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Carbohydrate Research 339 (2004) 1941–1952
Carbohydrate RESEARCH

Binuclear copper(II) complexes of 5-*N*-(β-ketoen)amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoses: synthesis, structure, and catecholoxidase activity

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Received 20 January 2004; received in revised form 10 May 2004; accepted 17 May 2004
Available online 25 June 2004

Abstract—The synthesis of 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**8**) was carried out via 5-azido-5-deoxy-1,2:3,4-*O*-diisopropylidene-α-D-glucofuranose (**6**), its reduction with Raney-Nickel and deprotection. 5-*N*-(β-Ketoen)amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoses (**8a**–**f**) were synthesized from 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose and β-ketoenolethers leading to ligands with symmetrically substituted double bonds (**8a**, **8b**) and *e*/*z* isomeric mixtures with unsymmetrical substitution (**8c**–**f**). Reaction of the ligands with Cu(II) ions leads to binuclear complexes of the general formula Cu_2L_2. In contrast to copper(II) complexes which are not derived from amino carbohydrates the metal centers in the compounds saturate their coordination sphere by complexation of additional solvent molecules, interaction with neighboring complex molecules, or free hydroxyl groups of the own ligand. Residues of the ketoen moiety, R^1 and R^2, also influence the electronic properties of the metal centers. The combination of factors leads to different catalytic properties of the complexes in catecholoxidase-like reactions.

Keywords: Amino carbohydrates; Schiff bases; Copper(II) complexes; Catecholoxidase activity

1. Introduction

Carbohydrates combine relevant properties as ligands for the synthesis of catalysts, such as chirality and polyfunctionality. They exist in a broad range of molecular sizes, obey unique conformational and configurational principles and can be selectively functionalized. Polysaccharides are able to form supramolecular structures such as fibers, gels, membranes, mono- and multilayers.[1–3] In most of the known examples for structurally characterized metal sugar complexes, commercial carbohydrates act as polyolato ligands to form metal complexes under deprotonation of one or more hydroxyl groups.[4–9] Another field of interest is the interaction of metal ions with *N*-glucosides[10–16] and inositols.[17–20]

Copper is one of the most important metals for transport, storage, and activation of molecular oxygen in nature. For the four-electron reduction of dioxygen binuclear (e.g., catechol oxidase[21,22]) or oligonuclear (e.g., ascorbate oxidase[23,24]) copper centers are favored. Studies on oligonuclear copper model compounds have been undertaken in recent years to elucidate the relationship between structure and reactivity of the active sites in enzymes and to develop new complexes with a useful catalytic performance.[25–31]

By complexation of copper(II) ions using condensation products of amino sugars and substituted

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0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.05.018

3-oxo-enamines—which are known for the protection of aminogroups in carbohydrate chemistry[32–34]—oligonuclear copper(II) complexes could be obtained. In contrast to similar compounds based on simple amino alcohols[35–41] instead of amino sugars these complexes show rare structures and catalytic reactivities depending on the used amino carbohydrate.[42–44]

2. Results and discussion

2.1. Ligand synthesis

Starting from glucuronic acid-3,6-lacton (**1**) we obtained 5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranuronicacid-3,6-lactone[45,46] (**3**), via acid catalyzed acetalization to 1,2-*O*-isopropylidene-α-D-glucurono-6,3-lactone[47,48] (**2**), and nucleophilic substitution with sulfuryl chloride in pyridine[49] according to literature procedures.

Reduction of the lactone with sodium borohydride and acetic acid in dimethoxyethane gives 5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**4**). In order to prevent the formation of 6-azido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose by direct reaction of **4** with sodium azide[50] the hydroxyl groups on C-3 and C-6 were protected, and **4** was reacted with 2,2-dimethoxypropane and sulfuric acid (cat.) to 5-chloro-5-deoxy-1,2:3,6-*O*-diisopropylidene-β-L-idofuranose (**5**). The nucleophilic substitution with sodium azide in *N*,*N*-dimethylformamide gave 5-azido-5-deoxy-1,2:3,6-*O*-diisopropylidene-α-D-glucofuranose (**6**) in good yield (80%). The product still contained 20% (^{1}H NMR) of the starting material **5**. Both have the same R_F value on silica gel in all solvent mixtures and all attempts of chromatographic separation failed. However, only **6** could be reduced with Raney-Nickel and hydrazine hydrate to 5-amino-5-deoxy-1,2:3,6-*O*-diisopropylidene-α-D-glucofuranose (**7**). The product was purified by column chromatography and residual **5** regained. Deprotection of **7** with sulfuric acid in methanol/water gave 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**8**) (Fig. 1).

