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A Sugar's Choice: Coordination to a Mononuclear or a Dinuclear Copper(II) Complex?

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We proposed a decisive role of the *number* of metal ions at the sugar binding site for carbohydrate-coordinating copper(II) complexes. To verify this hypothesis, we studied the binding of the representatively chosen carbohydrates D-ribose (**7**), D-mannose (**8**), D-glucose (**9**), and D-maltose (**10**) to structurally related mono- and dinuclear copper(II) complexes in alkaline solution. All carbohydrates coordinate to the metal complexes in a 1:1 molar ratio. Coordination of **7** or **8** to the dinuclear copper(II) complex **1** is about 0.5 order of magnitude stronger than the complex formation with related mononuclear complexes. On contrast, **9**, which is an epimer of **8,** coordinates stronger to either one of the mononuclear copper(II) complexes in alkaline aqueous solution.

Introduction

Considerable efforts have been directed toward carbohydrate recognition by synthetic receptors in relation to the important roles of saccharides in biological processes,[1,2] such as intercellular recognition, signal transduction, fertilization, or as targets of bacterial or viral infections of cells.[1−3] For imitation of these recognition events and a better understanding of the interactions involved, models need to be designed that discriminate isomeric or even epimeric sugars in aqueous solution. As the subtle steric differences between saccharides are difficult to take into account, the progress in the preparation of selective carbohydrate recognition sites is rather slow, although the design and synthesis of sugar binding sites by various methods is at the forefront of current research.[4−6] A mononuclear copper(II) complex, which by itself does not discriminate epimeric carbohydrates in solution, has been shown to distinguish biologically important natural saccharides, such as D-glucose and D-mannose or D-galactose, at neutral pH when incorporated into a polymer.[7,8] On contrast, the dinuclear copper(II) complex {*N*,*N*′-1,3-bis[(pyridin-2-ylmethyl)amino]propan-2-olato}dicopper(II) μ-acetato diperchlorate (**1**), Cu_2(bpdpo), allows a large discrimination between related saccharides in aqueous solution at pH 12.4.[9] We therefore proposed that the number of metal ions available for saccharide binding is decisive for the nature of preferred sugar coordination. We subsequently investigated the sugar coordination to dinuclear copper(II) complex **1** in comparison to the structurally closely related mononuclear copper(II) complexes {*N*,*N*′-1,3-bis[(pyridin-2-ylmethyl)amino]propan-2-ol}copper(II) diperchlorate (**2**), Cu(bpdpo), and {*N*-2-[(pyridin-2-ylmethyl)amino]ethanol}-copper(II) diperchlorate (**3**), Cu(paeo), under strong sugar binding conditions, i.e., in alkaline aqueous solution. The preparation of sugar recognition material and the evaluation of its sugar differentiation capability are based on the results reported herein and the topic of current work.

Experimental Section

General Remarks. Methanol, ethanol, chloroform, diethyl ether, pyridine-2-carbaldehyde, aminoethanol, copper(II) chloride dihydrate, and sodium sulfate were obtained from Merck, D-ribose (**7**), D-mannose (**8**), sodium hydroxide, and sodium tetrahydridoborate

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were obtained from Fluka, 1,3-diaminopropan-2-ol, copper(II) acetate monohydrate, sodium perchlorate, and copper(II) perchlorate hexahydrate were purchased from Aldrich, and D-glucose (**9**) and D-maltose (**10**) were obtained from Sigma. Pyridine-2-carbaldehyde and aminoethanol were distilled in a vacuum immediately prior to use. All other reagents and solvents had reagent grade quality or better and were used without further purification.

The melting points are uncorrected and were measured with a Büchi B-540. The IR spectra were obtained on a Bruker IFS 133V as thin films or KBr pellets with ν in cm^{-1}. The microanalysis was performed on a Elementar Vario EL. The mass spectra (EI) were obtained using a Varian Saturn GC/MS 2000 equipped with a CP-Sil 8 CB Lowbleed MS column, 25 m × 0.25 nm × 0.25 μm. The FAB-MS spectra were obtained using a Finnigan MAT SSQ 7000. The NMR experiments were performed on a Bruker DRX 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz) at 300 K; $CDCl_3$ or DMSO-d_6 was used as solvent, and residual $CHCl_3$ or CD_2HSOCD_3 was used as internal standard ($CHCl_3$, $\delta(^1H)$ 7.24, $\delta(^{13}C)$ 77.0; CD_2HSOCD_3, $\delta(^1H)$ 2.50, $\delta(^{13}C)$ 39.5). Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane with coupling constants J in Hz.

