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Catechol oxidase model compounds based on aminocarbohydrates: new structure types and investigations on the catalytic reaction

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Abstract

Recently, we reported the structure and properties of several copper(II) complexes with aminocarbohydrate-based ligands. Four of these complexes are capable of catalyzing the oxidation of 3,5-di-^{t}butyl-catechol (dtbc) to the corresponding quinone. The present work contains new compounds of this ligand series of which most form different structure types than the previously described. Investigations on the influence of possible inhibitors like kojic and cinnamic acid, as well as simple ligands like chloride ions and of the pH-value on the catalytic reaction are investigated.

Keywords: Aminocarbohydrate; 3,5-Di-^{t}butyl-catechol; Lineweaver–Burk plot

1. Introduction

Copper proteins play an important role in the biological transport, storage, and activation of dioxygen [1]. One group of these enzymes are the type **3** copper proteins hemocyanine, catechol oxidase and tyrosinase, which transport and activate dioxygen. They all have an identical active site with two triple histidine coordinated copper atoms [2–4]. Our concept for the synthesis of functional model compounds for this site is to use tridentate ligands derived from the condensation of a β-ketoenolether with an aminocarbohydrate (or its derivative, Scheme 1).

Reaction with copper(II) ions leads to copper complexes, which are coordinatively unsaturated and show a high tendency towards oligomerization. The residuals R^1 and R^2 are known to be useful for regulating important properties like redox potential and Lewis acidity of the central metal atom. Recently, we published the synthesis, spectroscopic and magnetic properties of some of these complexes [5]. Scheme 2 gives an overview of all these compounds.

In a former paper it turned out that only complexes with the set of substituents $R^1 = CH_3$; $R^2 = COCH_3$ were active in the catalytic oxidation of 3,5-di-^{t}butyl-catechol (dtbc). In this paper, we synthesized substances with other sets of substituents (**c**–**f**, Scheme 2), and carried out further investigations on the catalytic reaction of the known complexes **Cu1a**–**4a**. Inhibition experiments with the competitive inhibitor cinnamic acid gave an interesting hint on the mechanism of the reaction. A simple additional ligand

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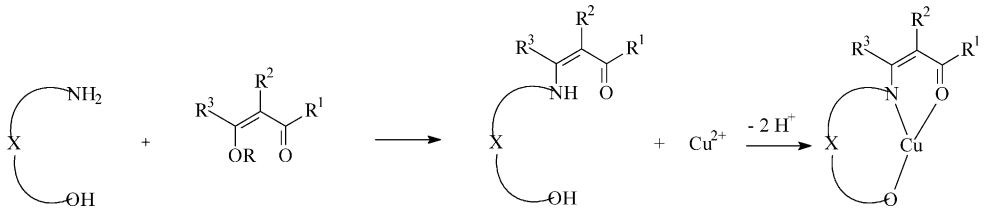
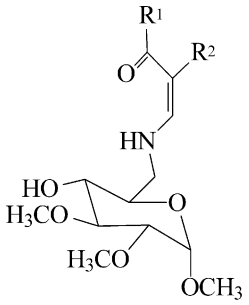


Scheme 1. Synthesis of coordinatively unsaturated copper complexes.



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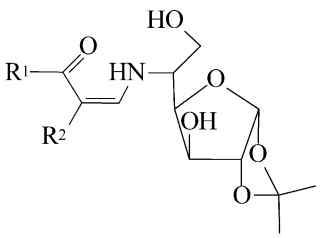

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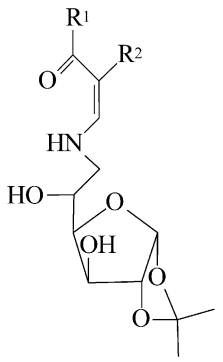

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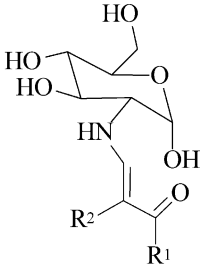

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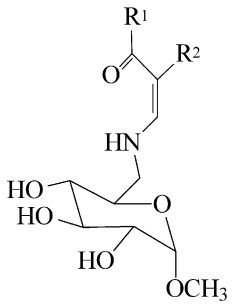

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a: $R^1 = CH_3$; $R^2 = COCH_3$
b: $R^1 = OC_2H_5$; $R^2 = CO_2C_2H_5$
c: $R^1 = CH_3$; $R^2 = CO_2C_2H_5$
d: $R^1 = CH_3$; $R^2 = H$
e: $R^1 = C_6H_5$; $R^2 = CO_2C_2H_5$
f: $R^1 = OC_2H_5$; $R^2 = CN$

Scheme 2. Overview of the ligands used in the present work.

like chloride ions may either inhibit or enhance the catalytic ability of the compounds by possible structural changes or by competitivity with the substrate. As the catechol oxidation to the corresponding *o*-quinone produces four protons, which are transferred to the dioxygen to form water, the reaction is sensible to the pH-value of the solution. Therefore, all investigations on the catalytic activity are carried out under the same circumstances to guarantee the comparability of the obtained results. In our case, we found out that the structure of one our catalysts is pH-dependent. **Cu3a**, which has the highest catecholase-like activity, has a dinuclear structure. A little additional base leads to a partly triple deprotonated ligand which is tetradentate and forms higher clusters. For all other combinations of substituents $R^{1,2}$, no dinuclear structure is found. Instead, different cluster compounds can be detected, the structure depending strongly on the substituents. This dependence of the compounds structure is also found for the compounds of types **1** and **5**, leading to either trinuclear $[Cu_3L_3]$ or $[Cu_3L_2(OAc)_2]$ or dinuclear $[Cu_2L_2]$ species. Nevertheless, activity can be found for all of this compounds. Structure-reactivity relationships are revealed.

2. Experimental

2.1. Procedures in kinetic measurements

All kinetic measurements were carried out in methanol due to the good solubility of the used substances. For detection of the reaction, the intense absorption of the resulting quinone (400 nm, $\varepsilon = 1900\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) was used. Blind measurements without the presence of a possible catalyst and in presence of the copper acetate monohydrate used for complex synthesis were carried out. The copper acetate measurement was used to decide if a complex shows activity or not. Therefore, a 10^{-4} M solution of the complex was made and 50 equivalents of di-^{t}butyl-catechol were added. The spectra were recorded every 2 min. In a repeated experiment, the slope of the absorption at 400 nm against time was recorded. The initial rate obtained from this slope was compared to the rate of copper acetate. Only for those complexes with higher rates, further investigations took place. At first, the above named amount of dtbc was added to different concentrations of the catalysts between 2×10^{-4} and 2×10^{-5} M (lower activity) or between 5×10^{-5} and 5×10^{-6} M (higher activity) to determine the kinetic behavior towards the variation of the catalyst concentration. To determine the rate constants for the variation of the substrate concentration, the amount of dtbc was varied to find out the region of concentration were saturation is observed. The initial rates of the reaction were obtained leading to a Lineweaver–Burk plot. To reduce the statistic error, every measurement was carried out at least three times, only measurements were taken into account where the discrepancy value of the linear fit was at least 0.985.

2.2. Inhibition experiments with cinnamic acid (*Cu1a*, *Cu3a*, *Cu4a*)

All inhibition experiments were carried out using a catalyst concentration of $1 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$. The first part of the investigations was the measurement of the inhibition curve. Therefore, each 2 ml of the catalyst solution were mixed with each 100, 90, 80, 70, 60, 50, 40, 30, 20 and 10 μl of a ca. 1×10^{-2} M[a] and of a ca. 1×10^{-3} M[a] solution of cinnamic acid which contains also $1 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ of the catalyst. The reaction with 3,5-di-^{t}butyl-catechol was monitored as a time-dependent slope for 5 min (s.a.) and the rates were determined. In a second part, the substrate (dtbc) concentration war varied at different constant inhibitor concentration and constant catalyst concentration. This measurements were carried out using the procedure described under “kinetic measurements” and interpreted on the base of the Michaelis–Menten model.

2.3. Preparation of the substances

The ligands of the types **1**, **2**, **4** and **5** bind to copper(II) ions as dianions, under deprotonation of the enaminic and one hydroxo group. In the compounds of type **3**, the second hydroxo group may be deprotonated as well, both di- and trianions are found in the complexes. Therefore the number of hydrogens is not taken into regard for the naming of the compounds, i.e. “**Cu3a**” means the copper complex with the deprotonated ligands, though **3a** is the neutral ligand. For copper compounds prepared with copper chloride instead of acetate a “Cl” is added, e.g. “**Cu5bCl**”.

The synthesis of the following compounds were already published: **Cu2a–f** [5,6b], **Cu1a**, **b** [5], **Cu3a**, **b**, **Cu3a′**, **Cu3e** [5,6a], **Cu4a–c** [5]. The synthesis of the type **3** compounds, however is described below in order to compare with other type **3** compounds.

2.3.1. General procedure for the synthesis of the ligands

One equivalent of the aminocarbohydrate was dissolved in methanol and mixed with 1.5 equivalent of triethylamine and 1 equivalent of corresponding the β-ketoenolether compound. After stirring of 2–24 h at room temperature, if no starting material was detected by TLC (silica gel, solvent see below), the solvent was evaporated. The crude product was cleaned by columnar chromatography or—if possible—recrystallized from suitable solvents.

2.3.2. General procedure for the synthesis of the copper complexes with copper acetate

0.5 mmol of the ligand and 1.0 mmol triethylamine were dissolved in 50 ml of methanol and 0.5 mmol of copper(II) acetate monohydrate were added. After stirring 24 h at room temperature and evaporation to dryness, the crude product was cleaned by extraction with different solvents (if none other mentioned with toluene). This solvent was evaporated to dryness and the complex was recrystallized (if possible) from the below mentioned solvents.

2.3.3. General procedure for the synthesis of the copper complexes with copper chloride

0.5 mmol of the ligand and 1.0 mmol triethylamine were dissolved in 50 ml tetrahydrofurane and 0.5 mmol copper(II) chloride were added. After 24 h at room temperature (under stirring), the precipitate was filtered off, the solution evaporated to dryness. The crude product was recrystallized from different solvents (see below).

*2.3.3.1. 6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranosid **(1a)**.* Procedure A. RF 0.27 (ethyl acetate). IR (ATR): [cm^{-1}] = 3488w, 2909w, 2833vw, 1662w, 1610vs, 1447w, 1396s, 1312s, 1251s, 1193w, 1151s, 1051vs, 980s, 749vs, 673vs. ^{1}H-NMR: δ [ppm]: 2.22; 2.44 (2s, 6H, 2 × CH_3); 2.89 (OH); 3.20 (dd, 9.45 Hz, 1H, H-2); 3.23 (dd, 1H, H-6′); 3.35; 3.70 (m, 4H + 3·OCH_3, H-3, H-4, H-5, H-6); 3.37; 3.46; 3.59 (3s, 9H, OCH_3); 4.81 (d, 3.50 Hz, 1H, H-1); 7.74 (d, 13.2 Hz, 1H, =CH–); 11.02 (td, 1H, NH). ^{13}C-NMR: δ [ppm]: 27.21; 31.83 (CH_3); 50.75; 55.42; 58.43 (OCH_3); 61.24 (C-6); 69.66 (C-5); 70.73 (C-4); 81.81 (C-3); 82.50 (C-2); 97.59 (C-1); 111.6 (=C<); 160.87 (=CH–); 194.49; 200.39 (C=O). UV-Vis (methanol): λ_{max}: 256 nm ($\log \varepsilon$ = 3.7421), 290 nm ($\log \varepsilon$ = 3.8200). MS (DCI with H_2O): *m/z*: 332 [M + 1]. Anal. calcd. for $C_{15}H_{25}NO_7$ (M = 331.37 g/mol): C, 54.37; H, 7.60; N, 4.23. Found: C, 53.94; H, 7.74; N, 3.94.

*2.3.3.2. 6-N-(2′,2′-Diethoxycarbonylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranosid **(1b)**.* Procedure A. IR (ATR): [cm^{-1}] = 3436w, 3283w, 2981w, 2907w, 2835w, 1712w, 1684s, 1656s, 1642s, 1608s, 1427w, 1376w, 1345w, 1293w, 1215s, 1155s, 1138s, 1049vs, 1020vs, 959w, 901w, 803s, 746w, 671w. ^{1}H-NMR: δ [ppm]: 1.21–1.32 (m, 6H, 2 × CH_3); 2.82 (OH); 3.19 (dd, 9.43 Hz, 1H, H-2); 3.29 (dd, 1H, H-6′); 3.37–3.72 (m, 4H + 3·OCH_3, H-3, H-4, H-5, H-6); 3.35; 3.45; 3.59 (3s, 9H, OCH_3); 4.10–4.24 (m, 4H, 2 × CH_2); 4.80 (d, 3.51 Hz, 1H, H-1); 7.98 (d, 14.0 Hz, 1H, =CH–); 9.27 (td, 1H, NH). ^{13}C-NMR: δ [ppm]: 14.30; 14.40 (CH_3); 50.15; 55.28; 58.41 (OCH_3); 59.60; 59.75 (CH_2); 60.34 (C-6); 69.84 (C-5); 70.58 (C-4); 81.79 (C-3); 82.61 (C-2); 90.05 (=C<); 97.45 (C-1); 160.71 (=CH–); 166.21; 169.14 (C=O). UV-Vis (methanol): λ_{max}: 279 nm ($\log \varepsilon$ = 4.6943), 222 nm ($\log \varepsilon$ = 4.1786). MS (DCI with H_2O): *m/z*: 392 [M + 1]. Anal. calcd. for $C_{17}H_{29}NO_9$ (M = 391.18 g/mol): C, 52.17; H, 7.47; N, 3.58. Found: C, 52.43; H, 7.59; N, 3.56.

*2.3.3.3. 6-N-(2′-Acetyl-2′-ethoxycarbonylvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranosid **(1c)**.* Procedure A. IR (ATR): [cm^{-1}] = 3437w, 2984w, 2937w, 2907w, 2834w, 1692s, 1633vs, 1580s, 1417s, 1364s, 1300s, 1239s, 1192s, 1155s, 1051vs, 1019vs, 958s, 900w, 808w, 746w, 669w. ^{1}H-NMR: δ [ppm]: *trans-form*: 1.22 (t, 3H, CH_3); 1.97 (s, 3H, CH_3); 3.14–3.17 (9.40 Hz, 1H, H-2); 3.33–3.61 (m, 5H + 3·OCH_3, H-3, H-4, H-5, H-6, H-6′); 3.33; 3.42; 3.56 (3s, 9H, OCH_3); 4.04–4.14 (q, 4H, CH_2); 4.77 (d, 3.52 Hz, 1H, H-1); 7.94 (d, 13.6 Hz, 1H, =CH–); 10.99 (td, 6.64 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form:* 14.41; 30.77 (CH_3); 50.45 (CH_2); 55.23; 58.36; 61.13 (OCH_3); 59.45 (C-6); 69.63

(C-5); 70.54 (C-4); 81.68 (C-3); 82.82 (C-2); 97.43 (C-1); 100.43 (=C<); 161.36 (=CH-); 167.80; 199.14 (C=O). *cis-form*: 14.30; 30.77 (CH_3); 50.24 (CH_2); 55.27; 58.40; 61.13 (OCH_3); 59.58 (C-6); 69.63 (C-5); 70.40 (C-4); 81.68 (C-3); 82.64 (C-2); 97.43 (C-1); 100.61 (=C<); 159.33 (=CH-); 168.75; 198.96 (C=O). UV-Vis (ethanol): λ_{max}: 294 nm ($\log \varepsilon$ = 4.1822), 234 nm ($\log \varepsilon$ = 4.1446). MS (DCI with H_2O): m/z = 2100: 362 (100%) [$M+1$]. Anal. calcd. for $C_{16}H_{27}NO_8$ (M = 361.17 g/mol): C, 53.21; H, 7.53; N, 3.88. Found: C, 52.94; H, 7.88; N, 3.82.

*2.3.3.4. 6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranosid (**1d**).* Procedure A. IR (ATR): [cm^{-1}] = 3260w, 2988vw, 2908w, 2833w, 1639vs, 1551vs, 1492s, 1445w, 1360w, 1281w, 1256w, 1195w, 1154w, 1047vs, 1021vs, 958s, 902w, 743s, 667w. ^{1}H-NMR: δ [ppm]: *cis-form:* 1.99 (s, 3H, CH_3); 3.12 (dd, 9.39 Hz, 1H, H-2); 3.17–3.54 (m, 5H + 3·OCH_3, H-3, H-4, H-5, H-6, H-6′); 3.31; 3.40; 3.54 (3 s, 9H, OCH_3); 4.90 (d, 7.33 Hz, 1H, CH); 4.74 (d, 3.51 Hz, 1H, H-1); 6.61 (dd, 12.8 Hz, 1H, =CH–); 9.75 (td, 6.24 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *cis-form:* 28.75 (CH_3); 49.21; 55.05; 61.03 (OCH_3); 58.33 (C-6); 70.37 (C-5); 70.32 (C-4); 81.61 (C-3); 82.74 (C-2); 93.86 (CH); 97.22 (C-1); 153.27 (=CH–); 197.35 (C=O). MS (DCI with H_2O): *m*/*z*: 290 (100%) [M + 1]. Anal. calcd. for $C_{13}H_{23}NO_6$ (M = 289.15 g/mol): C, 54.00; H, 8.02; N, 4.84. Found: C, 54.11; H, 8.02; N, 4.79.