Compound **8** reacts in methanol with the β-keto-enol ethers **a**–**f**[51–58] to give the ligands **8a**–**f** (Fig. 2). These compounds are chiral ligands differing in the residues R^1 and R^2. For the 5-*N*-(β-ketoen)amino-saccharides **8c**–**f** the synthesis leads to *e*/*z* isomers at the double bonds. Due to the electron delocalization between the donor nitrogen and the carbonyl groups, the C=C bonds lose their double bond characters. The corresponding isomers are stabilized by NH···O hydrogen bonds of different strength causing varying ratios of the *e*- and the *z*-isomeric forms (Fig. 3). Signals could be assigned to the different isomers by two-dimensional NMR. ^{1}H NOE NMR experiments show beside the expected signals cross peaks for an exchange of protons of the *e*/*z* isomeric forms in case of **8c**–**e**. Compound **8f** shows no isomerization at the

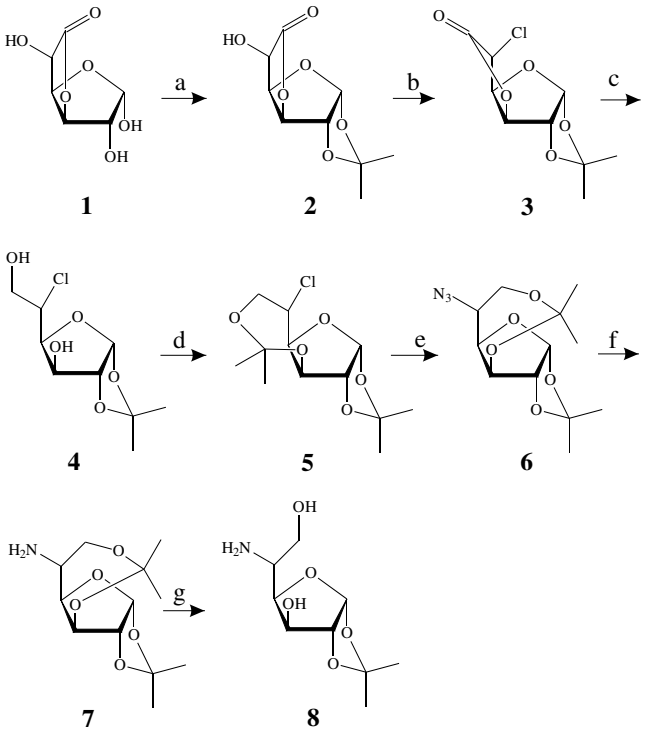
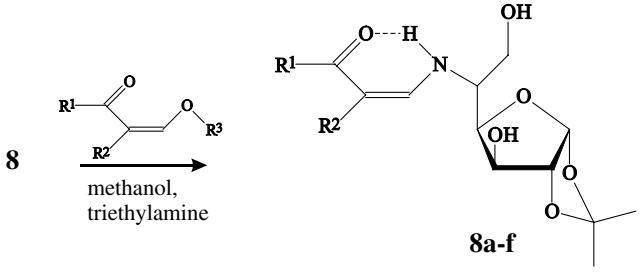


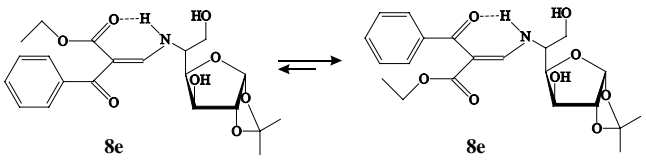
Figure 1. Synthesis of 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**8**). (a) Acetone, sulfuric acid (cat.); (b) sulfurylchloride, pyridine; (c) $NaBH_4$, acetic acid, dimethoxyethane; (d) 2,2-dimethoxypropane, sulfuric acid (cat.); (e) NaN_3, *N*,*N*-dimethylformamide; (f) Raney-nickel, hydrazine hydrate; (g) 0.8% sulfuric acid.