UV/Vis Spectroscopy. All experiments for the determination of binding constants were performed on an UV/vis J&M TIDAS spectrophotometer (software SPECTRALYS, version 1.55) with Suprasil standard cells (200−2000 nm) of 10 mm thickness and 700 μL volume at 25.0 ± 0.1 °C over a range of 200−900 nm. The experiments were done in unbuffered, Nanopure water, which pH was adjusted to pH 12.40 with NaOH prior to use for each set of titrations. Typically, 2.5 mM stock solutions of the metal complexes **1**, **2**, or **3** and 80 mM stock solutions of the carbohydrates **7**, **8**, **9**, or **10** were prepared separately and kept at 25 °C. The total concentration of the metal ion M_t (V_M = 800 μL; M_t = 2 mM) and the total volume of the resulting solutions (V_t = 1 mL) were kept constant during the titration experiments (V_{sugar} = 0−200 μL) by adding an appropriate amount of water. The UV/vis absorbances of the resulting mixtures were measured immediately after mixing. Likewise, the pH of the resulting was also measured immediately after mixing for the determination of the release of protons as a result of the coordination.

All spectrophotometric titration experiments were done in aqueous solution, which ionic strength was maintained constant with 0.1 M $NaClO_4$. The UV/vis spectra were recorded with Suprasil standard cells (200−2000 nm) of 10 mm thickness and 4.5 mL volume at 25.0 ± 0.1 °C over a range of 200−900 nm. The pH value was measured with a Beckman Φ 250 pH meter equipped with a refillable long combination Futura pH electrode of 0.7 mm thickness. Typically, 2 mL of stirred solutions containing copper(II) acetate or copper(II) perchlorate (4 mM), purified ligand (2 mM), and carbohydrate (2 or 10 mM) were titrated with freshly prepared 0.3 M aqueous NaOH. The UV/vis spectra were recorded in dependence of the pH value measured in the reaction vessel after equilibration. The spectral data were computed by the fitting procedures provided by the program Specfit.[10] The addition of at least equimolar amounts of acetonitrile in respect to the ligand paeo **5** prevented precipitation of copper(II) hydroxide during titration of **5** in the presence of copper(II) ions above pH 9. Formation of precipitate was not observed when the solution contained carbohydrate.

{*N*,*N*′-1,3-Bis[(pyridin-2-ylmethyl)amino]propan-2-ol}copper(II) Diperchlorate (2), Cu(bpdpo).[11,12] The raw product was prepared as described and purified by recrystallization from acetonitrile (5 mL) and subsequent slow diffusion of diethyl ether (20 mL) at ambient temperature, yielding **2** (1.90 g, 71%) as violet crystals. Mp (dec): 239 °C (CH_3CN/Et_2O). Anal. Found: C, 33.7; H, 3.8; N, 10.5. Calcd for $C_{15}H_{20}Cl_2CuN_4O_9$: C, 33.7; H, 3.8; N, 10.5. Other data: λ_{max} (H_2O)/nm 321 (ϵ/dm^3 mol^{-1} cm^{-1} 258), 656 (99); ν_{max} (KBr)/cm^{-1} 3485 s (NH), 3247 br (OH), 3080 br (=CH, arom) 2912 m (CH), 2887 m (CH), 1611 s (NH), 1570 s (NH), 1485 m (CH, arom), 1434 m (CH, arom), 1094 br, s (Cl−O), 771 m (=CH, arom) and 625 m (Cl−O); *m*/*z* (FAB) 434 (76%, M − ClO_4^-), 335 (100).