*2.3.3.5. 6-N-(2′-Benzoyl-2′-ethoxycarbonylvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranosid (**1e**).* Procedure A. IR (ATR): [cm^{-1}] = 3437w, 3310w, 3056vw, 2984w, 2937w, 2905w, 2834w, 1668vs, 1623vs, 1446w, 1424w, 1376w, 1306w, 1217w, 1154w, 1049s, 1019s, 958w, 808w, 785w, 727w, 699s, 666w, 615w. ^{1}H-NMR: δ [ppm]: *trans-form*: 0.85 (t, 3H, CH_3); 3.18 (dd, 9.40 Hz, 1H, H-2); 3.23–3.65 (m, 5H + 3·OCH_3, H-3, H-4, H-5, H-6, H-6′); 3.38; 3.45; 3.58 (3s, 9H, OCH_3); 3.91 (q, 2H, CH_2); 4.81 (d, 3.53 Hz, 1H, H-1); 7.24–7.53 (m, 5H, aromat.); 8.02 (d, 13.8 Hz, 1H, =CH–); 10.55 (td, 7.00 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 13.71 (CH_3); 50.37 (CH_2); 55.34; 58.43; 61.21 (OCH_3); 59.63 (C-6); 69.58 (C-5); 70.52 (C-4); 81.66 (C-3); 82.58 (C-2); 97.44 (C-1); 100.28 (=C<); 126.9–142.4 (C_{aromat}); 160.91 (=CH–); 169.04; 196.04 (C=O). *cis-form*: 13.55 (CH_3); 50.06 (CH_2); 55.34; 58.43; 61.21 (OCH_3); 59.27 (C-6); 69.70 (C-5); 70.45 (C-4); 81.66 (C-3); 82.58 (C-2); 97.44 (C-1); 100.28 (=C<); 126.9–142.4 (C_{aromat}); 160.63 (=CH–); 169.07; 194.15 (C=O). UV-Vis (ethanol): λ_{max}: 304 nm ($\log \varepsilon$ = 4.0340), 245 nm ($\log \varepsilon$ = 3.9679). MS (DCI with H_2O): *m*/*z*: 424 (100%) [M + 1]. Anal. calcd. for $C_{21}H_{29}NO_8$ (M = 423.19 g/mol): C, 59.60; H, 6.91; N, 3.31. Found: C, 59.89; H, 6.90; N, 3.19.

*2.3.3.6. 6-N-(2′-Ethoxycarbonyl-2′-nitrilvinyl)amino-1,2,3-O-trimethyl-6-deoxy-α-D-glucopyranosid (**1f**).* Procedure A. IR (ATR): [cm^{-1}] = 3457w, 3294w, 3234w, 2984w, 2937w, 2905w, 2835w, 2210s, 1677vs, 1622vs, 1465w, 1445w, 1428w, 1377w, 1345w, 1295w, 1241s, 1178w, 1153w, 1049s, 1018s, 957w, 902w, 843w, 784s, 731s, 616w. ^{1}H-NMR: δ [ppm]: *cis-form*: 1.29 (t, 3H, CH_3); 3.18 (dd, 9.21 Hz, 1H, H-2); 3.21–3.62 (m, 5H + 3·OCH_3, H-3, H-4, H-5, H-6, H-6′); 3.37; 3.47; 3.60 (3s, 9H, OCH_3); 4.18 (q, 2H, CH_2); 4.82 (d, 3.45 Hz, 1H, H-1); 7.34 (d, 13.9 Hz, 1H, =CH–); 9.01 (td, 6.85 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 14.74 (CH_3); 50.26 (CH–); 55.87; 60.78; 61.62 (OCH_3); 58.93 (C-6); 69.99 (C-5); 70.73 (C-4); 82.07 (C-3); 82.84 (C-2); 97.96 (C-1); 71.93 (=C<); 160.70 (=CH–); 168.24 (C=O). *cis-form*: 14.66 (CH_3); 49.95 (CH_2); 55.78; 60.95; 61.13 (OCH_3); 58.88 (C-6); 69.99 (C-5); 70.68 (C-4); 82.07 (C-3); 82.78 (C-2); 97.92 (C-1); 73.60 (=C<); 160.36 (=CH–); 162.51 (C=O). UV-Vis (methanol): λ_{max}: 282 nm ($\log \varepsilon$ = 4.3626), 202 nm ($\log \varepsilon$ = 4.1354). MS (DCI with H_2O): *m*/*z*: 345 (100%) [$M+1$]. Anal. calcd. for $C_{15}H_{24}N_2O_7$ (M = 344.16 g/mol): C, 52.35; H, 7.03; N, 8.14. Found: C, 51.81; H, 7.02; N, 7.85.

*2.3.3.7. 6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3a**).* Procedure A. mp 152 °C. [α] 29.3° (c1, methanol). IR (ATR): [cm^{-1}] = 3412s, 3284s, 2996w, 2948w, 2930w, 2888w, 1650vs, 1603vs, 1457vw, 1401vs, 1322s, 1255s, 1221s, 1190vw, 1163vw, 1128vw, 1087w, 1057w, 1001s, 978s, 939w, 847w, 788s, 669vw, 616w. ^{1}H-NMR: δ [ppm]: 1.25; 1.38 (6H, C-(CH_3)$_2$); 2.21; 2.37 (6H, 2 × CH_3); 3.43 (dd, 6.40 Hz, 1H, H-6′); 3.66 (dd, 13.2 Hz, 1H, H-6); 3.90 (s, 1H, H-4); 4.04 (s, 1H, H-5); 4.30 (s, 1H, H-3); 4.49 (d, 1H, H-2);

5.87 (d, 3.40 Hz, 1H, H-1); 7.81 (d, 13.4 Hz, 1H, =CH–); 10.97 (dt, 6.64 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: 26.11; 26.63 (CMe_2); 27.10; 31.83 (CH_3); 53.51 (C-6); 67.84 (C-5); 80.34 (C-4); 74.20 (C-3); 85.18 (C-2); 104.97 (C-1); 111.37 (CMe_2); 111.87 (=C<); 161.73 (=CH–); 195.71; 200.68 (C=O). UV-Vis (methanol): λ_{max}: 294 nm ($\log \varepsilon = 4.3173$), 260 nm ($\log \varepsilon = 4.2498$). MS (DCI with H_2O): *m/z*: 330 $[M + 1]^+$. Anal. calcd. for $C_{15}H_{23}NO_7$ (M = 329.35 g/mol): C, 54.70; H, 7.04; N, 4.25. Found: C, 54.59; H, 7.09; N, 4.22.

*2.3.3.8. 6-N-(2′,2′-Diethoxycarbonylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3b**).* Procedure A. mp 55 °C. IR (ATR): [cm^{-1}] = 3438s, 3294w, 2983s, 2937w, 1716w, 1655vs, 1608vs, 1424vw, 1376vw, 1346vw, 1210s, 1164w, 1066s, 1009s, 955vw, 883vw, 855vw, 801w, 753vw, 642vw, 617vw. ^{1}H-NMR: δ [ppm]: 1.20–1.50 (12H, 4 × CH_3); 3.39 (m, 1H, H-6′); 3.60 (m, 1H, H-6); 3.85–4.30 (4H, 2 × CH_2); 3.95 (m, 1H, H-4); 3.97 (s, 1H, H-5); 4.33 (s, 1H, H-3); 4.48 (d, 1H, H-2); 5.88 (d, 3.56 Hz, 1H, H-1); 7.98 (d, 14.3 Hz, 1H, =CH–); 9.26 (dt, 6.12 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: 14.09; 14.27 (CH_3); 26.16; 26.72 (CMe_2); 59.88; 59.92 (CH_2); 53.08 (C-6); 68.39 (C-5); 80.72 (C-4); 74.43 (C-3); 85.12 (C-2); 105.07 (C-1); 111.82 (CMe_2); 89.35 (=C<); 160.69 (=CH–); 168.81; 171.25 (C=O). UV-Vis (methanol): λ_{max}: 278 nm ($\log \varepsilon = 4.2105$), 223 nm ($\log \varepsilon = 4.3512$). MS (DCI with H_2O): *m/z*: 390 $[M + 1]^+$. Anal. calcd. for $C_{17}H_{27}NO_9$ (M = 389.40 g/mol): C, 52.44; H, 6.99; N, 3.60. Found: C, 52.02; H, 7.22; N, 3.06.

*2.3.3.9. 6-N-(2′-Acetyl-2′-ethoxycarbonylvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3c**).* Procedure A, colorless, viscous oil. IR (ATR): [cm^{-1}] = 3436w, 2985w, 2936w, 1691s, 1670s, 1631vs, 1568s, 1424s, 1380s, 1300s, 1249s, 1195s, 1163w, 1065s, 1008s, 853w, 790w, 665w. MS (DCI with H_2O): m/z = 2100: 360 $[M + 1]^+$. ^{1}H-NMR: δ [ppm]: *trans-form*: 1.23–2.41 (12 H, 4 × CH_3); 3.39 (m, 1H, H-6′); 3.62 (m, 1H, H-6); 4.15 (2H, CH_2); 3.94 (m, 1H, H-5); 4.05 (s, 1H, H-4); 4.32 (s, 1H, H-3); 4.50 (d, 1H, H-2); 5.89 (d, 3.56 Hz, 1H, H-1); 8.01 (d, 13.9 Hz, 1H, =CH–); 10.93 (dt, 6.92 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: 14.41; 30.62 (CH_3); 26.20; 26.81 (CMe_2); 59.78 (CH_2); 53.54 (C-6); 68.50 (C-5); 80.53 (C-4); 74.49 (C-3); 85.28 (C-2); 105.06 (C-1); 111.96 (CMe_2); 100.57 (=C<); 161.13 (=CH–); 168.90; 200.12 (C=O). UV-Vis (ethanol): λ_{max}: 294 nm ($\log \varepsilon = 4.2846$), 235 nm ($\log \varepsilon = 4.2500$). Anal. calcd. for $C_{16}H_{25}NO_8$ (M = 359.38 g/mol): C, 53.51; H, 7.02; N, 3.90. Found: C, 53.20; H, 6.98; N, 3.93.

*2.3.3.10. 6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3d**).* Procedure A. IR (ATR): [cm^{-1}] = 3374w, 3254w, 2986w, 2937w, 1639vs, 1550vs, 1496s, 1445w, 1375s, 1253s, 1213s, 1164s, 1067vs, 1007vs, 955s, 883w, 855w, 787w. ^{1}H-NMR: δ [ppm]: *cis-form*: 1.27; 1.43; 2.00 (9H, 3 × CH_3); 3.32 (m, 1H, H-6′); 3.51 (m, 1H, H-6); 3.90 (m, 1H, H-5); 3.97 (s, 1H, H-4); 4.33 (s, 1H, H-3); 4.50 (d, 1H, H-2); 4.97 (d, 7.23 Hz, 1H, CH); 5.89 (d, 3.42 Hz, 1H, H-1); 6.74 (d, 13.1 Hz, 1H, =CH–); 9.80 (dt, 6.30 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: 28.58 (CH_3); 26.23; 26.81 (CMe_2); 52.85 (C-6); 68.51 (C-5); 80.97 (C-4); 74.19 (C-3); 85.29 (C-2); 94.02 (CH); 105.12 (C-1); 111.73 (CMe_2); 154.52 (=CH–); 197.93 (C=O). UV-Vis (ethanol): λ_{max}: 300 nm ($\log \varepsilon = 4.2240$). MS (DCI with H_2O): *m/z*: 288 $[M + 1]^+$. Anal. calcd. for $C_{13}H_{21}NO_6$ (M = 287.31 g/mol): C, 54.38; H, 7.37; N, 4.88. Found: C, 54.04; H, 7.20; N, 4.72.

*2.3.3.11. 6-N-(2′-Ethoxycarbonyl-2′-benzoylvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3e**).* Procedure A. RF 0.1 (ethyl acetate/hexane 1:1). Yield: 76%. [α] 3.31° (c1, methanol). IR (ATR): [cm^{-1}] = 3434s, 2985w, 2940w, 2900vw, 1666vs, 1623vs, 1422s, 1376s, 1309s, 1211s, 1163vw, 1068s, 1006vs, 853s, 783vs, 697vs, 667vs, 614s. ^{1}H-NMR: δ [ppm]: *trans-form*: 0.86 (t, 3H, CH_3); 1.20; 1.37 (6H, CMe_2); 3.42 (m, 1H, H-6′); 3.55 (m, 1H, H-6); 3.54 (q, 2H, CH_2); 3.92 (m, 1H, H-5); 3.95 (s, 1H, H-4); 4.23 (s, 1H, H-3); 4.36 (d, 1H, H-2); 5.80 (d, 3.66 Hz, 1H, H-1); 7.20–7.46 (m, 5H, H_{aromat}) 8.02 (d, 14.1 Hz, 1H, =CH–); 10.51 (dt, 6.85 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 14.17 (CH_3); 26.61; 27.18 (CMe_2); 60.33 (CH_2); 53.91 (C-6); 68.63 (C-5); 81.05 (C-4); 74.77 (C-3); 85.58 (C-2); 105.46 (C-1); 100.58 (=C<); 112.28 (CMe_2); 127.40; 128.00; 130.45; 142.62 (C_{aromat}); 161.72 (=CH-); 168.68; 196.98 (C=O). *cis-form*: 14.03 (CH_3); 26.61; 27.18 (CMe_2); 60.08 (CH_2); 53.47 (C-6); 68.75 (C-5);

81.05 (C-4); 74.77 (C-3); 85.58 (C-2); 105.46 (C-1); 100.63 (=C<); 112.31 (CMe_2); 128.16; 128.66; 131.34; 141.65 (C_{aromat}); 161.72 (=CH–); 169.46; 196.01 (C=O). UV-Vis (ethanol): λ_{max}: 320 nm ($\log \varepsilon = 4.4517$), 299 nm ($\log \varepsilon = 4.4810$). MS (DCI with H_2O): *m/z*: 422 $[M + 1]^+$. Anal. calcd. for $C_{21}H_{27}NO_8$ ($M = 421.45$ g/mol): C, 59.85; H, 6.46; N, 3.32. Found: C, 59.35; H, 6.70; N, 3.17.

*2.3.3.12. 6-N-(2′-Ethoxycarbonyl-2′-nitrilvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranose (**3f**).* Procedure A. IR (ATR): [cm^{-1}] = 3398w, 3314w, 3234w, 2984w, 2940w, 2900w, 2218s, 1673vs, 1622vs, 1413s, 1376s, 1328s, 1245s, 1168s, 1069s, 1003s, 877s, 785s, 649w. ^{1}H-NMR: δ [ppm]: *cis-form*: 1.27–1.46 (9H, CMe_2, CH_3); 3.44 (m, 1H, H-6′); 3.61 (m, 1H, H-6); 3.96 (m, 1H, H-5); 4.03 (s, 1H, H-4); 4.18 (q, 2H, CH_2); 4.32 (s, 1H, H-3); 4.50 (d, 1H, H-2); 5.91 (d, 3.58 Hz, 1H, H-1); 7.39 (d, 14.0 Hz, 1H, =CH–); 9.08 (dt, 6.92 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: 14.70 (CH_3); 27.15; 26.61 (CMe_2); 53.04 (C-6); 61.17 (CH_2); 68.84 (C-5); 71.53 (=C<); 80.42 (C-4); 74.96 (C-3); 85.64 (C-2); 105.38 (C-1); 112.56 (CMe_2); 119.70 (CN); 160.89 (=CH–); 168.31 (C=O). UV-Vis (methanol): λ_{max}: 204 nm ($\log \varepsilon = 4.0902$), 282 nm ($\log \varepsilon = 4.3540$). MS (DCI with H_2O): *m/z*: 343 $[M+1]^+$. Anal. calcd. for $C_{15}H_{22}N_2O_7$ ($M = 342.35$ g/mol): C, 52.66; H, 6.48; N, 8.19. Found: C, 52.38; H, 6.51; N, 8.02.

*2.3.3.13. Methyl-6-N-(2′,2′-diacetylvinyl)amino-6-deoxy-α-*D*-glucopyranosid (**5a**).* Procedure A. RF 0.43 (ethyl acetate/methanol 2:1). IR (ATR): [cm^{-1}] = 3344s, 2996w, 2909w, 2841w, 1729vw, 1650w, 1605vs, 1445w, 1393s, 1357s, 1307s, 1248w, 1191w, 1143w, 1043s, 982s, 935w, 897w, 811w, 753w, 671s, 615w. ^{1}H-NMR: δ [ppm]: 2.29; 2.43 (2s; 6H, 2 × CH_3); 3.39 (OCH_3); 3.58 (dd, 6.34 Hz, 1H, H-6′); 3.84 (dd, 13.2 Hz, 1H, H-6); 3.68 (m, 2.71 Hz, 1H, H-5); 3.63 (dd, 9.86 Hz, 1H, H-4); 3.18 (dd, 9.36 Hz, 1H, H-3); 3.42 (dd, 9.70 Hz, 1H, H-2); 4.73 (d, 3.75 Hz, 1H, H-1); 8.12 (s, 1H, =CH–). ^{13}C-NMR: δ [ppm]: 25.65; 30.45 (CH_3); 54.27 (OCH_3); 50.18 (C-6); 70.24 (C-5); 71.29 (C-4); 72.05 (C-3); 73.48 (C-2); 100.05 (C-1); 110.61 (=C<); 162.34 (=CH–); 196.41; 200.15 (C=O). UV-Vis (methanol): λ_{max}: 290 nm ($\log \varepsilon = 4.2552$), 255 nm ($\log \varepsilon = 4.1891$). MS (DEI): *m/z*: 303 [M]. Anal. calcd. for $C_{13}H_{21}NO_7 \cdot H_2O$ ($M = 321.33$ g/mol): C, 48.60; H, 7.17; N, 4.36. Found: C, 48.97; H, 7.46; N, 4.12.