	R^1	R^2	R^3
8a	CH_3	$COCH_3$	OC_2H_5
8b	OC_2H_5	$COOC_2H_5$	OC_2H_5
8c	CH_3	$COOC_2H_5$	OC_2H_5
8d	Ch_3	H	CH_3
8e	C_6H_5	$COOC_2H_5$	OC_2H_5
8f	OC_2H_5	CN	OC_2H_5

Figure 2. Synthesis of the *N*-(β-ketoen)amino-saccharides **8a**–**f**.

double bond at temperatures up to 50 °C and mixture times up to 900 ms due to the electron-withdrawing influence of the nitrile group. ^{1}H NMR data for the most abundant isomers are listed in Table 1. The ^{13}C NMR data for the other observed isomers are also listed in Table 2.



	e : z
8c	1 : 7
8d	8 : 1
8e	1 : 2
8f	3.5 : 1

Figure 3. Different amounts of *E*- and *Z*-isomeric forms (determined by ^{1}H NMR).

Table 1. ^{1}H NMR data of the *N*-(β-ketoen)amino-saccharides

	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	N–H	=CH–	Other signals
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,6'}$	$J_{5,6'}$	$J_{X,NH}$	$J_{CH,NH}$	
8a	5.84 (d)	4.42 (d)	3.92 (d)	4.15 (dd)	3.77 (m)	3.62 (s)	3.62 (s)	10.87 (dd)	7.97 (d)	1.22, 1.38 (6H) CMe_2; 2.15, 2.28 (6H) 2×CH_3
	3.63 Hz	—	2.58 Hz	8.10 Hz	—	—	—	9.30 Hz	13.5 Hz	5.11 (m) OH-6, 5.70 (d) OH-3
8b	5.90 (d)	4.49 (d)	4.07 $\leftrightarrow_{m,2H}$ 4.22		3.70 $\leftrightarrow_{m,3H}$ 3.95			9.35 (dd)	8.03 (d)	1.20–1.45 (12H) 4×CH_3; 2.20, 3.19 OH
	3.61 Hz	—						9.04 Hz	14.2 Hz	4.07–4.22 (4H) 2×CH_2
8c	5.85 (d)	4.44 (d)	3.91 (d)	4.21 (dd)	3.58 $\leftrightarrow_{m,3H}$ 3.82			11.14 (dd)	7.97 (d)	1.22 (t, 3H) CH_3; 1.27, 1.40, 2.35 (3s, 9H)
(*Z*)	3.62 Hz	—	2.60 Hz	7.97 Hz				8.44 Hz	13.9 Hz	3×CH_3; 4.09 (q, 2H) CH_2
8d	5.86 (d)	4.44 (d)	4.17 (d)	4.09 (dd)	3.58 $\leftrightarrow_{m,3H}$ 3.82			9.93 (dd)	6.73 (dd)	4.93 (d, 1H, $J_{CH,CH}$ 7.39 Hz) CH
(*E*)	3.53 Hz	—	2.69 Hz	7.30 Hz				9.45 Hz	12.89 Hz	1.23, 1.41, 1.95 3×CH_3
8e	5.85 (d)	4.35 (d)	4.12 (d)	4.17 (dd)	3.77 $\leftrightarrow_{m,3H}$ 3.94			10.79 (dd)	8.05 (d)	4.08 (q, 2H) CH_2; 1.43, 1.24 (2s, 6H) C*Me*$_2$
(*Z*)	3.60 Hz	—	2.80 Hz	6.54 Hz				9.00 Hz	14.1 Hz	0.85 (t, 3H) CH_3; 7.24–7.48 (m, 5H) aromat.
8f	5.90 (d)	4.46 (d)	3.99 (d)	4.18 (dd)	3.77 (m)	3.83 (s)	3.83 (s)	9.17 (dd)	7.49 (d)	1.24 (t, 3H) CH_3; 1.26, 1.44 (2s, 6H) C*Me*$_2$
(*E*)	3.74 Hz	—	1.60 Hz	7.06 Hz	—	—	—	9.21 Hz	13.9 Hz	4.07 (q, 2H) CH_2