2-[(Pyridin-2-ylmethyl)amino]ethanol (5), paeo.[13] Compound **5** was prepared in a one-pot synthesis. Typically, pyridine-2-carbaldehyde (2.14 g, 0.02 mol) was added slowly to an ice-cooled solution of aminoethanol (1.22 g, 0.02 mol) in 30 mL of methanol. The resulting solution was stirred at ambient temperature for 2 h and subsequently treated with sodium tetrahydridoborate (1.89 g, 0.05 mol) in small portions. After additional 2 h, water (30 mL) was added and the reaction mixture was concentrated to about 20 mL using a rotavap. The remaining solution was extracted with dichloromethane (2 × 20 mL), and the organic layer was separated and subsequently dried with sodium sulfate. Filtration and evaporation of the solvent gave the amino ligand **5** (1.92 g, 63%) as an orange oil, which was used without further purification for the synthesis of **3**. Anal. Found: C, 60.8; H, 7.7; N, 18.2. Calcd for $C_8H_{12}N_2O$: C, 63.1; H, 7.9; N, 18.4. Other data: ν_{max} (film)/cm^{-1} 3305 br (OH), 3067 w (=CH, arom.), 2926 w (CH), 2843 w (CH), 1592 s (NH), 1570 s (NH), 1474 m (CH), 1434 m (CH), 1121 m (C−N), 1052 s (C−O) and 760 s (=CH, arom); δ_H (400 MHz; $CDCl_3$) 8.45 (1H, ddd, 4.9, 1.8, 0.8, pyr-H), 7.57 (1H, ddd, 7.7, 7.6, 1.8), 7.22 (1H, 7.7, 0.9, 0.8), 7.09 (1H, ddd, 7.6, 4.9, 0.9), 3.84 (2H, s, pyr-C*H*$_2$N), 3.60 (2H, t, 5.2, −NCH$_2$C*H*$_2$OH), 3.30 (2H, br s, OH, NH), 2.74 (2H, t, 5.2, NC*H*$_2$CH$_2$OH); δ_C (100 MHz; $CDCl_3$) 159.3, 149.0, 136.6, 122.4, 122.0, 60.7, 54.3, 51.0; *m*/*z* (EI) 153 (100%, MH^+), 121 (33), 93 (10), 65 (5).

2-[(Pyridin-2-ylmethylen)amino]ethanol (6).[13] An analytical sample of **6**, which was typically not isolated during the one-pot synthesis of **5**, was obtained by adding pyridine-2-carbaldehyde (2.14 g, 0.02 mol) slowly to an ice-cooled solution of aminoethanol (1.22 g, 0.02 mol) in 30 mL of methanol. After the sample was stirred for 2 h at ambient temperature, the solvent was evaporated yielding **6** as a yellowish waxy solid (2.97 g, 99%). Mp: 31 °C. Anal. Found: C, 64.5; H, 6.7; N, 18.4. Calcd for $C_8H_{10}N_2O$: C, 64.0; H, 6.7; N, 18.7. Other data: ν_{max} (film)/cm^{-1} 3287 br (OH), 3058 w (=CH, arom), 2922 w (CH), 2872 w (CH), 1650 s (C=N), 1588 s (NH) 1568 s (NH), 1470 m (CH), 1436 m (CH), 1149 w (C−N), 1063 s (C−O) and 773 s (=CH, arom); δ_H (400 MHz, DMSO-d_6, 300 K) δ = 8.63 (1H, ddd, 4.9, 1.8, 1.0, pyr-H), 8.32 (1H, s, *H*C=N), 7.95 (1H, ddd, 7.5, 4.9, 1.3, pyr-H), 7.85 (1H, ddd, 7.8, 7.5, 1.8, pyr-H), 7.43 (1H, ddd, 7.8, 1.3, 1.0, pyr-H), 4.65 (1H, br s, OH) 3.70 (4H, s); δ_C (100 MHz; DMSO-d_6) 162.7, 154.2, 149.2, 136.7, 124.9, 1204., 63.1, 60.5; *m*/*z* (EI) 151 (40%, MH^+), 119 (100), 92 (65), 65 (30).

