **1997**, *36*, 979–988.

[10] K. K.-S. Ng, S. Park-Snyder, W. I. Weis, *Biochemistry* **1998**, *37*, 17965–17976.

[11] N. Habermann, G. Jung, M. Klaassen, P. Klüfers, *Chem. Ber.* **1992**, *125*, 809–814.

[12] J. Burger, C. Gack, P. Klüfers, *Angew. Chem.* **1995**, *107*, 2950–2951; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2647–2649.

[13] P. Klüfers, T. Kunte, *Angew. Chem.* **2001**, *113*, 4356–4358; *Angew. Chem. Int. Ed.* **2001**, *40*, 4210–4212.

[14] P. Klüfers, T. Kunte, *Eur. J. Inorg. Chem.* **2002**, 1285–1289.

[15] P. Klüfers, O. Krotz, M. Oßberger, *Eur. J. Inorg. Chem.* **2002**, 1919–1923.

[16] S. Yano, *Coord. Chem. Rev.* **1988**, *92*, 113–156.

[17] T. Tanase, M. Nakagoshi, A. Teratani, M. Kate, Y. Yamamoto, S. Yano, *Inorg. Chem.* **1994**, *33*, 5–6.

[18] T. Tanase, T. Onaka, M. Nakagoshi, I. Kinoshita, K. Shibata, M. Doe, J. Fujii, S. Yano, *Chem. Commun.* **1997**, 2115–2116.

[19] T. Tanase, Y. Yasuda, T. Onaka, S. Yano, *J. Chem. Soc. Dalton Trans.* **1998**, 345–351.

[20] T. Tanase, T. Onaka, M. Nakagoshi, I. Kinoshita, K. Shibata, M. Doe, J. Fujii, S. Yano, *Inorg. Chem.* **1999**, *38*, 3150–3159.

[21] T. Tanase, S. Tamakoshi, M. Doi, M. Mikuriya, H. Sakurai, S. Yano, *Inorg. Chem.* **2000**, *39*, 692–704.

[22] T. Tanase, H. Inukai, T. Onaka, M. Kato, S. Yano, S. J. Lippard, *Inorg. Chem.* **2001**, *40*, 3943–3953.

[23] Y. Mikata, Y. Shinohara, K. Yoneda, Y. Nakamura, K. Esaki, M. Tanahashi, I. Brudzińska, S. Hirohara, M. Yokoyama, K. Mogami, T. Tanase, T. Kitayama, K. Takashiba, K. Nabeshima, R. Takagi, M. Takatani, T. Okamoto, I. Kinoshita, M. Doe, A. Hamazawa, M. Morita, F. Nishida, T. Sakakibara, C. Orvig, S. Yano, *J. Org. Chem.* **2001**, *66*, 3783–3789.

[24] S. Yano, Y. Mikita, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2097–2113.

[25] Y. Mikata, Y. Sugai, S. Yano, *Inorg. Chem.* **2004**, *43*, 4778–4780.

[26] T. Storr, Y. Sugai, C. A. Barta, Y. Mikata, M. J. Adam, S. Yano, C. Orvig, *Inorg. Chem.* **2005**, *44*, 2698–2705.

[27] T. Storr, M. Obata, C. L. Fisher, S. R. Bayly, D. E. Green, I. Brudzińska, Y. Mikata, B. O. Patrick, M. J. Adam, S. Yano, C. Orvig, *Chem. Eur. J.* **2005**, *11*, 195–203.

[28] Y. Mikata, Y. Sugai, M. Obata, M. Harada, S. Yano, *Inorg. Chem.* **2006**, *45*, 1543–1551.

[29] J. C. Irvine, J. C. Earl, *J. Chem. Soc.* **1922**, *121*, 2376–2381.

[30] A. K. Sah, C. P. Rao, P. K. Saarenketo, E. K. Wegelius, E. Kolehmainen, K. Rissanen, *Eur. J. Inorg. Chem.* **2001**, *11*, 2773–2781.

[31] M. E. Cucciolito, R. D. Litto, G. Roviello, F. Ruffo, *J. Mol. Catal. A* **2005**, *236*, 176–181.

[32] T. Klabunde, C. Eicken, J. C. Sacchettini, B. Krebs, *Nat. Struct. Biol.* **1998**, *5*, 1084–1090.

[33] A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gatti, A. Marchesini, R. Petruzzelli, A. Finazzi-Agró, *J. Mol. Biol.* **1989**, *206*, 513–529.

[34] R. Wegner, M. Gottschaldt, H. Görls, E.-G. Jäger, D. Klemm, *Angew. Chem.* **2000**, *112*, 608–612; *Angew. Chem. Int. Ed.* **2000**, *39*, 595–599.

[35] A. Fragoso, M. L. Kahn, A. Castineiras, J.-P. Sutter, O. Kahn, R. Cao, *Chem. Commun.* **2000**, 1547–1548.

[36] A. K. Sah, C. P. Rao, P. K. Saarenketo, K. Rissanen, G. A. Van Albada, J. Reedijk, *Chem. Lett.* **2002**, 348–349.

[37] A. K. Sah, M. Kato, T. Tanase, *Chem. Commun.* **2005**, 675–677.

[38] A. K. Sah, T. Tanase, M. Mikuriya, *Inorg. Chem.* **2006**, *45*, 2083–2092.

[39] P. H. Gross, R. W. Jeanloz, *J. Org. Chem.* **1967**, *32*, 2759–2763.

[40] Z. Györgydeák, *Liebigs Ann. Chem.* **1991**, 1291–1300.

[41] J. Zhao, X. Zhou, A. M. Santos, E. Herdtweck, C. C. Romão, F. E. Kühn, *Dalton Trans.* **2003**, 3736–3742.

[42] C. J. Matthews, K. Avery, Z. Xu, L. K. Thompson, L. Zhao, D. O. Miller, K. Biradha, K. Poirier, M. J. Zaworotko, C. Wilson, A. E. Goeta, J. A. K. Howard, *Inorg. Chem.* **1999**, *38*, 5266–5276.

[43] O. Kahn, in: *Molecular Magnetism*, VCH, Weinheim, **1993**.

[44] F. Tuna, L. Patron, Y. Journaux, M. Andruh, W. Plass, J.-C. Trombe, *J. Chem. Soc. Dalton Trans.* **1999**, 539–545.

[45] L. Merz, W. Haase, *J. Chem. Soc. Dalton Trans.* **1978**, 1594–1598.

[46] E. Ruiz, C. De Graaf, P. Alemany, S. Alvarez, *J. Phys. Chem. A* **2002**, *106*, 4938–4941.

[47] G. Sheldrick, *SHELXS* and *SHELXL*, University of Göttingen, **1997**.

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