*2.3.3.14. Methyl-6-N-(2′,2′-diethoxycarbonylvinyl)-amino-6-deoxy-α-*D*-glucopyranosid (**5b**).* Procedure A. RF 0.60 (ethyl acetate/methanol 2:1). IR (ATR): [cm^{-1}] = 3383s, 3290s, 2981w, 2933w, 2906w, 2841w, 1712w, 1655vs, 1635vs, 1607vs, 1427w, 1377w, 1345w, 1302w, 1217s, 1139w, 1041s, 1004s, 897w, 801s, 751w, 672w, 616w. ^{1}H-NMR: δ [ppm]: 1.28; 1.32 (2s; 6H, 2 × CH_3); 3.39 (OCH_3); 3.53 (dd, 6.57 Hz, 1H, H-6′); 3.77 (dd, 13.3 Hz, 1H, H-6); 3.59 (m, 2.12 Hz, 1H, H-5); 3.63 (dd, 9.55 Hz, 1H, H-4); 3.19 (dd, 8.90 Hz, 1H, H-3); 3.42 (dd, 9.65 Hz, 1H, H-2); 4.16; 4.21 (2q, 4H, CH_2); 4.72 (d, 3.74 Hz, 1H, H-1); 8.13 (s, 1H, =CH–). ^{13}C-NMR: δ [ppm]: 13.01; 13.38 (CH_3); 54.22 (OCH_3); 59.23; 59.33 (CH_2); 49.79 (C-6); 70.54 (C-5); 71.24 (C-4); 72.07 (C-3); 73.52 (C-2); 100.00 (C-1); 88.75 (=C<); 160.64 (=CH-); 166.83; 168.58 (C=O). UV-Vis (methanol): λ_{max}: 279 nm ($\log \varepsilon = 4.8409$), 223 nm ($\log \varepsilon = 4.5783$). MS (DEI): *m/z*: 363 [M]. Anal. calcd. for $C_{15}H_{25}NO_9 \cdot H_2O$ ($M = 381.38$ g/mol): C, 47.24; H, 7.09; N, 3.67. Found: C, 48.34; H, 7.26; N, 3.58.

*2.3.3.15. Methyl-6-N-(2′-acetyl-2′-ethoxycarbonyl-vinyl)amino-6-deoxy-α-*D*-glucopyranosid (**5c**).* Procedure A. IR (ATR): [cm^{-1}] = 3375s, 2984w, 2932w, 2901w, 2841w, 1691s, 1672s, 1631vs, 1569s, 1417s, 1364s, 1300s, 1241s, 1192s, 1139w, 1044vs, 1006vs, 897w, 805w, 754w, 670w. ^{1}H-NMR: δ [ppm]: *trans-form*: 1.21 (t; 3H, CH_3); 2.37 (s, 3H, CH_3); 3.28 (OCH_3); 3.19–3.71 (m, 6H + 1·OCH_3, H-6′, H-6, H-5, H-4, H-3, H-2); 4.12 (q, 2H, CH_2); 4.66 (d, 3.55 Hz, 1H, H-1); 7.94 (d, 13.73 Hz, 1H, =CH–); 10.94 (td, 6.83 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 14.86; 31.24 (CH_3); 55.74 (OCH_3); 60.24 (CH_2); 50.84 (C-6); 70.28 (C-5); 71.29 (C-4); 72.25 (C-3); 74.37 (C-2); 99.96 (C-1); 100.86 (=C<); 161.54 (=CH–); 167.73; 200.07 (C=O). *cis-form*: 14.74; 31.24 (CH_3); 55.74 (OCH_3); 60.10 (CH_2); 50.85 (C-6); 70.50 (C-5); 71.79 (C-4); 72.25 (C-3); 74.37 (C-2); 99.96 (C-1); 100.82 (=C<); 161.54 (=CH–); 167.84; 199.98 (C=O). UV-Vis (methanol): λ_{max}: 234 nm ($\log \varepsilon = 4.2076$), 294 nm ($\log \varepsilon = 4.2481$). MS (DEI): *m/z*: 333 (100%) $[M + 1]$. Anal. calcd. for $C_{14}H_{23}NO_8$ ($M = 333.34$ g/mol): C, 50.45; H, 6.95; N, 4.20. Found: C, 49.52; H, 7.19; N, 4.05.

*2.3.3.16. Methyl-6-N-(2′-acetylvinyl)amino-6-deoxy-α-D-glucopyranosid (**5d**).* Procedure A. RF 0.43 (ethyl acetate/methanol 2:1). IR (ATR): [cm^{-1}] = 3300s, 3004vw, 2912w, 2841vw, 1638vs, 1543vs, 1495s, 1445w, 1357w, 1254w, 1192w, 1144w, 1106w, 1041vs, 1005vs, 899w, 751w, 670w, 617w. ^{1}H-NMR: δ [ppm]: *cis-form*: 2.02 (s, 3H, CH_3); 3.39 (OCH_3); 3.17 (dd, 8.97 Hz, 1H, H-3); 3.42 (dd, 9.59 Hz, 1H, H-2); 3.35–3.70 (m, 4H, H-6′, H-6, H-5, H-4); 5.05 (d, 7.29 Hz, 1H, CH); 4.70 (d, 3.72 Hz, 1H, H-1); 6.91 (d, 13.73 Hz, 1H, =CH–). ^{13}C-NMR: δ [ppm]: *cis-form*: 27.11 (CH_3); 54.23 (OCH_3); 49.12 (C-6); 71.15 (C-5); 72.06 (C-4); 73.57 (C-2); 99.91 (C-1); 93.07 (CH); 154.52 (=CH–); 197.51 (C=O). UV-Vis (methanol): λ_{max}: 298 nm ($\log \varepsilon$ = 4.7475). MS (DEI): *m/z*: 261 [M]. Anal. calcd. for $C_{11}H_{19}NO_6 \cdot H_2O$ (M = 279.29 g/mol): C, 47.31; H, 7.52; N, 5.02. Found: C, 47.70; H, 7.63; N, 4.88.

*2.3.3.17. Methyl-6-N-(2′-benzoyl-2′-ethoxycarbonylvinyl)amino-6-deoxy-α-D-glucopyranosid (**5e**).* Procedure A. IR (ATR): [cm^{-1}] = 3409w, 3294w, 2984vw, 2907w, 2841w, 1666vs, 1623vs, 1553s, 1446s, 1424s, 1376w, 1306s, 1214w, 1143w, 1044vs, 1011vs, 897w, 751s, 698s, 666w. ^{1}H-NMR: δ [ppm]: *trans-form*: 1.19 (t; 3H, CH_3); 3.25 (s, 3H, OCH_3); 3.54 (q, 2H, CH_2); 3.20–3.67 (m, 6H + 1·OCH_3, H-6′, H-6, H-5, H-4, H-3, H-2); 4.63 (d, 3.75 Hz, 1H, H-1); 7.20–7.45 (m, 5H, H_{aromat}); 7.97 (d, 13.98 Hz, 1H, =CH–); 10.48 (td, 6.50 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 14.14 (CH_3); 55.76 (OCH_3); 60.80 (CH_2); 50.34 (C-6); 70.95 (C-5); 71.79 (C-4); 72.29 (C-3); 74.34 (C-2); 99.96 (C-1); 100.59 (=C<); 127.4–142.8 (C_{aromat}); 161.71 (=CH–); 168.69; 196.61 (C=O). *cis-form*: 14.59 (CH_3); 55.76 (OCH_3); 60.20 (CH_2); 50.74 (C-6); 70.43 (C-5); 71.39 (C-4); 72.29 (C-3); 74.34 (C-2); 99.96 (C-1); 100.87 (=C<); 127.4–142.8 (C_{aromat}); 161.27 (=CH–); 169.42; 195.33 (C=O). UV-Vis (methanol): λ_{max}: 244 nm ($\log \varepsilon$ = 3.5001), 302 nm ($\log \varepsilon$ = 3.5327). MS (DEI), *m/z*: 394 (70%) [M + 1]. Anal. calcd. for $C_{19}H_{25}NO_8$ (M = 395.41 g/mol): C, 57.71; H, 6.37; N, 3.54. Found: C, 57.94; H, 6.77; N, 3.31.

*2.3.3.18. Methyl-6-N-(2′-ethoxycarbonyl-2′-nitrilvinyl)amino-6-deoxy-α-D-glucopyranosid (**5f**).* Procedure A. IR (ATR): [cm^{-1}] = 3429w, 3302w, 2984w, 2920w, 2853w, 2209s, 1677vs, 1621vs, 1550vw, 1533vw, 1445w, 1377s, 1345s, 1297w, 1241s, 1178w, 1044s, 897w, 782w, 671w, 616w. ^{1}H-NMR: δ [ppm]: *cis-form*: 1.32 (t; 3H, CH_3); 3.31 (s, 3H, OCH_3); 4.21 (q, 2H, CH_2); 3.15–3.76 (m, 6H + 1·OCH_3, H-6′, H-6, H-5, H-4, H-3, H-2); 4.69 (d, 3.80 Hz, 1H, H-1); 7.36 (d, 13.8 Hz, 1H, =CH–); 9.12 (td, 6.76 Hz, 1H, NH). ^{13}C-NMR: δ [ppm]: *trans-form*: 14.57 (CH_3); 56.54 (OCH_3); 49.98 (CH_2); 50.13 (C-6); 70.67 (C-5); 71.56 (C-4); 72.13 (C-3); 74.21 (C-2); 99.87 (C-1); 71.65 (=C<); 160.75 (=CH-); 167.34 (C=O). *cis-form*: 14.87 (CH_3); 56.54 (OCH_3); 50.03 (CH_2); 49.89 (C-6); 70.53 (C-5); 71.39 (C-4); 72.13 (C-3); 74.21 (C-2); 99.87 (C-1); 72.89 (=C<); 159.87 (=CH-); 161.67 (C=O). UV-Vis (ethanol): λ_{max}: 282 nm ($\log \varepsilon$ = 4.2960), 354 nm ($\log \varepsilon$ = 3.0794). MS (ESI in methanol): *m/z*: 339 [M + Na]$^+$. Anal. calcd. for $C_{15}H_{24}N_2O_7$ (M = 344, 37 g/mol): C, 52.32; H, 7.02; N, 8.13. Found: C, 52.41; H, 7.08; N, 7.18.

*2.3.3.19. bis-(6-N-(2′,2′-Diacetylvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopyranoso)-bis-μ-acetato-tricopper(II) (**Cu1a**).* Procedure B. The residue was extracted with diethylether. While slow evaporation of the ether blue crystals precipitate. Yield: 187 mg (38.7%). IR (KBr): ν [cm^{-1}] = 3321vw, 2980s, 2915s, 2845s, 1721vw, 1647w, 1626w, 1592vs, 1545vs, 1475w, 1395vs, 1352s, 1282s, 1196w, 1147s, 1081vs, 1047vs, 1022s, 995s, 955s, 937s, 745s, 647vs, 615vs. UV-Vis (MeOH): λ_{max}: 659 nm ($\log \varepsilon$ = 2.5038), 357 nm ($\log \varepsilon$ = 3.4031). MS (DEI): m/z = 2100: 967 $[Cu_3L_2(OAc)_2]^+$, 908 $[Cu_3L_2OAc]^+$, 849 $[Cu_3L_2]^+$, 785 $[Cu_2L_2]^+$, 515 $[Cu_2LOAc]^+$, 452 $[CuLOAc]^+$, 393 $[CuL]^+$. Anal. calcd. for $C_{34}H_{54}N_2O_{18}Cu_3$ $[Cu_3L_2(OAc)_2]$ (M = 967.42 g/mol): C, 42.21; H, 5.42; N, 2.90. Found: C, 41.79; H, 5.54; N, 2.87.

*2.3.3.20. tris-(6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopyranoso)-tricopper(II) (**Cu1aCl**).* Procedure C. IR (ATR): ν [cm^{-1}] = 2908w, 2834w, 1646w, 1585vs, 1392s, 1355s, 1283s, 1194w, 1155w, 1102w, 1047s, 995s, 935s, 735w, 672w, 646w. UV-Vis (methanol): λ_{max}: 639 nm ($\log \varepsilon$ = 2.6798), 266 nm ($\log \varepsilon$ = 4.2565). MS (ESI in methanol): *m/z*: 1202 (20%, 3Cu) $[Cu_3L_3 + Na]^+$, 807 (100%, 2Cu) $[Cu_2L_2 + Na]^+$, 416 (25%, 1 Cu) $[CuL + Na]^+$, 354 (80%, 0Cu)

$[L+Na]^+$. Anal. calcd. for $C_{45}H_{69}N_3O_{21}Cu_3$ $[Cu_3L_3]$ (M = 1178.70 g/mol): C, 45.86; H, 5.90; N, 3.56. Found: C, 45.22; H, 6.06; N, 3.45; Cl, 0.44.

*2.3.3.21. bis-(6-N-(2′,2′-Diethoxycarbonylvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-bis-μ-acetato-tricopper(II) (**Cu1b**).* Procedure B. Extraction of the residue with diethylether, the solution is evaporated to dryness. Yield: 174 mg (33,9%), green powder. IR (KBr): ν [cm^{-1}] = 3436w, 3279w, 2980s, 2934s, 2907s, 2836w, 1702s, 1684s, 1657s, 1613vs, 1553s, 1499w, 1553s, 1430s, 1399w, 1379w, 1346w, 1272w, 1244s, 1218s, 1156w, 1139w, 1061vs, 1047vs, 1024vs, 959s, 918w, 802s, 791s, 734s, 621w. UV-Vis (toluene): λ_{max}: 664 nm ($\log\varepsilon$ = 2.6385), 397 nm ($\log\varepsilon$ = 3.1670), 346 nm ($\log\varepsilon$ = 3.2487). MS (FAB): *m/z*: 1028 $[Cu_3L_2(OAc)]^+$, 969 $[Cu_3L_2]^+$, 905 $[Cu_2L_2]^+$, 453 $[CuL]^+$, 392 $[L+H]^+$. Anal. calcd. for $C_{38}H_{60}N_2O_{22}Cu_3$ $[Cu_3L_2(OAc)_2]$ (M = 1087.53 g/mol): C, 42.08; H, 5.49; N, 2.73. Found: C, 42.39; H, 5.39; N, 2.77.

*2.3.3.22. tris-(6-N-(2′,2′-Diethoxycarbonyl-vinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-tricopper(II) (**Cu1bCl**).* Procedure C. IR (ATR): ν [cm^{-1}] = 2980w, 2933w, 2905w, 2836w, 1704w, 1665s, 1603vs, 1497w, 1466s, 1430s, 1403w, 1379s, 1344s, 1277s, 1247s, 1222w, 1196w, 1133w, 1050s, 1023s, 982s, 959s, 925w, 787s, 743w, 618w. UV-Vis (methanol): λ_{max}: 636 nm ($\log\varepsilon$ = 2.6478), 281 nm ($\log\varepsilon$ = 4.3264), 246 nm ($\log\varepsilon$ = 4.1132). MS (ESI in methanol): *m/z*: 1380 (6%, 3 Cu) $[Cu_3L_3+Na]^+$, 928 (20%, 2Cu $[Cu_2L_2+Na]^+$, 414 (100%, 0Cu) $[L+Na]^+$. Anal. calcd. for $C_{51}H_{81}N_3O_{27}Cu_3$ $[Cu_3L_3]$ (M = 1358.86 g/mol): C, 45.08; H, 6.01; N, 3.09. Found: C, 45.00; H, 6.14; N, 3.13; Cl, 0.92.

*2.3.3.23. tris-(6-N-(2′-Acetyl-2′-ethoxycarbonyl-vinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-tricopper(II) (**Cu1c**).* Procedure B. IR (ATR): ν [cm^{-1}] = 2981w, 2931w, 2905w, 2838w, 1693s, 1636vs, 1604vs, 1552vs, 1424vs, 1365s, 1299w, 1264s, 1241w, 1194w, 156w, 1048vs, 1022s, 958s, 898w, 812w, 771w, 679s, 620w. UV-Vis (methanol): λ_{max}: 636 nm ($\log\varepsilon$ = 2.9173), 291 nm ($\log\varepsilon$ = 4.0834), 242 nm ($\log\varepsilon$ = 4.2279). MS (ESI in methanol): *m/z*: 1291 (50%, 3Cu) $[Cu_3L_3+Na]^+$, 869 (100%, 2Cu) $[Cu_2L_2+Na]^+$, 845 (30%, 2Cu) $[Cu_2L_2]^+$, 445 (30%, 1Cu) $[CuL+Na]^+$, 384 (50%, 0Cu) $[L+Na]^+$. Anal. calcd. for $C_{48}H_{75}N_3O_{24}Cu_3$ $[Cu_3L_3]$ (M = 1268.78 g/mol): C, 45.44; H, 5.96; N, 3.31. Found: C, 45.18; H, 5.98; N, 3.16.