{*N*-2-[(Pyridin-2-ylmethyl)amino]ethanol}copper(II) Diperchlorate−Acetonitrile (3), Cu(paeo). *Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of material should be prepared, and the samples should be handled with care!* A solution of copper(II) perchlorate hexahydrate (2.44 g, 6.57 mmol) in 5 mL of methanol

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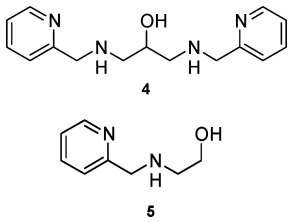

Figure 1. Amino ligands bpdpo (**4**) and paeo (**5**).

was added to a solution of ligand **5** (1 g, 6.57 mmol) in 20 mL of methanol at ambient temperature. The blue solution was heated at 70 °C and hot filtrated after 15 min. Evaporation of the solvent yielded a blue oil, which solidified upon standing. Crystallization by diffusion of diethyl ether into an acetonitrile solution gave the light blue crystalline copper complex **3** (1.53 g, 51%). Mp (dec): 203 °C. Anal. Found: C, 26.2; H, 3.3; N, 9.1. Calcd for $C_8H_{12}Cl_2CuN_2O_9 \cdot CH_3CN$: C, 26.3; H, 3.3; N, 9.2. Other data: λ_{max} (H_2O)/nm 313 (ϵ/dm^3 mol^{-1} cm^{-1} 132), 626 (89); ν_{max} (KBr)/cm^{-1} 3411 br (OH), 3252 (=CH, arom), 2959 m (CH), 2854 m (CH), 1612 s (NH), 1573 s (NH), 1483 m (CH, arom), 1450 m (CH, arom), 1094 br, s (Cl−O), 769 m (=CH, arom) and 628 m (Cl−O); m/z (FAB) 314 (60%, M − ClO_4^-), 215 (100, M − $2ClO_4^-$), 184 (32), 136(15), 107 (7).

Results and Discussion

Ligand and Complex Syntheses. The pentadentate *N*,*O*-ligand 1,3-bis[(pyridin-2-ylmethyl)amino]propan-2-ol (**4**), bpdpo, forms mono- or binuclear copper(II) complexes depending on the amount of copper salt available for coordination.[11,12,14] This property of the ligand is favorable for our purpose to compare carbohydrate coordination to metal complexes, which differ in the *number* of metal centers only. On the other hand, steric hindrance around the metal site due to the bulkiness of ligand **4** may diminish the carbohydrate coordination and consequently limit a fair comparison of the saccharide binding capability of mono- and dinuclear copper(II) complexes in solution. Therefore, we used the structurally closely related, but sterically less demanding, tripodal *N*-ligand 2-[(pyridin-2-ylmethyl)amino]-ethanol (**5**), paeo (Figure 1), for the preparation of mononuclear copper(II) complex **3**, Cu(paeo), and studied its coordination to carbohydrates as well.

The amino ligand **5** was previously synthesized in two steps and characterized as an amber oil.[13] However, we developed a one-pot synthesis avoiding benzene as solvent, characterized **5** in more detail, and report herein for the first time the mononuclear copper(II) complex **3** derived from **5**. Aminoethanol was reacted with pyridine-2-carbaldehyde in methanol yielding the Schiff base 2-[(pyridin-2-ylmethylene)-amino]ethanol (**6**), which typically was not isolated but subsequently reduced with sodium tetrahydridoborate to afford **5** as an orange oil after workup. The N=C valence bond vibration at 1650 cm^{-1} in the IR spectrum of **6** is absent in the spectrum of **5** indicating complete reduction. Similarly, the ^{1}H NMR spectrum of **6** shows one signal for the proton of the CH=N moiety at 8.57 ppm that is absent after reduction of the Schiff base yielding **5**, which displays a singlet at 3.84 ppm for the resulting CH_2 group instead (see Supporting Information). Reacting **5** with copper(II) perchlorate in methanol at ambient temperature yielded a blue oil, from which microcrystalline **3** was obtained by slow addition of diethyl ether to a saturated solution in acetonitrile. We confirmed the composition of **3** by elemental analysis and mass spectrometry. The infrared spectrum of **3** demonstrates the coordination of **5** to the copper(II) ions, as e.g. the C−H deformation vibration of the pyridyl group shifts from 1474 and 1434 cm^{-1} to 1483 and 1450 cm^{-1}, respectively, while the signal of the N−H deformation vibration of the secondary amino group changes from 1592 to 1612 cm^{-1} (see Supporting Information). As the signals for the deformation vibration of the hydroxyl group remain unaffected in **3** and **5**, whereas the C−O stretch vibration at 1052 cm^{-1} of **5** is overlaid by strong perchlorate stretch vibrations at 1092 cm^{-1} in **3**, the coordination of the hydroxyl group to the copper(II) center in **3** cannot be unambiguously assigned. All attempts to obtain a single-crystal suitable for X-ray structure analysis have failed so far. For the planned study of the sugar coordination ability of the complexes of **1**−**3** in *solution*, however, we focused on the determination of the complex composition under the conditions used for strong carbohydrate binding, i.e., at alkaline pH. Under these conditions the hydroxyl groups in the metal-coordinating ligands **4** and **5** may be deprotonated to form strongly coordinating alkoxide groups.

Composition of the Metal Complexes at Alkaline pH. The composition of the metal complexes **1**−**3** may differ in solution from that in solid state. We therefore took advantage of the spectrophotometric titration method developed by Zuberbühler and co-workers to determine the distribution of species related to **1**−**3** from multiwavelength spectroscopic UV/vis data, which were recorded in dependence of the pH value at constant ionic strength (Figure 2).[10]

Dinuclear complex **1** is formed above pH 9, when a 2:1 molar ratio of copper(II) ions and the ligand is provided (Figure 2A),[12] while a mononuclear complex from **4** is formed in the presence of molar amounts of copper(II) ions (Figure 2B). Mononuclear complexes only are derived from ligand **5** (Figure 2C). The structures proposed for the corresponding mono- and dinuclear copper(II) complexes at pH 12.40, which is subsequently used for carbohydrate coordination,[15] are different in number of hydroxyl groups coordinated to the metal centers (Figure 3).

As protons from both the metal-coordinating backbone ligand and the coordinating water molecules may be abstracted under these conditions, equilibrium structures are proposed for **2** and **3**.

Carbohydrate Coordination to the Metal Complexes. The binding strength of metal complexes formed from polyalcohols or sugar-type ligands, which contain hydroxyl or carbonyl oxygen donor atoms only, is weak in neutral or acidic aqueous solutions.[16] In alkaline solutions, however,

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(15) For a comprehensive investigation of the carbohydrate stability at pH 12.40, see ref 8.

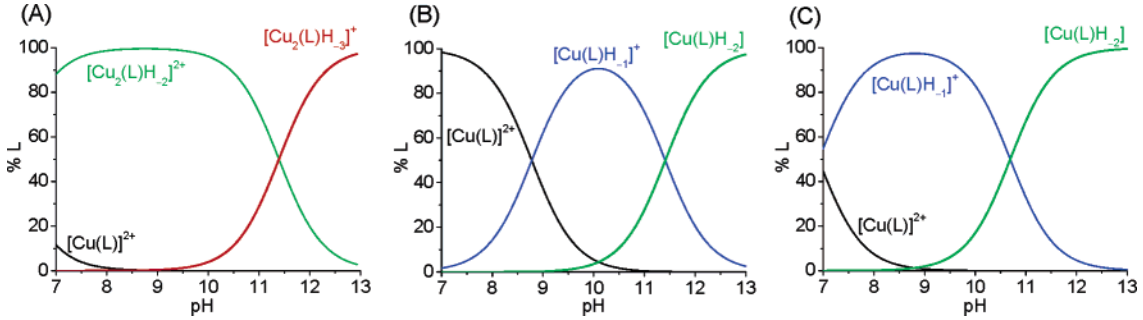

Figure 2. Distribution of species between pH 7 to 13 related to (A) Cu_2(bpdpo) (**1**), (B) Cu(bpdpo) (**2**), and (C) Cu(paeo) (**3**) as calculated from UV/vis spectra, which were recorded in dependence of the pH value. Note: L = bpdpo (**4**; A, B) or paeo (**5**; C).