*2.3.3.24. tris-(6-N-(2′-Acetyl-2′-ethoxycarbonyl-vinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-tricopper(II) (**Cu1cCl**).* Procedure C. IR (ATR): ν [cm^{-1}] = 3447w, 2981w, 2933w, 2908w, 2835w, 1692s, 1635vs, 1603vs, 1574vs, 1441s, 1414s, 1364s, 1299w, 1265w, 1240w, 1192w, 1156w, 1140vw, 1047s, 1020s, 957s, 899w, 811w, 772s, 745s, 669s, 615s. UV-Vis (methanol): λ_{max}: 596 nm ($\log\varepsilon$ = 2.9699), 293 nm ($\log\varepsilon$ = 4.1919), 235 nm ($\log\varepsilon$ = 4.2104). MS (ESI in methanol): *m/z*: 1291 (30%, 3Cu) $[Cu_3L_3+Na]^+$, 868 (70%, 2Cu) $[Cu_2L_2+Na]^+$, 846 (30%, 2Cu) $[Cu_2L_2]^+$, 446 (40%, 1Cu) $[CuL+Na]^+$, 384 (100%, 0Cu) $[L+Na]^+$. Anal. calcd. for $C_{48}H_{75}N_3O_{24}Cu_3$ $[Cu_3L_3]$ (M = 1268.78 g/mol): C, 45.44; H, 5.96; N, 3.31. Found: C, 45.97; H, 6.34; N, 3.36; Cl, 0.26.

*2.3.3.25. tris-(6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-tricopper(II) (**Cu1d**).* Procedure B. IR (ATR): ν [cm^{-1}] = 3465vw, 2923s, 2853w, 1642w, 1599s, 1551vs, 1518vs, 1415vs, 1372s, 1225w, 1186w, 1156w, 1082s, 1044s, 959s, 924w, 895vw, 748w, 677w, 616w. UV-Vis (methanol): λ_{max}: 650 nm ($\log\varepsilon$ = 2.8073), 317 nm ($\log\varepsilon$ = 3.9464), 287 nm ($\log\varepsilon$ = 3.9731). MS (ESI in methanol): *m/z*: 1075 (10%, 3Cu) $[Cu_3L_3+Na]^+$, 723 (100%, 2Cu) $[Cu_2L_2+Na]^+$, 701 (30%, 2Cu) $[Cu_2L_2]^+$, 373 (80%, 1Cu) $[CuL+Na]^+$, 312 (20%, 0Cu) $[L+Na]^+$. Anal. calcd. for $C_{39}H_{63}N_3O_{18}Cu_3$ $[Cu_3L_3]$ (M = 1052.58 g/mol): C, 44.50; H, 6.03; N, 3.99. Found: C, 44.24; H, 6.57; N, 3.34.

*2.3.3.26. tris-(6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-*D*-glucopyranoso)-tricopper(II) (**Cu1dCl**).* Procedure C. IR (ATR): ν [cm^{-1}] = 2908s, 2849w, 1599vs, 1563vw, 1515vs, 1457s, 1412vs, 1379vs, 1253vw, 1224vw, 1192w, 1155w, 1047vs, 959s, 923s, 871s, 747s, 669s, 615w. UV-Vis (methanol): λ_{max}: 578 nm ($\log\varepsilon$ = 2.6777), 310 nm ($\log\varepsilon$ = 3.8437), 293 nm ($\log\varepsilon$ = 3.8490). MS (ESI in methanol): *m/z*: 1075 (15%, 3Cu) $[Cu_3L_3+Na]^+$,

724 (90%, 2Cu) $[Cu_2L_2 + Na]^+$, 374 (100%, 1Cu) $[CuL + Na]^+$, 312 (50%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{39}H_{63}N_3O_{18}Cu_3$ $[Cu_3L_3]$ (M = 1052.58 g/mol): C, 44.50; H, 6.03; N, 3.99. Found: C, 43.81; H, 6.16; N, 3.93; Cl, 0.40.

2.3.3.27. tris-(6-N-(2′-Benzoyl-2′-ethoxycarbonyl-vinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopy-ranoso)-tricopper(II) ***(Cu1e)****.* Procedure B. IR (ATR): ν [cm^{-1}] = 3437vw, 3056vw, 2976w, 2932s, 2901s, 2837w, 1673s, 1625s, 1600vs, 1550vs, 1422vs, 1279s, 1134w, 1047s, 1021s, 956s, 821w, 778w, 698s, 672s, 617w. UV-Vis (methanol): λ_{max}: 630 nm ($\log\varepsilon$ = 2.9362), 302 nm ($\log\varepsilon$ = 4.1658), 248 nm ($\log\varepsilon$ = 4.2638). MS (ESI in methanol): *m/z*: 1477 (15%, 3Cu) $[Cu_3L_3 + Na]^+$, 993 (30%, 2Cu) $[Cu_2L_2 + Na]^+$, 446 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{63}H_{81}N_3O_{24}Cu_3$ $[Cu_3L_3]$ (M = 1454.99 g/mol): C, 52.01; H, 5.61; N, 2.89. Found: C, 52.07; H, 5.43; N, 3.03.

2.3.3.28. tetra-(6-N-(2′-Benzoyl-2′-ethoxycarbonyl-vinyl)amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopy-ranoso)-tetracopper(II) ***(Cu1eCl)****.* Procedure C. IR (ATR): ν [cm^{-1}] = 3056vw, 2976w, 2929w, 2905w, 2829w, 1676s, 1599vs, 1454vs, 1422vs, 1365s, 1279vs, 1186vw, 1132s, 1047vs, 956s, 824w, 777w, 744w, 697s, 643w, 616w. UV/VIS (methanol): λ_{max}: 610 nm ($\log\varepsilon$ = 2.8481), 294 nm ($\log\varepsilon$ = 4.1153), 250 nm ($\log\varepsilon$ = 4.3033). MS (ESI in methanol): *m/z*: 1963 (2%, 4Cu) $[Cu_4L_4 + Na]^+$, 1477 (40%, 3Cu) $[Cu_3L_3 + Na]^+$, 993 (80%, 2Cu) $[Cu_2L_2 + Na]^+$, 446 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{84}H_{108}N_4O_{32}Cu_4$ $[Cu_4L_4]$ (M = 1939.97 g/mol): C, 52.01; H, 5.61; N, 2.89. Found: C, 51.89; H, 5.62; N, 2.91; Cl, 0.81.

2.3.3.29. tris-(6-N-(2′-Ethoxycarbonyl-2′-nitrilvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopyra-noso)-tricopper(II) ***(Cu1f)****.* Procedure B. IR (ATR): ν [cm^{-1}] = 2984vw, 2932w, 2839vw, 2205s, 1680s, 1632vs, 1587s, 1554s, 1522w, 1467vw, 1428s, 1399s, 1379s, 1348s, 1296vw, 1263w, 1244w, 1206w, 1141w, 1064s, 1044s, 1017s, 989vw, 960s, 917vw, 764w, 679w, 619w. UV-Vis (methanol): λ_{max}: 657 nm ($\log\varepsilon$ = 2.2137), 283 nm ($\log\varepsilon$ = 4.1599), 207.2 ($\log\varepsilon$ = 3.9964). MS (ESI in methanol): *m/z*: 1238 (40%, 3Cu) $[Cu_3L_3 + Na]^+$, 833 (70%, 2Cu) $[Cu_2L_2 + Na]^+$, 367 (100%, 0Cu) $[L+Na]^+$. Anal. calcd. for $C_{45}H_{66}N_6O_{21}Cu_3$ $[Cu_3L_3]$ (M = 1217.68 g/mol): C, 44.39; H, 5.46; N, 6.90. Found: C, 44.38; H, 5.34; N, 7.01.

2.3.3.30. tris-(6-N-(2′-Ethoxycarbonyl-2′-nitrilvinyl)-amino-6-deoxy-1,2,3-O-trimethyl-α-D-glucopyra-noso)-tricopper(II) ***(Cu1fCl)****.* Procedure C. IR (ATR): ν [cm^{-1}] = 2984vw, 2932w, 2839vw, 2205s, 1680s, 1632vs, 1587s, 1554s, 1522w, 1467vw, 1428s, 1399s, 1379s, 1348s, 1296vw, 1263w, 1244w, 1206w, 1141w, 1064s, 1044s, 1017s, 989vw, 960s, 917vw, 764w, 679w, 619w. UV-Vis (methanol): λ_{max}: 617 nm ($\log\varepsilon$ = 2.1923), 291 nm ($\log\varepsilon$ = 4.2348), 221 ($\log\varepsilon$ = 4.1044). MS (ESI in methanol): *m/z*: 1238 (40%, 3Cu) $[Cu_3L_3 + Na]^+$, 833 (70%, 2Cu) $[Cu_2L_2 + Na]^+$, 367 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{45}H_{66}N_6O_{21}Cu_3$ $[Cu_3L_3]$ (M = 1217.68 g/mol): C, 44.39; H, 5.46; N, 6.90. Found: C, 44.02; H, 5.76; N, 7.22; Cl, 0.37.

2.3.3.31. bis-(6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-D-glucofuranoso)-dicopper(II) ***(Cu3a)****.* Procedure B with exact equimolar amounts. The crude product was extracted with toluene and recrystallized from a mixture of toluene, chloroform and ethanol (2:2:1). A dark blue solid was isolated. IR (ATR): ν [cm^{-1}] = 3314w, 2961s, 2925vs, 2854s, 2683vw, 1724w, 1650w, 1585vs, 1448s, 1387vs, 1310w, 1259s, 1214w, 1163w, 1067vs, 1010vs, 955w, 852w, 798s, 732vw, 617vw. UV-Vis (toluene): λ_{max}: 620 ($\log\varepsilon$ = 2.7924), 365 ($\log\varepsilon$ = 3.1550). MS (ESI in methanol): *m/z*: 781 $[Cu_2L_2]$, 720 $[CuL_2]$, 423 [CuL + MeOH], 391 [CuL]. Anal. calcd. for $C_{30}H_{42}N_2O_{14}Cu_2$ $[Cu_2L_2]$ (M = 781.76 g/mol): C, 46.09; H, 5.42; N, 3.58. Found: C, 45.67; H, 5.38; N, 3.36.

2.3.3.32. penta-(6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-D-gluco-furanoso)-2,4-pentandionato-heptacopper(II) ***(Cu3a′)****.* Procedure B with 2 mmol triethylamine. The residue was washed twice with toluene. The solid, not soluble precipitate was heated under reflux in toluene/methanol 1:1 (ca. 4 h) until nearly all substance was dissolved. After cooling down the solution was filtered. By slow evaporation of the methanol **Cu3a′** crystallizes in form of dark green crystals. IR (ATR): ν

[cm^{-1}] = 3372w, 2985w, 2936w, 2881w, 2845vw, 1645w, 1596vs, 1521s, 1442s, 1384vs, 1280s, 1214s, 1164w, 1066s, 1010s, 940s, 872s, 793w, 646s, 615w. UV-Vis (methanol): λ_{max}: 269 nm ($\log \varepsilon = 4.8063$), 304 nm ($\log \varepsilon = 4.5201$). MS (ESI in methanol): *m/z*: 2100 (3%, 7Cu) $[Cu_7L_5 + Na]^+$, 1648 (15%, 5Cu) $[Cu_5L_4 + Na]^+$, 1256 (100%, 4Cu) $[Cu_4L_3 + Na]^+$. Anal. calcd. for $C_{80}H_{111}O_{37}N_5Cu_7$ $[Cu_7L_5Acac]$ (M = 2174.20 g/mol): C, 44.19; H, 5.15; N, 3.22. Found: C, 44.26; H, 5.54; N, 3.39.

*2.3.3.33. tris-(6-N-(2′,2′-Diacetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-chloro-tricopper(II) (**Cu3aCl**).* Procedure C with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3381s, 2988w, 2926s, 2853w, 1733w, 1650w, 1592vs, 1447w, 1384vs, 1284w, 1214w, 1163w, 1065w, 1010s, 943w, 876w, 796w, 646s, 613s. UV-Vis (methanol): λ_{max}: 268 nm ($\log \varepsilon = 4.2855$), 654 nm ($\log \varepsilon = 2.8552$). MS (ESI in methanol): *m/z*: 1646 (7%, 5Cu) $[Cu_5L_4 + Na]^+$, 1256 (20%, 4Cu) $[Cu_4L_3 + Na]^+$, 1195 (70%, 3Cu) $[Cu_3L_3 + Na]^+$, 803 (62%, 2Cu) $[Cu_2L_2 + Na]^+$, 781 (30%, 2Cu) $[Cu_2L_2]^+$, 352 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{45}H_{63}O_{21}N_3Cu_3Cl$ $[Cu_3L_3Cl]$ (M = 1208.10 g/mol): C, 44.74; H, 5.26; N, 3.48; Cl, 2.93. Found: C, 44.58; H, 5.31; N, 3.40; Cl, 2.58.

*2.3.3.34. bis-(6-N-(2′,2′-Diethoxycarbonylvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-dicopper(II) (**Cu3b**).* Procedure B with 2 mmol triethylamine. The isolation was carried out in the same way described for **Cu3a**. Yield: 144 mg (66%). IR (ATR): ν [cm^{-1}] = 3434w, 2980s, 2933s, 2902s, 1738w, 1714w, 1686w, 1653vs, 1616vs, 1570vs, 1503w, 1441s, 1426s, 1376s, 1342s, 1286s, 1212s, 1166s, 1122s, 1064vs, 1009vs, 847s, 803w, 785w, 732w, 677w. UV-Vis (toluene): λ_{max}: 626 nm ($\log \varepsilon = 2.7789$), 346 nm ($\log \varepsilon = 3.5013$). MS (ESI in methanol): *m/z*: 933 $[Cu_2L_2 + MeOH]^+$, 452 $[CuL + H]^+$. Anal. calcd. for $C_{34}H_{50}N_2O_{18}Cu_2$ $[Cu_2L_2]$ (M = 901.86 g/mol): C, 45.28; H, 5.59; N, 3.11. Found: C, 45.47; H, 5.48; N, 3.21.

*2.3.3.35. tris-(6-N-(2′,2′-Diethoxycarbonylvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-tetracopper(II) (**Cu3b′**).* Procedure B with 2 mmol triethylamine. Yield: 144 mg (66%). IR (ATR): ν [cm^{-1}] = 3434w, 2980s, 2933s, 2902s, 1738w, 1714w, 1686w, 1653vs, 1616vs, 1570vs, 1503w, 1441s, 1426s, 1376s, 1342s, 1286s, 1212s, 1166s, 1122s, 1064vs, 1009vs, 847s, 803w, 785w, 732w, 677w. UV-Vis (methanol): λ_{max}: 620 nm ($\log \varepsilon = 2.6018$), 280 nm ($\log \varepsilon = 4.2199$), 224 nm ($\log \varepsilon = 3.9993$). MS (ESI in methanol): *m/z*: 1436 $[Cu_4L_3 + Na]^+$, 986 $[Cu_3L_2 + Na]^+$, 923 $[Cu_2L_2 + Na]^+$, 412 $[L + Na]^+$. Anal. calcd. for $C_{51}H_{74}N_3O_{27}Cu_4$ $[Cu_4L_3]$ (M = 1415.35 g/mol): C, 43.28; H, 5.27; N, 2.97. Found: C, 43.47; H, 5.38; N, 3.01.

*2.3.3.36. penta-(6-N-(2′,2′-Diethoxycarbonylvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-heptacopper(II) (**Cu3bCl**).* Procedure C with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3373w, 2982w, 2937w, 2901w, 1661s, 1611vs, 1425s, 1376s, 1339s, 1284s, 1214s, 1164w, 1067s, 1012s, 955w, 857w, 788s, 674s, 615w. UV-Vis (methanol): λ_{max}: 649 nm ($\log \varepsilon = 2.0145$), 284 nm ($\log \varepsilon = 4.1991$), 248 nm ($\log \varepsilon = 4.2527$). MS (ESI in methanol): *m/z*: 2397 (3%, 7Cu) $[Cu_7L_5 + Na]^+$, 1887 (6%, 5Cu) $[Cu_5L_4 + Na]^+$, 1436 (100%, 4Cu) $[Cu_4L_3 + Na]^+$. Anal. calcd. for $C_{85}H_{121}N_5O_{45}Cu_7$ $[Cu_7L_5]$ (M = 2377.74 g/mol): C, 42.94; H, 5.13; N, 2.95. Found: C, 42.82; H, 5.25; N, 3.05.