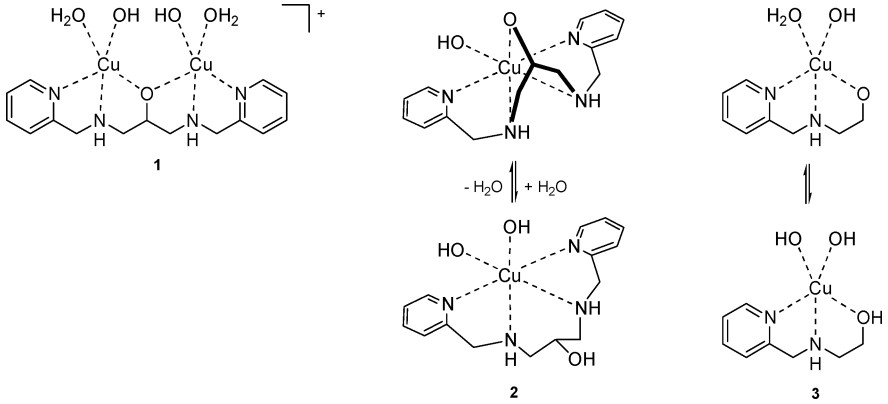

Figure 3. Proposed structures for the dominating species of the metal complexes Cu_2(bpdpo) (**1**), Cu(bpdpo) (**2**), and Cu(paeo) (**3**) at pH 12.40 and 25 °C.

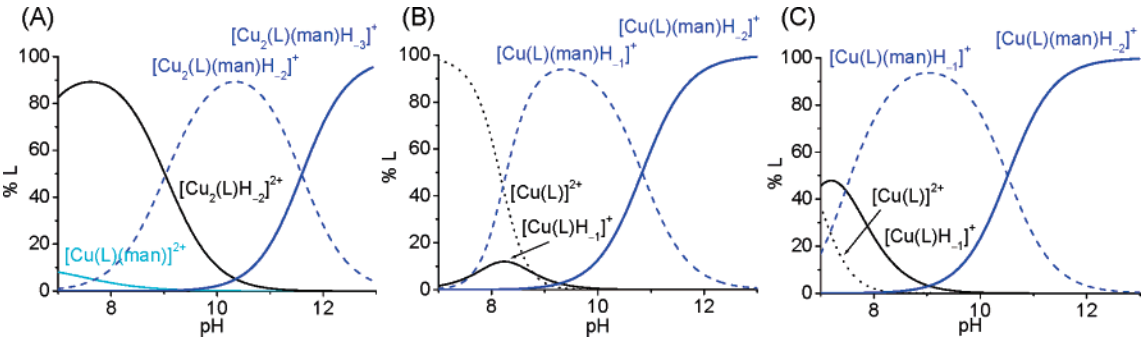

Figure 4. Representative examples for the distribution of species derived from D-mannose (**8**) and (A) Cu_2(bpdpo) (**1**), (B) Cu(bpdpo) (**2**), and (C) Cu(paeo) (**3**). The species distributions are determined from UV/vis spectra, which were recorded in dependence of the pH value between 7 and 13 Note: L = bpdpo (A, B) or paeo (C); complexes related to D-mannose (**8**) are shown in blue.

the hydroxyl groups of the carbohydrates can be deprotonated, resulting in sugar anions with enhanced coordination ability. We used UV/vis spectroscopy at highly alkaline pH to explore the differences in coordination of the metal complexes **1**−**3** to selected carbohydrates, namely D-ribose (**7**), D-mannose (**8**), D-glucose (**9**), and D-maltose (**10**). The stability of the carbohydrates under these conditions has been established earlier.[8] We confirmed a 1:1 composition for all sugar complexes investigated that is independent of both the metal complex used and the nature or amount of sugar applied. The complex stoichiometry has been concluded from the number of spectroscopic states, which gives evidence for only two species, namely the metal complex and the corresponding carbohydrate−metal complex assembly.[8,17] A 1:1 binding is visualized in Job plots by applying the method of continuous variations (see Supporting Information). Spectrophotometric titration experiments support that the sugar-containing species maintain the coordination mode throughout a pH between 7 and 13. The sugar-containing complexes dominate above pH 9 and undergo a second deprotonation, when the pH of the solution exceeds 10 (Figure 4).

The comparison of sugar coordination to the metal complexes **1**−**3** is facilitated when the number of species present is minimized. We therefore determined the binding strength of the carbohydrate complexes derived from complexes **1**−**3** at pH 12.40 from saturation isotherm plots (see Supporting Information and Table 1).[15]

All carbohydrate complexes derived from mononuclear copper(II) complex Cu(bpdpo) (**2**) show comparable apparent binding constants ($pK_{app} = -\log(K_{app})^{-1}$), which are typically about 0.5 order of magnitude larger than those derived from

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Table 1. Apparent Binding Constants (pK_{App}) for 1:1 Complexes Derived from **1**−**3** and **7**−**10** at pH 12.40 and 25 °C

	$pK_{app} \pm \Delta pK_{app}$[a]		
carbohydrate	Cu_2(bpdpo) (**1**)	Cu(bpdpo) (**2**)	Cu(paeo) (**3**)
D-ribose (**7**)	4.07 ± 0.02	3.49 ± 0.04	3.12 ± 0.03
D-mannose (**8**)	4.06 ± 0.03	3.44 ± 0.04	3.07 ± 0.03
D-glucose (**9**)	2.56 ± 0.03	3.66 ± 0.02	3.15 ± 0.02
D-maltose (**10**)	2.94 ± 0.03	3.55 ± 0.04	3.07 ± 0.05

[a] The error of the mean of the apparent binding constants ($pK_{app} = -\log(K_{app})^{-1}$) is given as 95% confidence limit determined from the standard deviation of 53 data points obtained from two independent measurements, using six different wavelengths between 600 and 700 nm each.

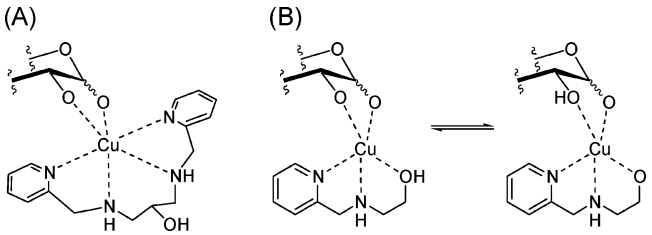

Figure 5. Proposed structures of carbohydrate complexes derived from **7**−**10** and (A) Cu(bpdpo) (**2**) as well as (B) Cu(paeo) (**3**) at pH 12.40 and 25 °C.

Cu(paeo) (**3**). The steric constraints of the pentadentate ligand bpdpo (**4**) do therefore not hamper the carbohydrate coordination capability of **2** and imply *chelation*, rather than monodentate coordination, to the metal complex. The bpdpo ligand **4** coordinates the metal center in tetradentate fashion (Figure 5A). In contrast, carbohydrate coordination to the mononuclear complex **3** may result in equilibrium structures, as both protonation and deprotonation of the tridentate ligand paeo (**5**) and of the carbohydrates **7**−**10** will occur under the conditions applied but cannot be discriminated experimentally (Figure 5B).

Evidence for a third deprotonation of the sugar−**3** complex is not provided by the spectrophotometric titration data nor supported by the pH-stat titration experiments of **3** with carbohydrate solution at pH 12.4. A similar coordination behavior between various carbohydrates and mononuclear copper(II) complexes has been observed earlier.[8]

On contrast to complexes **2** and **3**, the nature of complexation varies strongly for closely related carbohydrates upon coordination to dinuclear copper(II) complex **1** (Table 1, Figure 6).

D-Ribose (**7**) or D-mannose (**8**) chelate the *dinuclear* copper(II) complex **1** up to 1 order of magnitude stronger than that for **2** or **3**.[9] We demonstrated earlier that mononuclear copper(II) complexes form chelates with a sugar involving the sugar hydroxyl groups at C-1 and C-2.[8] Both copper(II) centers in a **7**−**1** or **8**−**1** complex will therefore participate in the sugar complexation.