*2.3.3.37. penta-(6-N-(2′-Ethoxycarbonyl-2′-acetyl-vinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-gluco-furanoso)-heptacopper(II) (**Cu3c**).* Procedure B with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3302vw, 2983w, 2936w, 2877w, 1692s, 1616vs, 1573vs, 1384vs, 1260vs, 1164w, 1065vs, 1008vs, 955w, 774w, 677w, 616w. UV-Vis (methanol): λ_{max}: 600 nm ($\log \varepsilon = 2.9809$), 294 nm ($\log \varepsilon = 4.0262$), 243 nm ($\log \varepsilon = 4.2408$). MS (ESI in methanol): *m/z*: 2249 (0.8%, 7Cu) $[Cu_7L_5 + Na]^+$, 1766 (2%, 5Cu) $[Cu_5L_4 + Na]^+$, 1346 (30%, 4Cu) $[Cu_4L_3 + Na]^+$, 1285 (5%, 3Cu) $[Cu_3L_3 + Na]^+$, 453 (15%, 1Cu) $[CuL + Na]^+$, 382 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{80}H_{111}N_5O_{40}Cu_7$ $[Cu_7L_5]$ (M = 2227.61 g/mol): C, 43.14; H, 5.02; N, 3.14. Found: C, 43.28; H, 5.07; N, 3.17.

*2.3.3.38. penta-(6-N-(2′-Ethoxycarbonyl-2′-acetyl-vinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-gluco-furanoso)-chloro-heptacopper(II) (**Cu3cCl**).* Pro-cedure C. The product was purified by one addi-

tional extraction with benzene. IR (ATR): ν [cm^{-1}] = 3381vw, 2982w, 2937w, 1694s, 1615vs, 1385s, 1261s, 1216w, 1164w, 1066s, 1009s, 861w, 774w, 643s, 615s. UV-Vis (methanol): λ_{max}: 642 nm ($\log \varepsilon$ = 2.8372), 300 nm ($\log \varepsilon$ = 4.0005), 244 nm ($\log \varepsilon$ = 4.2691). MS (ESI in methanol): *m/z*: 2249 (3%, 7Cu) $[Cu_7L_5 + Na]^+$, 1766 (60%, 5Cu) $[Cu_5L_4 + Na]^+$, 1745 (50%, 5Cu) $[Cu_5L_4]^+$, 1347 (90%, 4Cu) $[Cu_4L_3 + Na]^+$, 1285 (70%, 3Cu) $[Cu_3L_3 + Na]^+$, 864 (30%, 2Cu) $[Cu_2L_2 + Na]^+$, 841 (100%, 2Cu) $[Cu_2L_2]^+$, 453 (40%, 1Cu) $[CuL + Na]^+$. Anal. calcd. for $C_{86}H_{117}N_5O_{40}Cu_7Cl$ $[Cu_7L_5Cl{\cdot}C_6H_6]$ (*M* = 2340.17 g/mol): C, 44.14; H, 5.00; N, 2.99; Cl, 1.51. Found: C, 44.74; H, 5.13; N, 3.09; Cl, 1.49.

*2.3.3.39. penta-(6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-hepta-copper(II) (**Cu3d**).* Procedure B with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3255w, 2985w, 2931w, 1710vw, 1617s, 1561vs, 1406s, 1375s, 1340w, 1257w, 1212w, 1164w, 1068vs, 1010vs, 956w, 833w, 735w, 677w, 616w. UV-Vis (methanol): λ_{max}: 637 nm ($\log \varepsilon$ = 2.6139), 380 nm ($\log \varepsilon$ = 3.3227), 321 nm ($\log \varepsilon$ = 3.5612), 269 nm ($\log \varepsilon$ = 3.6585), 240 nm ($\log \varepsilon$ = 3.6585), 205 nm ($\log \varepsilon$ = 3.8070). MS (ESI in methanol): *m/z*: 2234 (2%, 8Cu) $[Cu_8L_6 + Na]^+$, 1889 (10%, 7Cu) $[Cu_7L_5 + Na]^+$, 1541 (30%, 6Cu) $[Cu_6L_4 + Na]^+$, 1478 (15%, 5Cu) $[Cu_5L_4 + Na]^+$, 1130 (50%, 4Cu) $[Cu_4L_3 + Na]^+$, 782 (30%, 3Cu) $[Cu_3L_2 + Na]^+$, 719 (60%, 2Cu) $[Cu_2L_2 + Na]^+$, 697 (100%, 2Cu) $[Cu_2L_2]^+$. Anal. calcd. for $C_{78}H_{110}N_6O_{36}Cu_8$ $[Cu_8L_6]$ (*M* = 2210.13 g/mol): C, 42.27; H, 5.00; N, 3.79%. Found: C, 42.35; H, 5.77; N, 3.75.

*2.3.3.40. tetra-(6-N-(2′-Acetylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-chloro-pentacopper(II) (**Cu3dCl**).* Procedure C with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3358s, 2985s, 2917s, 1705w, 1600vs, 1551vs, 1455w, 1396vs, 1385vs, 1253w, 1211s, 1169w, 1125w, 1062vs, 1010vs, 957s, 885s, 841s, 819s, 748w, 650w, 619w. UV-Vis (methanol): λ_{max}: 615 nm ($\log \varepsilon$ = 2.4913), 311 nm ($\log \varepsilon$ = 4.0264). MS (ESI in methanol): *m/z*: 1478 (20%, 5Cu) $[Cu_5L_4 + Na]^+$, 1130 (100%, 4Cu) $[Cu_4L_3 + Na]^+$, 782 (30%, 3Cu) $[Cu_3L_2 + Na]^+$, 720 (60%, 2Cu) $[Cu_2L_2 + Na]^+$, 698 (80%, 2Cu) $[Cu_2L_2 + 1]^+$. Anal. calcd. for $C_{52}H_{74}N_4O_{24}Cu_5Cl$ $[Cu_5L_4Cl]$ (*M* = 1492.36 g/mol): C, 41.85; H, 5.00; Cl, 2.38; N, 3.75%. Found: C, 41.54; H, 5.69; Cl, 2.38; N, 3.64.

*2.3.3.41. penta-(6-N-(2′-Ethoxycarbonyl-2′-phenyl-carbonylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-diacetato-octacopper(II) (**Cu3e**).* 290 mg (0.69 mmol) **3e** were heated under reflux together with 125 mg (0.69 mmol) $Cu(OAc)_2$ and 200 μl (2.76 mmol) TEA in 50 ml toluene/hexane 4:1 for 5 h. After cooling to room temperature, the precipitate was filtered off. The solution was evaporated to dryness, yielding a dark green powder, which was recrystallized from acetone/diethylether. Yield: 105 mg (32%), dark green crystals. IR (ATR): ν [cm^{-1}] = 3429vw, 2982w, 2937w, 1708vw, 1669s, 1620vs, 1568vs, 1554s, 1449s, 1415vs, 1382s, 1283s, 1262s, 1213s, 1164w, 1068s, 1010s, 732w, 699w, 642w, 617vw. UV-Vis (toluene): λ_{max}: 320 nm ($\log \varepsilon$ = 4.4517), 299 nm ($\log \varepsilon$ = 4.4810). MS (ESI in methanol): *m/z*: 2618 (0.5%, 8 Cu) $[Cu_8L_5 + Na]^+$, 2499 (1%, 6Cu) $[Cu_6L_5 + Na]^+$, 1994 (3%, 5Cu) $[Cu_5L_4]^+$, 1532 (20%, 4Cu) $[Cu_4L_3 + Na]^+$, 444 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{109}H_{126}N_5O_{44}Cu_8$ $[Cu_8L_5(OAc)_2]$ (*M* = 2718.59 g/mol): C, 48.16; H, 4.67; N, 2.58. Found: C, 48.54; H, 4.69; N, 2.64.

*2.3.3.42. tetra-(6-N-(2′-Ethoxycarbonyl-2′-phenyl-carbonylvinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-tetracopper(II) (**Cu3eCl**).* Procedure C with 2 mmol triethylamine. Like the mass spectrum shows, the ligand was partly hydrolyzed at the ethyl ester group during the reaction. By oligomerization a nearly statistic mixture of tetranuclear compounds is formed. {IR (ATR): ν [cm^{-1}] = 3311w, 3064vw, 2982w, 2936w, 1730w, 1651w, 1589s, 1572s, 1515s, 1485s, 1456s, 1427s, 1372w, 1302s, 1199s, 1163s, 1116w, 1067vs, 1012vs, 954w, 851w, 770s, 699vs, 615w. UV-Vis (methanol): λ_{max}: 615 nm ($\log \varepsilon$ = 2.6894), 302 nm ($\log \varepsilon$ = 4.0188), 230 nm ($\log \varepsilon$ = 4.0875).} MS (ESI in methanol): *m/z*: 1879 (20%, 4Cu), 1865 (80%, 4Cu), 1851 (100%, 4Cu), 1847 (100%, 4Cu), 1833 (100%, 4Cu), 1819 (80%, 4Cu), 1805 (20%, 4Cu).

*2.3.3.43. tris-(6-N-(2′-Ethoxycarbonyl-2′-nitrilvinyl)-amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofura-noso)-tetracopper(II) (**Cu3f**).* Procedure B with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3381vw,

3294vw, 3230vw, 2985w, 2937w, 2204s, 1679vs, 1643vs, 1623vs, 1570vs, 1423s, 1399s, 1376s, 1340s, 1294w, 1241s, 1210s, 1164w, 1118vw, 1067s, 1008vs, 956w, 916vw, 883w, 847w, 786s, 765s, 677s, 618w. UV-Vis (methanol): λ_{max}: 642 nm ($\log\varepsilon = 2.5518$), 284 nm ($\log\varepsilon = 4.1833$), 210 nm ($\log\varepsilon = 4.0307$). MS (ESI in methanol): *m/z*: 1295 (4%, 4Cu) $[Cu_4L_3 + Na]^+$, 890 (2%, 3Cu) $[Cu_3L_2 + Na]^+$, 365 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{45}H_{58}N_6O_{21}Cu_4$ $[Cu_4L_3]$ ($M = 1273.18$ g/mol): C, 42.45; H, 4.59; N, 6.60%. Found: C, 42.80; H, 4.58; N, 6.95.

*2.3.3.44. penta-(6-N-(2′-Ethoxycarbonyl-2′-nitril-vinyl)amino-6-deoxy-1,2-O-isopropyliden-α-*D*-glucofuranoso)-chloro-heptacopper(II)* ***(Cu3fCl)****.* Procedure C with 2 mmol triethylamine. IR (ATR): ν [cm^{-1}] = 3311w, 2984w, 2933w, 2204s, 1680w, 1633vs, 1510w, 1468w, 1425w, 1376s, 1339s, 1255w, 1206w, 1163w, 1067w, 1011s, 955w, 852w, 789w, 763w, 669w, 615w. UV-Vis (methanol): λ_{max}: 624 nm ($\log\varepsilon = 2.7830$), 288 nm ($\log\varepsilon = 4.1932$), 225 nm ($\log\varepsilon = 4.1706$). MS (ESI in methanol): *m/z*: 2164 (2%, 7Cu) $[Cu_7L_5 + Na]^+$, 1678 (2%, 5Cu) $[Cu_5L_4]^+$, 1296 (100%, 4Cu) $[Cu_4L_3 + Na]^+$. Anal. calcd. for $C_{75}H_{97}N_{10}O_{35}Cu_7Cl$ $[Cu_7L_5Cl]$ (M = 2178.93 g/mol): C, 41.34; H, 4.49; N, 6.43; Cl, 1.63. Found: C, 41.80; H, 4.58; N, 6.58; Cl, 1.39.

*2.3.3.45. bis-(Methyl-6-N-(2′,2′-diacetylvinyl)amino-6-deoxy-α-*D*-glucopyranoso)-μ-diacetato-tricopper(II)* ***(Cu5a)****.* Procedure B. IR (ATR): [cm^{-1}] = 3363w, 3278w, 2996w, 2925w, 1581vs, 1392s, 1306s, 1191w, 1143w, 1106w, 1044s, 939w, 899vw, 820w, 752w, 675s, 618w. UV-Vis (methanol): λ_{max}: 656 nm ($\log\varepsilon = 2.5196$), 289 nm, 263 nm ($\log\varepsilon = 4.1337$). MS (FAB in NBA): *m/z*: 912 (3%, 2 Cu) $[Cu_2L_2(OAc)_2 + H]^+$, 853 (2%, 3Cu) $[Cu_2L_2OAc+H]^+$, 793 (3%, 3 Cu) $[Cu_3L_2+H]^+$, 729 (3%, 2Cu) $[Cu_2L_2+H]^+$, 304 (100%, 0Cu) $[L+H]^+$. Anal. calcd. for $C_{30}H_{44}N_2O_{18}Cu_3$ $[Cu_3L_2(OAc)_2]$ (M = 911.32 g/mol): C, 39.54; H, 4.87; N, 3.07. Found: C, 39.86; H, 4.71; N, 3.03.

*2.3.3.46. hexa-(Methyl-6-N-(2′,2′-diacetylvinyl)-amino-6-deoxy-α-*D*-glucopyranoso)-chloro-hexakupfer(II)* ***(Cu5aCl)****.* Procedure C. IR (ATR): ν [cm^{-1}] = 3373w, 2923w, 2837vw, 1585vs, 1466w, 1393s, 1357w, 1283w, 1190vw, 1141vw, 1024s, 940w, 894w, 745vw, 672w, 644w, 613w. UV-Vis (methanol): λ_{max}: 660 nm ($\log\varepsilon = 2.6029$), 291 nm, 267 nm ($\log\varepsilon = 4.2453$). MS (ESI in methanol): *m/z*: 1117 (15%, 3Cu) $[Cu_3L_3 + Na]^+$, 753 (91%, 2Cu) $[Cu_2L_2 + Na]^+$, 387 (71%, 1 Cu) $[CuL + Na]^+$, 326 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{78}H_{114}N_6O_{42}Cu_6Cl$ $[Cu_6L_6Cl]$ (M = 2224.50 g/mol): C, 42.12; H, 5.17; N, 3.78; Cl, 1.59. Found: C, 42.13; H, 5.26; N, 3.77; Cl, 1.56.

*2.3.3.47. bis-(Methyl-6-N-(2′,2′-diethoxycarbonyl-vinyl)amino-6-deoxy-α-*D*-glucopyranoso)dicopper(II)* ***(Cu5b)****.* Procedure B. IR (ATR): ν [cm^{-1}] = 3377w, 3309w, 2982w, 2932w, 2901w, 1709w, 1681s, 1637vs, 1608vs, 1566vs, 1424s, 1379s, 1344s, 1294w, 1221s, 1139w, 1044s, 1016s, 897w, 841w, 802w, 751w, 680s, 618w. UV-Vis (methanol): λ_{max}: 684 nm ($\log\varepsilon = 2.5855$), 280 nm ($\log\varepsilon = 4.0402$), 223 nm ($\log\varepsilon = 3.8957$). MS (ESI in methanol): *m/z*: 871 (5%, 2Cu) $[Cu_2L_2 + Na]^+$, 386 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{30}H_{46}N_2O_{18}Cu_2$ $[Cu_2L_2]$ (M = 849.79 g/mol): C, 42.40; H, 5.46; N, 3.30. Found: C, 43.13; H, 6.63; N, 3.48.

*2.3.3.48. tetra-(Methyl-6-N-(2′,2′-diethoxycarbonyl-vinyl)amino-6-deoxy-α-*D*-glucopyranoso)-chloro-tetracopper(II)* ***(Cu5bCl)****.* Procedure C. IR (ATR): ν [cm^{-1}] = 3384w, 2980w, 2932w, 2901w, 1657s, 1607vs, 1499w, 1466w, 1430s, 1379w, 1345w, 1279w, 1228w, 1091w, 1044s, 1017s, 893w, 789w, 750w, 671w, 615w. UV-Vis (methanol): λ_{max}: 626 nm ($\log\varepsilon = 2.7444$), 282 nm ($\log\varepsilon = 4.2966$), 246 nm ($\log\varepsilon = 4.1549$), 226 nm ($\log\varepsilon = 4.0836$). MS (ESI in methanol): *m/z*: 871 (5%, 2Cu) $[Cu_2L_2 + Na]^+$, 386 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{60}H_{92}N_4O_{36}Cu_4Cl$ $[Cu_4L_4Cl]$ (M = 1731.24 g/mol): C, 41.63; H, 5.36; N, 3.24; Cl, 2.05. Found: C, 41.23; H, 5.71; N, 3.35; Cl, 1.38.

*2.3.3.49. bis-(Methyl-6-N-(2′-acetyl-2′-ethoxycarbonylvinyl)amino-6-deoxy-α-*D*-glucopyranoso)-dicopper(II)* ***(Cu5c)****.* Procedure B. IR (ATR): ν [cm^{-1}] = 3382w, 2978w, 2931w, 2906w, 1661s, 1600vs, 1439s, 1435s, 1381w, 1368s, 1270s, 1230w, 1095w, 1051s, 899w, 837w, 791w, 752w, 673s, 620s. UV-Vis (methanol): λ_{max}: 631 nm ($\log\varepsilon = 2.4761$), 292 nm ($\log\varepsilon = 4.1013$), 238 nm ($\log\varepsilon = 4.2460$). MS (ESI in methanol): *m/z*: 811 (40%,

2Cu) $[Cu_2L_2 + Na]^+$, 356 (70%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{28}H_{42}N_2O_{16}Cu_2$ $[Cu_2L_2]$ (M = 789.74 g/mol): C, 42.58; H, 5.36; N, 3.55. Found: C, 42.37; H, 5.27; N, 3.56.

2.3.3.50. octa-(Methyl-6-N-(2′-acetyl-2′-ethoxycarbonylvinyl)amino-6-deoxy-α-D-glucopyranoso)-chloro-octacopper(II) ***(Cu5cCl)***. Procedure C. IR (ATR): ν [cm^{-1}] = 3375w, 2980w, 2929w, 2901w, 1682s, 1603vs, 1440s, 1403s, 1365s, 1266s, 1190w, 1094w, 1048s, 893w, 832w, 770w, 670s, 615s. UV-Vis (methanol): λ_{max}: 648 nm ($\log\varepsilon$ = 2.5314), 294 nm ($\log\varepsilon$ = 4.0890), 242 nm ($\log\varepsilon$ = 4.2480). MS (ESI in methanol): *m/z*: 1601 (4%, 4Cu) $[Cu_4L_4 + Na]^+$, 1206 (70%, 3Cu) $[Cu_3L_3 + Na]^+$, 811 (100%, 2Cu) $[Cu_2L_2 + Na]^+$, 788 (30%, 2Cu) $[Cu_2L_2]^+$, 356 (70%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{112}H_{168}N_8O_{84}Cu_8Cl$ $[Cu_8L_8Cl]$ (M = 3194.40 g/mol): C, 42.11; H, 5.30; N, 3.67; Cl, 1.11. Found: C, 41.97; H, 5.27; N, 3.26; Cl, 0.60.

2.3.3.51. tris-(Methyl-6-N-(2′-acetylvinyl)amino-6-deoxy-α-D-glucopyranoso)-tricopper(II) ***(Cu5d)***. Procedure B. IR (ATR): ν [cm^{-1}] = 3310s, 2988w, 2920w, 2841w, 1638s, 1557vs, 1403vs, 1257w, 1192w, 1144w, 1044vs, 1013vs, 898w, 839w, 751w, 676s, 616w. UV-Vis (methanol): λ_{max}: 654 nm ($\log\varepsilon$ = 2.4626), 287 nm ($\log\varepsilon$ = 3.6221). MS (ESI in methanol): *m/z*: 991 (4%, 3Cu) $[Cu_3L_3 + Na]^+$, 345 (100%, 1Cu) $[CuL + Na]^+$. Anal. calcd. for $C_{33}H_{51}N_3O_{18}Cu_3$ $[Cu_3L_3]$ (M = 966.11 g/mol): C, 41.03; H, 5.32; N, 4.35. Found: C, 41.39; H, 5.66; N, 4.19.

2.3.3.52. hexa-(Methyl-6-N-(2′-acetylvinyl)amino-6-deoxy-α-D-glucopyranoso)-chloro-hexacopper(II) ***(Cu5dCl)***. Procedure C. IR (ATR): ν [cm^{-1}] = 3328w, 2909w, 2838w, 1640w, 1604vs, 1520vs, 1454w, 1386s, 1284vw, 1261vw, 1225w, 1190w, 1139w, 1043vs, 1008vs, 926w, 896w, 840vw, 746w, 669w, 618w. UV-Vis (methanol): λ_{max}: 622 nm ($\log\varepsilon$ = 2.4804), 306 nm ($\log\varepsilon$ = 4.0128). MS (ESI in methanol): *m/z*: 990 (12%, 3Cu) $[Cu_3L_3 + Na]^+$, 668 (100%, 2Cu) $[Cu_2L_2 + Na]^+$, 346 (72%, 1Cu) $[CuL + Na]^+$. Anal. calcd. for $C_{66}H_{102}N_6O_{36}Cu_6Cl$ $[Cu_6L_6Cl]$ (M = 1967.66 g/mol): C, 40.29; H, 5.22; N, 4.27; Cl, 1.80. Found: C, 40.30; H, 5.25; N, 4.25; Cl, 2.24.

2.3.3.53. bis-(Methyl-6-N-(2′-benzoyl-2′-ethoxycarbonylvinyl)amino-6-deoxy-α-D-glucopyranoso)-dicopper(II) ***(Cu5e)***. Procedure B. IR (ATR): ν [cm^{-1}] = 3313w, 3056w, 2984w, 2927w, 2857w, 1741w, 1670s, 1600vs, 1570vs, 1522s, 1420s, 1282s, 1205w, 1107w, 1035vs, 897vw, 777w, 752w, 698s, 669s, 617w. UV-Vis (methanol): λ_{max}: 666 nm ($\log\varepsilon$ = 2.3880), 300 nm ($\log\varepsilon$ = 3.9902), 247 nm ($\log\varepsilon$ = 4.1384). MS (ESI in methanol): *m/z*: 913 (4%, 2Cu) $[Cu_2L_2]^+$, 418 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{38}H_{46}N_2O_{16}Cu_2$ $[Cu_2L_2]$ (M = 913.88 g/mol): C, 49.94; H, 5.07; N, 3.07. Found: C, 49.91; H, 5.16; N, 3.03.

2.3.3.54. hexa-(Methyl-6-N-(2′-benzoyl-2′-ethoxycarbonylvinyl)amino-6-deoxy-α-D-glucopyranoso)-chloro-hexacopper(II) ***(Cu5eCl)***. Procedure C. IR (ATR): ν [cm^{-1}] = 3331w, 3062w, 2925w, 1677s, 1602vs, 1576s, 1521s, 1489vw, 1456s, 1422s, 1365s, 1279s, 1205w, 1110s, 1033vs, 970s, 898w, 774w, 753w, 696s, 669w, 616w. UV-Vis (methanol): λ_{max}: 644 nm ($\log\varepsilon$ = 2.7748), 296 nm ($\log\varepsilon$ = 4.0741), 249 nm ($\log\varepsilon$ = 4.2296). MS (ESI in methanol): *m/z*: 1394 (20%, 3Cu) $[Cu_3L_3 + Na]^+$, 937 (100%, 2Cu) $[Cu_2L_2 + Na]^+$, 480 (72%, 1Cu) $[CuL + Na]^+$. Anal. calcd. for $C_{114}H_{138}N_6O_{48}Cu_6Cl$ $[Cu_6L_6Cl]$ (M = 2777.10 g/mol): C, 49.31; H, 5.01; N, 3.03; Cl, 1.28. Found: C, 49.25; H, 5.17; N, 2.85; Cl, 1.31.

2.3.3.55. bis-(Methyl-6-N-(2′-ethoxycarbonyl-2′-nitrilvinyl)amino-6-deoxy-α-D-glucopyranoso)-dicopper(II) ***(Cu5f)***. Procedure B. IR (ATR): ν [cm^{-1}] = 3373s, 3298s, 2985w, 2911w, 2837w, 2207s, 1679vs, 1622vs, 1568s, 1424s, 1400s, 1378s, 1344s, 1294w, 1241s, 1176vw, 1142w, 1106w, 1044s, 1014s, 897w, 838w, 784w, 760w, 678s, 616w. UV-Vis (methanol): λ_{max}: 713 nm ($\log\varepsilon$ = 1.8574), 282 nm ($\log\varepsilon$ = 4.1130), 206 nm ($\log\varepsilon$ = 3.9058). MS (ESI in methanol): *m/z*: 777 (20%, 2Cu) $[Cu_2L_2 + Na]^+$, 339 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{26}H_{36}N_4O_{14}Cu_2$ $[Cu_2L_2]$ (M = 755.69 g/mol): C, 41.32; H, 4.80; N, 7.41. Found: C, 41.35; H, 4.91; N, 7.50.

2.3.3.56. hexa-(Methyl-6-N-(2′-ethoxycarbonyl-2′-nitrilvinyl)amino-6-deoxy-α-D-glucopyranoso)-chloro-hexacopper(II) ***(Cu5fCl)***. Procedure C. IR (ATR): ν [cm^{-1}] = 3380s, 3301s, 2991w, 2917w,

2845w, 2212s, 1686vw, 1635vs, 1520s, 1475w, 1441s, 1414s, 1382s, 1351s 1298w, 1245s, 1181vw, 1146w, 1112w, 1049s, 1020s, 903w, 842w, 790w, 766w, 683s, 620w. UV-Vis (methanol): λ_{max}: 684 nm ($\log \varepsilon = 2.0342$), 278 nm ($\log \varepsilon = 4.2634$), 210 nm ($\log \varepsilon = 4.0064$). MS (ESI in methanol): *m/z*: 1148 (2%, 3 Cu) $[Cu_3L_3 + Na]^+$, 777 (8%, 2Cu) $[Cu_2L_2 + Na]^+$, 339 (100%, 0Cu) $[L + Na]^+$. Anal. calcd. for $C_{78}H_{108}N_{12}O_{28}Cu_6Cl$ $[Cu_6L_6Cl]$ (M = 2302.50 g/mol): C, 40.69; H, 4.73; N, 7.65; Cl, 1.54. Found: C, 40.93; H, 4.62; N, 7.48; Cl, 1.40.

3. Results and discussion

3.1. Structure of the new compounds

Table 1 gives an overview of the structures of the new compounds.

Type **1**: The structure of **Cu1a** and **b** was that of a trinuclear species, in which a copper acetate monomer was inserted into two CuL monomers (Scheme 3) [5]. For the compounds **Cu1c–f**, one signal in the mass spectrum hints on a composition of $[Cu_3L_3]$ of the compounds. By MS–MS ion trap and CID experiments, this peak could be proofed to be the one of the most stable species. A peak of dimeric species $[Cu_2L_2]$ is found to be a fragment of this. The heptanuclear cluster of the compound **Cu3a′** [6] (Scheme 5b) gives a hint on the possible structure of this compounds. Three of its copper atoms form a trinuclear subunit with a central Cu_3O_3 six-membered ring in tub conformation, so that it forms two sides of a cubane subunit. One can assume that the trimeric structure of **Cu1c–f** looks similar, but with the central ring in chair conformation.

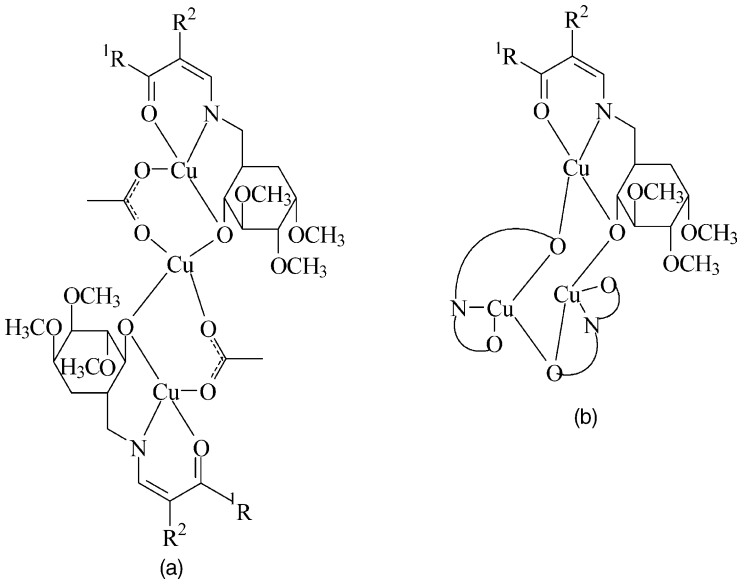
If copper chloride is used for the synthesis of the compounds instead of copper acetate, the structures of the acetate containing compounds **Cu1a** and **b** have to change. For all compounds, the UV-Vis-spectra show a hypsochromic shift compared with the compounds synthesized with copper acetate. Elemental analysis indicates that chloride is present in the compounds. For **Cu1aCl–Cu1dCl** and **Cu1fCl**, the mass spectra and the elemental analysis hint on trinuclear species, of the above mentioned $[Cu_3L_3]$ structure. For **Cu1eCl**, a tetrameric composition is found, hinting on a heterocubane-like structure like those found for 2-aminocyclohexanol derived compounds of our type [5]. The chloride content measured by elemental analysis, however, is too low compared with the calculated value for one chloride bridging two complexes of the calculated formula. It is possible that the isolated compound contains only partly chloride-bridged species, in which two trimeric or tetrameric specie (in case of **Cu1eCl**) are bridged by one axial chloride ligand as found for the corresponding compounds of type **5**.

Type **5**: The ligands of type **5** differ from their type **1** equivalent only by the fact, that the carbohydrate hydroxo groups in 2- and 3-positions are not methylated. The structures of the compounds should therefore be similar. Indeed, a $[Cu_3L_2(OAc)_2]$ composition is found for **Cu5a**. **Cu5d** is a trimeric $[Cu_3L_3]$ species with the same structure than the corresponding type **1** complex **Cu1d**, too. A different structure is found for the other compounds of type **5**, **Cu5b**, **c**, **e**, **f**, which are dimeric $[Cu_2L_2]$ species. As the ligands of type **5** formally could be regarded as derivatives

Table 1
Overview of the nuclearity of the new substances

Type	**a**	**b**	**c**	**d**	**e**	**f**
1	$Cu_3L_2(OAc)_2$	$Cu_3L_2(Oac)_2$	Cu_3L_3	Cu_3L_3	Cu_3L_3	Cu_3L_3
3	$Cu_2L_2/Cu_7L_5(acac)$[b]	Cu_2L_2/Cu_4L_3[b]	Cu_7L_5	Cu_7L_5	$Cu_8L_5(OAc)_2$ (H_2O)	Cu_4L_3
5	$Cu_3L_2(OAc)_2$	Cu_2L_2	Cu_2L_2	Cu_3L_3	Cu_2L_2	Cu_2L_2
	aCl	**bCl**	**cCl**	**dCl**	**eCl**	**fCl**
1	Cu_3L_3[a]	Cu_3L_3[a]	Cu_3L_3[a]	Cu_3L_3[a]	Cu_4L_4[a]	Cu_3L_3[a]
3	Cu_7L_5Cl	Cu_7L_5	Cu_7L_5Cl	Cu_5L_4Cl	Mixture of species	Cu_7L_5Cl
5	$(Cu_3L_3)_2Cl$	$(Cu_2L_2)_2Cl$	$(Cu_4L_4)_2Cl$	$(Cu_2L_2)_2Cl$	$(Cu_3L_3)_2Cl$	$(Cu_3L_3)_2Cl$

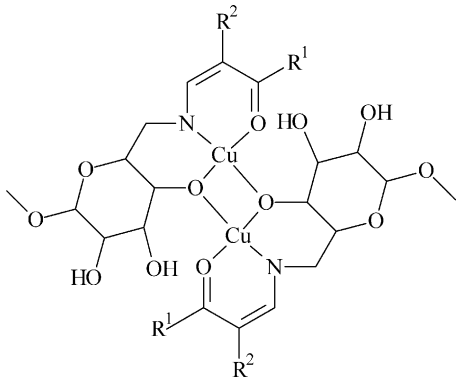
[a] Containing some chloride, possibly from a $(Cu_nL_n)_2Cl$ species.
[b] Depending on the pH-value during the synthesis: first prepared with stoichiometric amount of base, second with excess of base.



Scheme 3. Structures of the $[Cu_3L_2(OAc)_2]$ species of **Cu1a**, **b** (a) and of the $[Cu_3L_3]$ species of **Cu1c–f**.

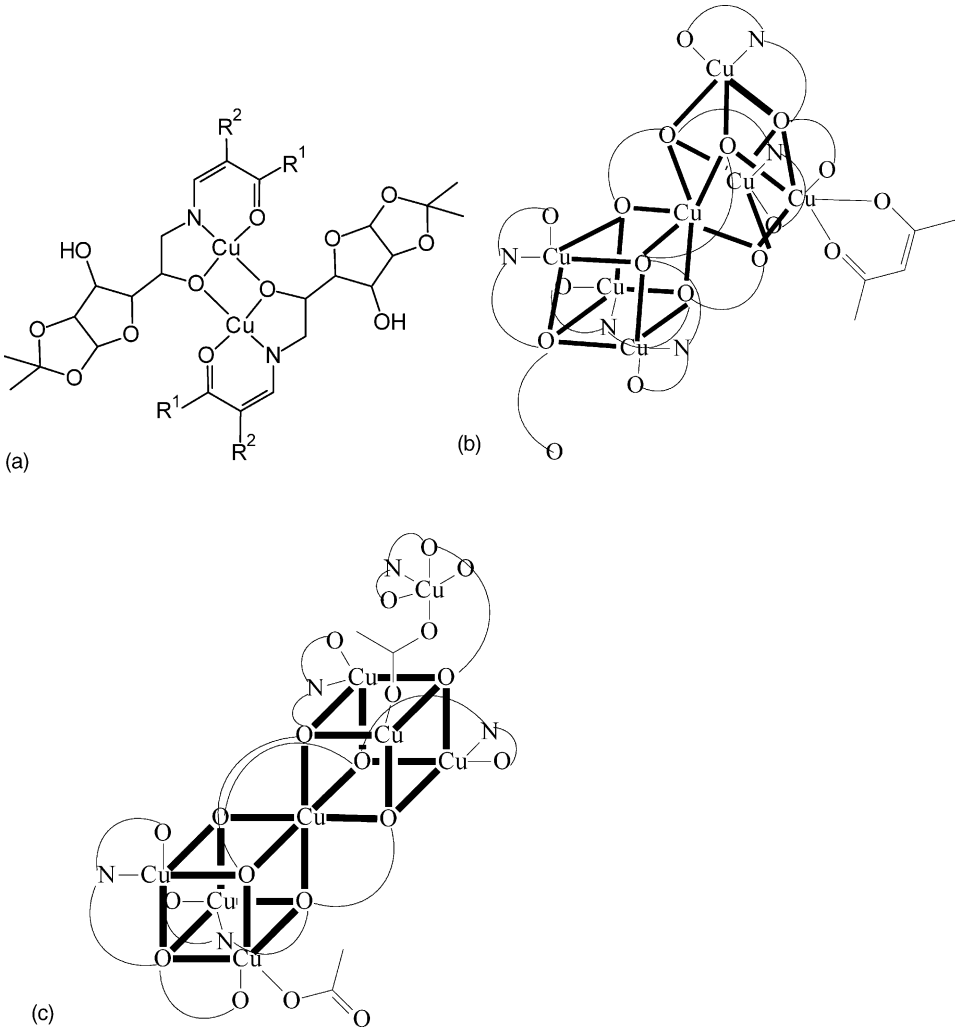
of 3-aminopropanol derivatives, one could expect the structure displayed in Scheme 4 [5–7].