The opposite is true for coordination of D-glucose (**9**) or glucose-derived disaccharide D-maltose (**10**). Here, the complex formation with the *mononuclear* complexes **2** or **3** is, presumably due to steric reasons, up to 1 order of magnitude stronger than coordination to **1**. The number of metal ions bound by the ligand bpdpo reverses the preference of sugar coordination. The use of multinuclear instead of mononuclear copper(II) complexes is therefore not generally superior for coordination of any biologically interesting carbohydrate. Multipoint interactions are only favorable for carbohydrates that enable coordination by a *cis*,*cis*-triol, such as **7** or **8**. Carbohydrates that chelate the metal complex with a *cis*-diol, such as **9**, enable strong coordination to mononuclear copper(II) complexes **2** or **3** only (Figure 6).

Conclusions

We investigated the coordination of selected carbohydrates to structurally closely related mono- and dinuclear copper(II) complexes Cu_2(bpdpo) (**1**), Cu(bpdpo) (**2**), and Cu(paeo) (**3**) in aqueous alkaline solution. Depending on the amount of metal ions provided, mononuclear copper(II) species related to **2** or **3** or dinuclear species related to **1** are formed and maintained in this molar ratio of ligand to copper(II) ions in a pH range from 7 to 13. All carbohydrates

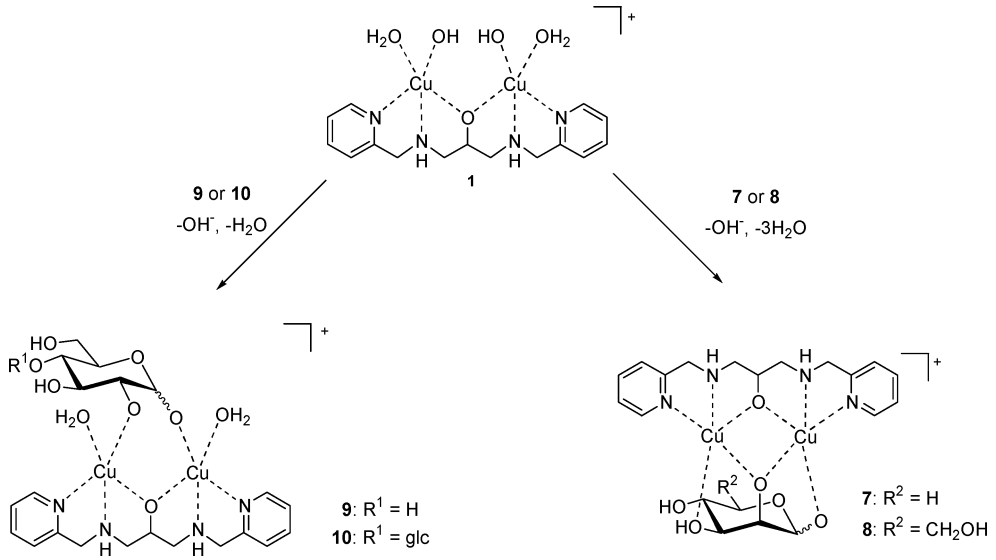

Figure 6. Proposed structures of the complexes derived from Cu_2(bpdpo) (**1**) and D-ribose (**7**), D-mannose (**8**), D-glucose (**9**), or D-maltose (**10**) at pH 12.40 and 25 °C.

investigated coordinate the metal complexes **1**−**3** in a 1:1 molar ratio. Sugar coordination to the mononuclear complex **2** is preferred over **3**. While D-mannose or D-ribose binding to the dinuclear complex **1** is favored over coordination to the mononuclear complexes, the binding preference is reversed for the glucose-type sugars **9** and **10**. As a large variety of biologically important saccharides are based on D-glucose, such as D-maltose, D-cellobiose, or D-lactose, while others are derived from D-ribose moieties, such as nucleosides and nucleotides, our results underline the importance of the appropriate choice of the metal complex for the preparation of carbohydrate-selective synthetic receptors. The preparation of such material and the evaluation of its sugar differentiation ability is a topic of current work.

Supporting Information Available: Representative plots for the characterization of complex formation between the sugars **7**−**10** and the metal complexes **1**−**3** including saturation isotherms, number of spectroscopic states, and Job plots as well as images of ^{1}H, ^{13}C NMR, IR, FAB-MS, and EI spectra for the characterization of mononuclear copper(II) complex **2** and the new compounds **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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