Different structures are found for the compounds synthesized with chloride. Like for the compounds of type **1**, a hypsochromic shift of the d-d bands are found in the UV-Vis spectra, indicating that chloride is bound to the copper atoms of the complexes. In contrast to the compounds of type **1**, the elemental analysis shows a defined composition $[Cu_nL_n]_2Cl$ for all complexes, where one chloride is bound to two oligomeric clusters. For **Cu5aCl**, which has to change its structure compared with **Cu5a**, a trimeric species $[Cu_3L_3]_2Cl$ can be detected. Remarking is, that the same structure is found for **Cu5eCl** and **Cu5fCl**, whose analogous complexes synthesized with copper acetate, **Cu5e** and **Cu5f**, are dimers. **Cu5bCl** and **Cu5dCl**, show their original dimeric, respectively trimeric structure bridged by one chloride in a $[Cu_2L_2]_2Cl$ or $[Cu_3L_3]_2Cl$ composition. For the compound **Cu5cCl** a composition of $[Cu_4L_4]_2Cl$ is found which might be interpreted by a structure of two heterocubane-like subunits, bridged by one chloride.



Scheme 4. Structure of the complexes **Cu5b**, **c**, **e** and **f**.

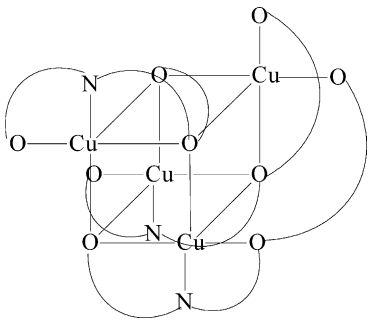
Type **3**: The structures of the complexes with type **3** ligands are the most complex of the discussed compounds. All other ligands are tridentate, using a carbonyl oxygen atom, the ketoenamin nitrogen atom and one alkoxo oxygen atom for the copper binding. The ligands of type **3** are able to use both of their free hydroxo (alkoxo) oxygen atoms for metal binding. The compound **Cu3a** (Scheme 5) was previously synthesized and characterized as a dimeric compound with two magnetically nearly isolated copper atoms. It is synthesized from the ligand and copper acetate by addition of exact two equivalents of triethylamine. If a small excess of base is used, green crystals are obtained build up by a compound **Cu3a′** of the formula $[Cu_7L_5(acac)]\cdot H_2O\cdot CH_3OH\cdot C_6H_6\cdot C_7H_8$ containing a



Scheme 5. Structures of **Cu3a** (a), **Cu3a′** (b) and **Cu3e** (c) [5,6].

heptanuclear cluster [6]. The structure of **Cu3e** turned out to be an octanuclear compound of the formula $[Cu_8L_5(OAc)_2(H_2O)]\cdot EtOH\cdot 1.5H_2O\cdot 1.5Et_2O\cdot MeOH$ [6].

The mass spectrum of **Cu3a′** shows, in addition to the molecular mass at $m/z = 2100$ peaks for the compositions of $[Cu_7L_5 + Na]^+$ (*M*-acac, $m/z = 2078$), $[Cu_5L_4]^+$ ($m/z = 1648$), and $[Cu_4L_3]^+$ ($m/z = 1256$). The peak at $m/z = 2100$ is proofed to be the one of the molecular structure by MS–MS-ion trap experiments. This method was used to find the molecular weights of all other compounds of this type. However, the mass spectrum shows that there is an equilibrium of several species and that the resulting structure of the compounds of type **3** is very sensitive to influences like pH-value, etc. A closer look on the heptanuclear structure of **Cu3a′** and on the octanuclear structure of **Cu3e** shows, that they consist of a dimeric and a trimeric subunit and of two or three copper atoms which carry no own ligand and are bound by the additional alkoxo (or hydroxo) oxygen atom in 3-position of the glucofuranose ring. The higher oligomers could therefore be regarded as the products of tri- and dimeric species, which are present in equilibrium and form higher oligomers. For **Cu3b**, a dimeric compound was isolated and characterized



Scheme 6. Structure of the tetranuclear structure of **Cu3b′**.

before [5]. The structure of **Cu3b′** is that of a tetranuclear species with $[Cu_4L_3]$ composition, whose structure should be very similar to the one of a subunit of the heptanuclear cluster of **Cu3a′** (Scheme 6).

The same structure is found for **Cu3f**. **Cu3c** and **Cu3d** have heptanuclear structures like **Cu3a′**. The chloride-containing compounds **Cu3aCl**, **Cu3bCl**, **Cu3cCl** and **Cu3fCl** show all heptanuclear clusters, of which **Cu3aCl**, **Cu3cCl** and **Cu3fCl** each contain one chloride ion (possibly at one of the positions occupied by a 2,4-pentandionato ligand in the structure of **Cu3a′**). No chloride can be found in **Cu3bCl**, but a structural change from a tetra- to a heptanuclear structure is observed. **Cu3dCl** shows a pentanuclear structure of the composition $[Cu_5L_4Cl]$. A possible structure for this composition may be that of a dinuclear and a trinuclear subunit bridged by a chloride ligand, so that all complexes consist of trinuclear and dinuclear subunits, with either additional copper atoms bound by the second alkoxo/hydroxo function of the ligand or bridging chloride.

Isolated dimeric and trimeric species, like they are predominant in the structures of the other ligand types, can only be isolated for the complexes with **3a** and **3b**. The reason for this may be that the substituents R^1 and R^2 lead to a Lewis acidity of the copper centers which allows only double deprotonation of the ligand at certain circumstances, whereas the other ligands are at all circumstances at least partly triple deprotonated.

3.2. Activity of the new compounds, influence of chloride

Both chloride-free and chloride-containing substances were examined as potential catalyst for the oxidation of 3,5-di-^{t}butyl-catechol. The results (only for the new compounds) are displayed in Fig. 1, the kinetic data in Table 2.

For the complexes of type **1**, activity was found for the new compounds **Cu1c**, **Cu1d** and **Cu1e**. The maximum activity is found for **Cu1d**, the activity follows the order **d** > **e** > **a** ≈ **c** >> **b**. The same order between **d** and **e** is found for the chloride-containing compounds, while **Cu1cCl** and **Cu1bCl** are not active. The activities of the chloride-containing compounds of type **1** are generally higher than the activities of the analogous chloride-free compounds, with exception of **Cu1d** and **Cu1dCl**, whose activities are nearly identical. In this case, one may suggest that the chloride bridged dimerization of $[Cu_3(\mathbf{1d})_3]$ trimers observed as the difference between the chloride-free and chloride-containing substances, is broken in solution, so that the same amount of chloride-free trimers is present in solution and the same activity is measured. The second trimer carries the chloride and is not involved in the catalytic reaction (chloride is known to inhibit catechol oxidase). For **Cu1aCl**, the enhancement of the activity could be a result from the structural change from the $[Cu_3(\mathbf{1a})_2(OAc)_2]$ structure to a trimeric $[Cu_3(\mathbf{1a})_3]$ structure (Scheme 3).

The highest activity of all our compounds is found for **Cu3a**, all copper acetate derived compounds with other substitution patterns for R^{1-3} are not active or, in case of **Cu3e**, their kinetic data are not determinable cause of a decomposition in solution, so that no exact catalyst concentration is determinable. The structure of **Cu3a** is, like mentioned above, unique among the complexes of type **3**, from no other ligand of type **3** a dimeric complex like **Cu3a** can be isolated. The heptanuclear complex **Cu3a′** shows only ca. 2% of the activity of **Cu3a**, while it is not determinable whether this is the activity of **Cu3a′** itself or if **Cu3a′** decomposes to a little amount of **Cu3a**.

This behavior changes dramatically for the chloride-containing substances. While the activity of **Cu3aCl** is two magnitudes lower than the one of **Cu3a**, due to the structural change from a dimeric to a trimeric species, the chloride-containing compounds of the other substitution patterns become moderately active. The order found is **d** > **c** > **b** > **a**. Again, the complex with $R^1 = C_6H_5$ and $R^2 = CO_2C_2H_5$ (**Cu3eCl**) shows decomposition in solution (change of UV-Vis-spectrum), so that no kinetic data are

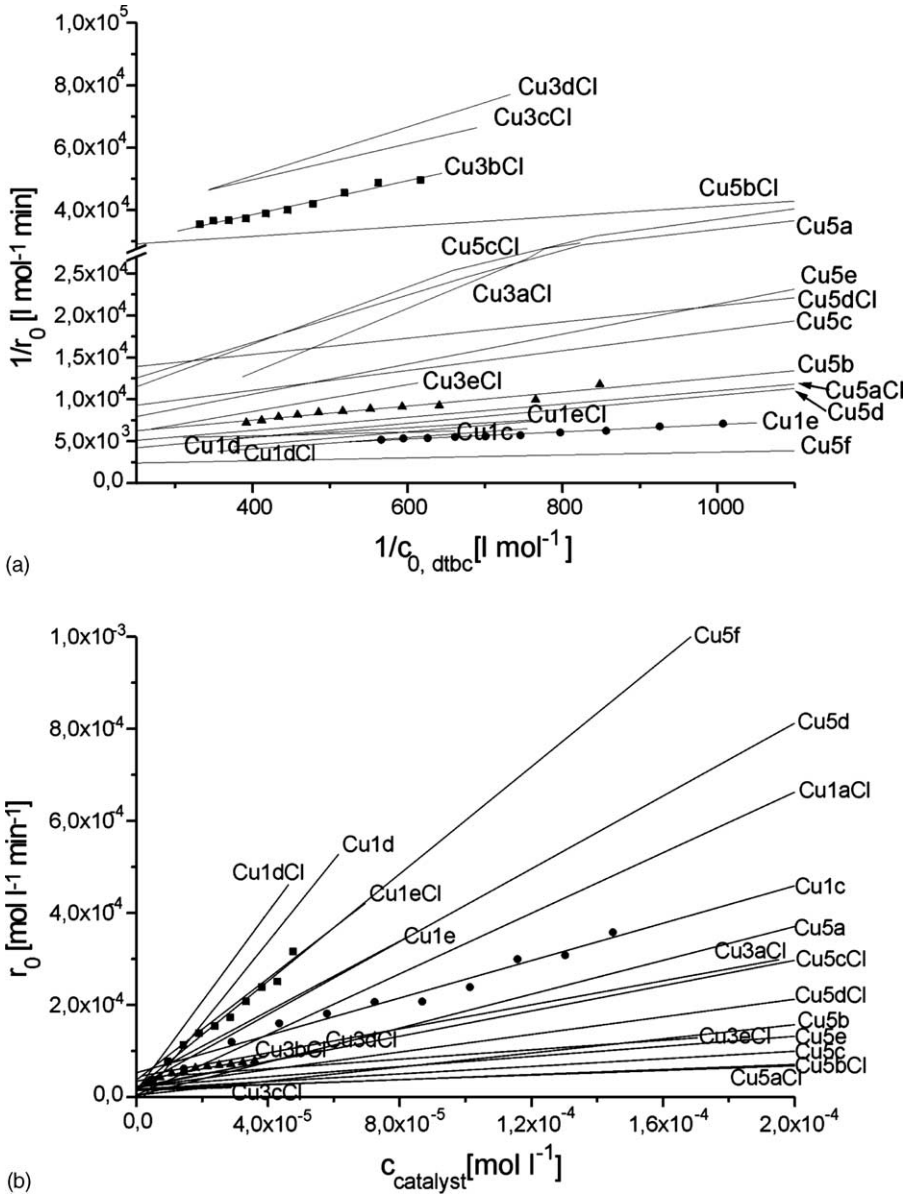


Fig. 1. (a) *Lineweaver-Burk* plots (all investigations were carried out at least three times with different constant catalyst concentrations); (b) r vs. c_{cat} plot for the variation of the catalyst concentration (only for the new compounds, for **Cu1a** and **Cu3a** see [5]).

determinable. The reason for the found reactivities is that the structures of the chloride-containing compounds are lower molecular (no heptanuclear cluster).

The activities of the compounds of type **5** follow the order **f** >> **d** > **a** > **e** > **c** > **b**. The complexes **Cu5d** and **Cu5a** have different structures than the other four complexes and therefore a comparison between all complexes is difficult. The most striking is, that of the dinuclear complexes, **Cu5f** is one magnitude more active than the other complexes **Cu5e**, **c** and **b**. The substituents $R^1 = OC_2H_5$ and $R^2 = CN$ are the most electron-withdrawing of the whole examined

Table 2
Kinetic data of the compounds of type **1**, **3** and **5** in dependence on the copper salt used for synthesis

	Type **1** acetate	Type **1** chloride	Type **3** acetate	Type **3** chloride	Type **5** acetate	Type **5** chloride
a[a]	138 ± 8 8.94 (±0.05) × 10^{-4} 102 ± 4	187.5 ± 3.9 7.02 (±0.11) × 10^{-3} 198.5 ± 5.1	9471 ± 255; **Cu3a′**: 23.7 ± 1.4 5.90 (±0.04) × 10^{-3}; **Cu3a′**: 2.19 (±0.04) × 10^{-3} 9927 ± 392; **Cu3a′**: 22.8 ± 0.6	53.8 ± 3.4 2.20 (±0.07) × 10^{-3} 48.2 ± 0.2	117.5 ± 4.5 2.43 (±0.06) × 10^{-3} 116.9 ± 3.7	131.8 ± 9.3 4.62 (±0.08) × 10^{-3} 38.6 ± 1.2
b[a]	Activity ≤ $Cu(OAc)_2$	Activity ≤ $Cu(OAc)_2$	Activity ≤ $Cu(OAc)_2$	71.1 ± 4.8 2.39 (±0.14) × 10^{-3} 77.7 ± 1.3	68.8 ± 3.4 1.67 (±0.06) × 10^{-3} 45.9 ± 2.6	23.2 ± 1.6 5.99 (±0.10) × 10^{-4} 16.2 ± 2.0
c	179.4 ± 3.6 1.40 (±0.09) × 10^{-3} 123.9 ± 3.9	Activity ≤ $Cu(OAc)_2$	Activity ≤ $Cu(Oac)_2$	86.4 ± 3.5 2.20 (±0.04) × 10^{-3} 101.2 ± 3.6	40.8 ± 1.9 1.72 (±0.05) × 10^{-3} 50.8 ± 1.5	752.3 ± 71.6 1.32 (±0.07) × 10^{-2} 84.9 ± 5.7
d	561.7 ± 12.9 5.0 (±0.2) × 10^{-3} 510.4 ± 5.4	572.4 ± 12.9 3.96 (±0.18) × 10^{-3} 585.2 ± 6.5	Activity ≤ $Cu(Oac)_2$	117.2 ± 12.0 1.20 (±0.16) × 10^{-3} 103.7 ± 5.0	224.7 ± 8.6 3.35 (±0.06) × 10^{-3} 236.3 ± 6.5	53.6 ± 0.8 6.44 (±0.04) × 10^{-4} 57.2 ± 2.2
e	237.6 ± 4.6 1.75 (±0.04) × 10^{-3} 224.3 ± 4.6	332.1 ± 8.0 1.56 (±0.07) × 10^{-3} 311.3 ± 7.5	Active, but decomposes in solution	Active, but decomposes in solution	92.2 ± 4.3 5.25 (±0.07) × 10^{-3} 98.3 ± 1.4	Activity ≤ $Cu(OAc)_2$ Activity ≤ $Cu(OAc)_2$
f	–	–	–	–	615.3 ± 6.5 8.77 (±0.11) × 10^{-3} 761.2 ± 7.2	

First row: k_{cat} (h^{-1}); second row: K_M ($mol\,l^{-1}$) (both from the Lineweaver–Burk plots); third row: k (h^{-1}) from the variation of the catalyst concentration..

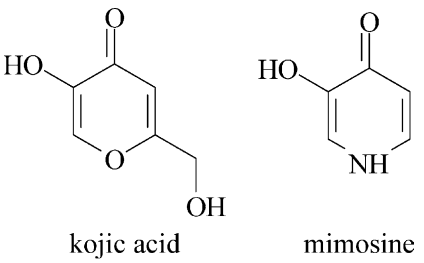
[a] For the kinetic data of the compounds synthesized with copper acetate see also [5].

series, and are therefore the set of substituents which is most suitable for the stabilization of a dicopper(I) state as a possible transition state in the catalytic reaction. The ability of the substituation patterns of **Cu5a** and **d** to stabilize the copper(I) oxidation state is less than the one of **Cu5f**. One could therefore think, that the different structures of **Cu5a** and **d** are improving the activity of this compounds.

For all chloride-containing substances of type **5**, significant lower activities are found, **Cu5fCl**, whose chloride-containing analogue **Cu5f** is highly active, shows no activity. For **Cu5aCl**, **Cu5bCl** and **Cu5cCl**, a remarkable difference is found for the values for k_{cat} (from the *Michaelis–Menten* interpretation of the variation of the substrate concentration) and for k (from the variation of the catalyst concentration). This values should be equal, if no inhibition is occurring. For a competitive inhibition, k_{cat} should be equal for the chloride-free and chloride-containing substances, and the value K_M should be higher for the chloride-containing compound. Therefore an inhibition of the activity of the compounds by chloride is detected, but it is not competitive like the one of kojic acid or cinnamic acid (see below).

3.3. Inhibition of the activity of *Cu1a*, *3a* and *4a* by cinnamic acid

The kinetic data of the active compounds **Cu1a–4a** were determined recently [5]. The low rate constants of **Cu2a** (2.83(3) h^{-1}) makes this compound not suitable for inhibition experiments. With a competitive inhibitor, one can obtain valuable information about the catalyst-substrate adduct and the mechanism of the reaction. Well-known competitive inhibitors of catechol oxidase are, e.g. kojic acid and mimosine [8], which have a chinoid structure (Scheme 7).



Scheme 7. Structure of competitive inhibitors for catechol oxidase.

Recently, Battaini et al. [8] published the mechanism of the inhibition of some model compounds with kojic acid. We tried to adapt this procedure to our compounds, but if kojic acid is added to the compounds **Cu1a–4a**, a pale green solid precipitates, which can be identified as copper kojate. Obviously, kojic acid is a better ligand for copper(II) than our ligands, so that it is not suitable for our purpose. Carboxylate ions are also known to inhibit catechol oxidase, and are also known to hold the copper atoms in the correct distance of 2.8–3.2 Å. Cinnamic acid was chosen for its molecular size being adequate.

The inhibition experiments were carried out measuring the activity at constant substrate (3,5-di-^{t}butylcatechol) and catalyst concentrations and varying concentration of cinnamic acid. The activity of **Cu3a** decreases to almost zero when one equivalent of the cinnamic acid is added, possibly due to structural changes. The inhibition curves of **Cu1a** and **4a** are displayed in Fig. 2.

As can be seen, the first equivalent of the inhibitor increases the activity of both compounds, than the activity decreases in the expected way.

To proof that cinnamic acid acts as a competitive inhibitor, kinetic measurements were carried out at different constant inhibitor concentrations and interpreted using the Michaelis–Menten model. If the inhibition by cinnamic acid is competitive, one should get the same r_{max} (k_{cat}) value for every concentration of cinnamic acid, but an increasing slope of the curve, indicated by an increasing K_M value. The results are given in Table 3 and Fig. 3 for **Cu1a** and in Table 4 and Fig. 4 for **Cu4a**.

Indeed, for both compounds, the values for v_{max} (k_{cat}) stay identical during the variation of the inhibitor concentration within their error ranges. For **Cu4a**, the

Table 3
Kinetic measurements at different concentrations of cinnamic acid for **Cu1a**

Graph no.	$c_{cinammic\ acid}$ (mol l^{-1})	k_{cat} (h^{-1})	K_M (mol l^{-1})
0	0	175.4 ± 7.5	1.28 (±0.08) × 10^{-3}
1	1 × 10^{-4}	119.2 ± 3.1	6.49 (±0.4) × 10^{-4}
2	4 × 10^{-4}	190.7 ± 12.5	2.88 (±0.14) × 10^{-3}
3	8 × 10^{-4}	187.4 ± 16.1	2.65 (±0.13) × 10^{-3}
4	2.0 × 10^{-3}	169.2 ± 6.5	2.52 (±0.06) × 10^{-3}
5	4.0 × 10^{-3}	170.4 ± 17.1	4.42 (±0.16) × 10^{-3}
6	6.0 × 10^{-3}	179.2 ± 6.5	8.80 (±0.71) × 10^{-3}

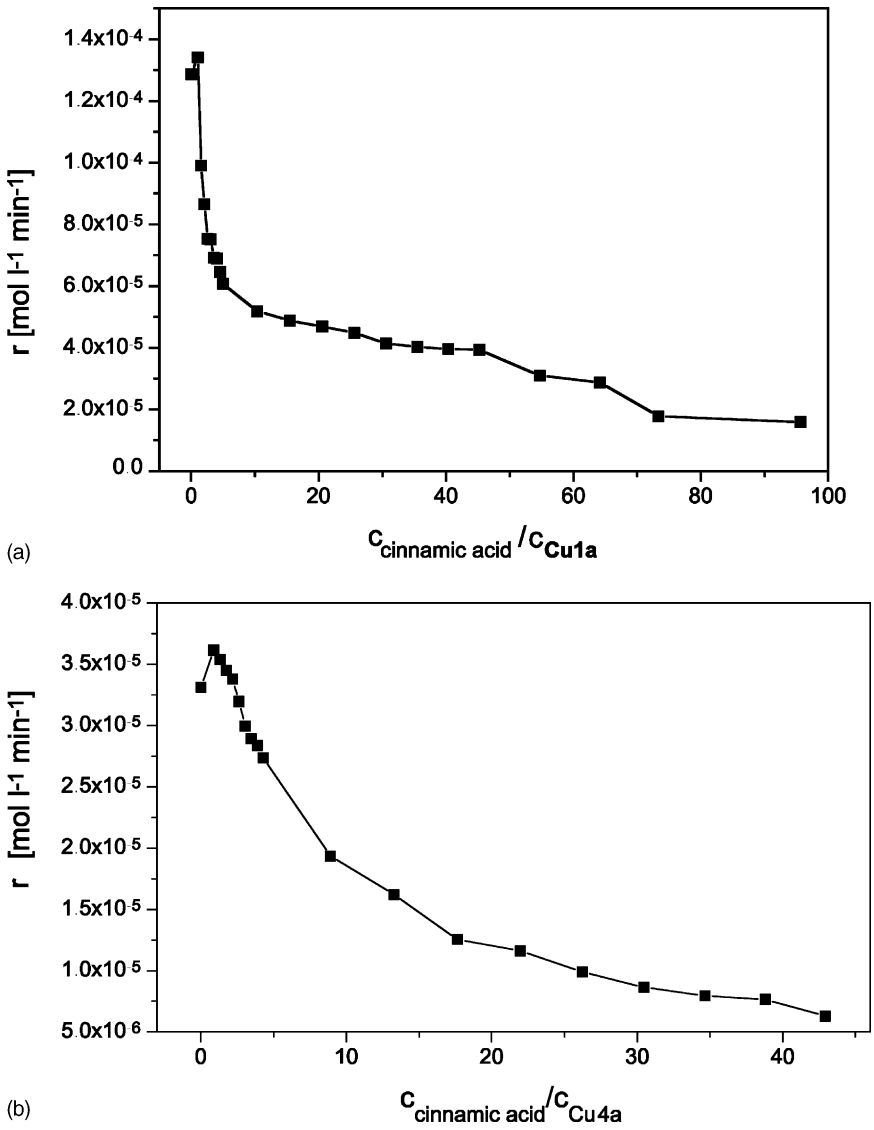


Fig. 2. Inhibition of the catechol oxidase activity of **Cu1a** and **Cu4a** by cinnamic acid.

K_M values increase like expected, for **Cu1a**, a general tendency of increase is found, but the values for the experiments No. 2–4 are nearly identical, only the last two values show a significant increase. Having a closer look on the error ranges of the measurements 2 and 3, one finds relative high values, which allow to ignore that this values are higher than expected.

Both the inhibition of **Cu1a** and **4a** can therefore be regarded as competitive.

Therefore, one can assume, that substrate and inhibitor bind to the catalyst in the same way. The fact that the first equivalent of inhibitor enhances the activity of the compounds can be interpreted that way that the active species is formed by two monomers of the complex and a bridging catecholate anion (Scheme 8). A binding of the catecholate to the non-dissociated complex is less probable, because of the following reasons:

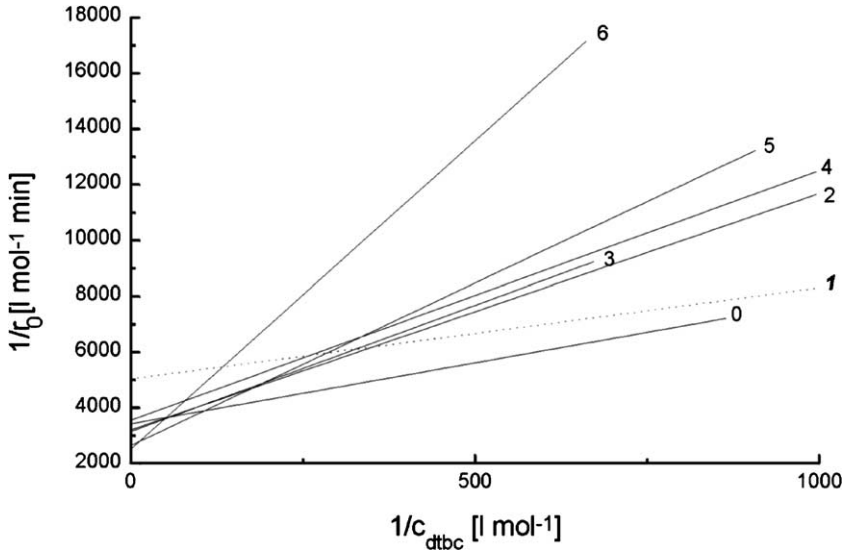


Fig. 3. Kinetic measurements at different concentrations of cinnamic acid for **Cu1a**.

1. This would lead to a species with two five-coordinated copper atoms. The binding of a second catecholate (as a substrate) would fulfill the coordination sphere of the copper atoms, the copper complex should be stable.
2. The protons from the dtbc molecules have to be "stored" somewhere until they are transferred to the oxygen atoms and form water. Therefore, the alkoxo oxygen groups should be protonated and their bonds to the copper atoms should be at least

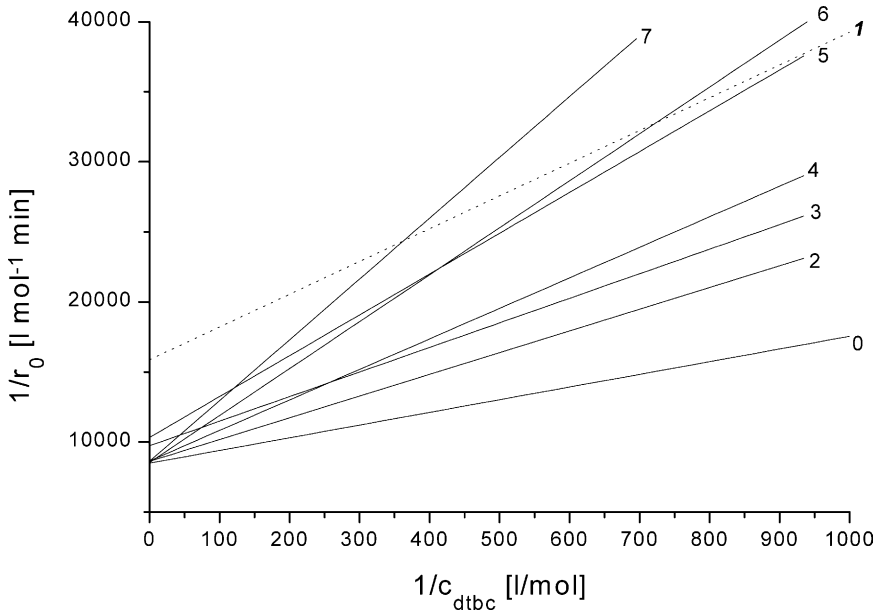
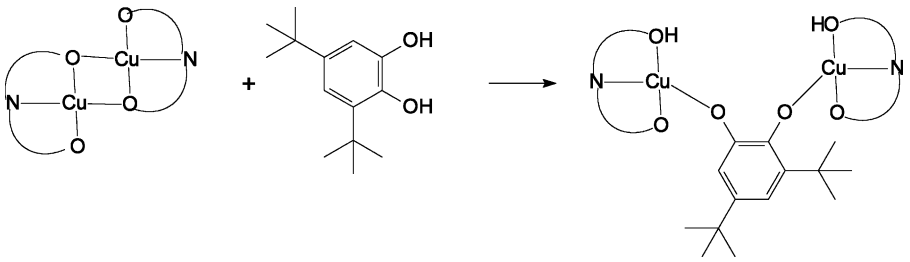


Fig. 4. Kinetic measurements at different concentrations of cinnamic acid for **Cu1a**.



Scheme 8. Formation of the active species.

Table 4
Kinetic measurements at different concentrations of cinnamic acid for **Cu4a**

Graph no.	$c_{\text{cinammic acid}}$ (mol l^{-1})	k_{cat} (mol l^{-1} min^{-1})	K_{M} (mol l^{-1})
0	0	63.8 ± 4.6	4.40 (±0.22) × 10^{-3}
1	1 × 10^{-4}	37.8 ± 1.8	2.94 (±0.14) × 10^{-3}
2	4 × 10^{-4}	69.6 ± 3.4	3.60 (±0.16) × 10^{-3}
3	8 × 10^{-4}	61.7 ± 1.8	3.60 (±0.10) × 10^{-3}
4	1.6 × 10^{-3}	69.4 ± 3.0	5.04 (±0.14) × 10^{-3}
5	2.4 × 10^{-3}	58.1 ± 2.2	5.64 (±0.12) × 10^{-3}
6	3.2 × 10^{-3}	70.3 ± 4.5	7.86 (±0.94) × 10^{-3}
7	5.0 × 10^{-3}	69.6 ± 8.1	1.008 (±0.044) × 10^{-2}

weakened (OH groups being weaker ligands than O^- groups).

3. For a μ-η^2; η^2-peroxo-species, which is discussed as the binding mode of dioxygen in the mechanism of catechol oxidase [1,4], the sites occupied by the alkoxo oxygen atoms are needed.

It is known from titration of the compounds **Cu1a**–**4a** with tetrachlorocatechol [5], that the catechol indeed binds as catecholate (dianion) to this complexes. Furthermore, a first order kinetics is found both for catalyst and substrate (at low concentrations) concentrations. Therefore this catecholate is either not oxidized during the reaction until no other substrate is present, or that it is fastly exchanged by a new catechol molecule after oxidation.

4. Conclusion

The structure and therefore the catalytic ability of copper(II) complexes with aminocarbohydrate-based β-ketoenaminic ligands is highly dependent on a couple of different influences. A little change in the pH, for example, leads to the formation of a heptanuclear cluster compound **Cu3a′** with low activity, whereas the dinuclear species **Cu3a** is—to our knowledge—the most active catalyst known for this reaction [9–20]. The structural changes caused by additional ligands (chloride), which are not competitive inhibitors, may either suppress the activity of the complexes (complexes of type **5**, **Cu3a**) or make an inactive compound active (other complexes of type **3**, type **1**). This structural changes could be a dimerization of the oligomers found for the chloride-free compounds or simply be caused by the fact that the compounds prepared with acetate contain some acetate ligands [$Cu_3L_2(OAc)_2$] (**Cu1a**, **Cu1b** and **Cu5a**).

The most striking feature from the investigations on the competitive inhibition of the reaction is, that a first equivalent of the inhibitor enhances the activity of the compounds **Cu1a** and **Cu4a**. Together with the fact, that the complexes are saturated with two equivalents of tetrachlorocatechol in form of bridging, dianionic catecholate ions, and that (at low concentrations) *first order* kinetics were found for the compounds [5], this leads to the conclusion that the active form of the compounds consists of two monomeric subunits with a bridging catecholate (Scheme 8). This catecholate is not oxidized during the reaction or is substituted fastly by a new catechol. This is in total agreement with the observation made for the reaction of a copper(II) complex based on a β-ketoenaminic derivative of a steroid aminoalcohol ligand with dtbc under inert gas atmosphere. There a dicopper(I) complex could be isolated which caries one catechol molecule [21].

The substituents R^1–R^3 proof to have the expected high influence on the structure and reactivity of the complexes. For the compounds of type **3**, only **Cu3a** (R^1 = CH_3, R^2 = $COCH_3$) gives a highly active,

dimeric complex. For the compounds of type **1**, **Cu1a** is the only active of the literature-known compounds [5]. The influences of its substituents are very similar to those of **Cu1c** ($R^2 = CO_2C_2H_5$), which is also true for its activity. For most compounds, R^2 has an electron-withdrawing effect. This should help to stabilize the intermediate copper(I) oxidation state and therefore enhance the activity.

Despite of this, the electron-withdrawing substituent R^2 is missing in the most active compound of this type **Cu1d** (R^2 = H). This should destabilize the copper(I) oxidation state compared with the other compounds and therefore decrease the reactivity. The opposite is observed. Similar behavior for compounds with no copper(I)-stabilizing residuals was also found for the steroid aminoalcohol derived compounds [21] and should have the same origin.

Acknowledgements

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