Table 2. ^{13}C NMR data of the *N*-(β-ketoen)amino-saccharides

	C-1	C-2	C-3	C-4	C-5	C-6	–CO–	=C<	=CH–	Other signals
8a	104.35	84.86	73.19	84.86	60.30	60.50	197.81, 193.86	110.70	161.00	27.09, 31.49 CH_3; 26.62, 26.07 C*Me*$_2$; 110.38 *C*Me$_2$
8b	104.85	85.30	74.33	78.77	62.47	62.47	168.98, 166.96	90.14	160.09	14.30 CH_3; 59.89 CH_2 26.72, 26.10 C*Me*$_2$; 111.92 *C*Me$_2$
8c	102.99	83.74	73.01	76.64	60.41	58.06	197.85, 165.96	98.80	159.02	58.21 CH_2; 29.07, 12.72 2×CH_3, 25.06, 24.42 C*Me*$_2$; 110.18 *C*Me$_2$
	103.22	83.59	72.28	76.97	60.06	58.29	195.29, 167.29	99.11	158.86	58.21 CH_2; 29.15, 12.64 2×CH_3, 25.06, 24.42 C*Me*$_2$; 110.26 *C*Me$_2$
8d	105.16	85.72	74.97	79.61	63.08	60.22	197.99	94.60	153.75	29.15 CH_3; 27.14, 26.53 C*Me*$_2$; 112.11 *C*Me$_2$ *second isomer not detected*
8e	105.08	85.71	75.02	78.72	61.84	60.17	196.71, 168.76	100.68	161.18	62.44 CH_2; 14.06 CH_3, 27.16, 26.49 C*Me*$_2$; 112.22 *C*Me$_2$; 127.30–142.91 C_{arom}
	105.28	85.59	74.47	79.07	60.75	59.83	195.56, 169.40	100.80	160.47	62.63 CH_2; 13.91 CH_3, 27.16, 26.49 C*Me*$_2$; 112.16 *C*Me$_2$; 127.30–142.91 C_{arom}
8f	105.34	85.72	74.22	78.69	60.12	62.34	168.16	71.49	160.37	61.28 CH_2; 14.73 CH_3; 27.10, 26.49 C*Me*$_2$; 112.39 *C*Me$_2$; 119.75 CN
	105.01	85.72	75.32	78.15	60.84	61.49	171.23	72.92	166.18	61.12 CH_2; 14.53 CH_3; 27.10, 26.49 C*Me*$_2$; 112.39 *C*Me$_2$; 117.15 CN

2.2. Synthesis and structure of the copper(II) complexes

Ligands **8a–f** may react under deprotonation of the amino function at C-5 and the hydroxyl group at C-6 to give cuban-like structures analogous to amino ethanol derivatives,[37] or via an amino propanol-like reaction under complexation of the nitrogen and the hydroxyl group on C-3 of the furanose ring leading to binuclear structures.[38–40] All of the synthesized ligands form stable binuclear complexes of the general formula Cu_2L_2 with

copper(II) ions after deprotonation of the 3-OH and the NH group, due to the favored formation of six-membered chelate rings at the copper centers (Fig. 4).

Dissolving the complexes in the specified solvents and slow evaporation while standing in air gave for all complexes, except of **9d**, blue to violet crystals suitable for X-ray crystal structure analysis. Selected bond lengths and angles are included in Table 3.

Crystals of **9a**[42,43] consist of two different binuclear formula units. Figure 5 shows one of the molecules witch coordinates a water molecule at one of the copper centres. In the other unit a methanol is bound to one of the copper ions.

The asymmetric unit of **9b** contains two molecules (one is shown in Fig. 6). Both dimers are identical in formula and basic structure but differ in their three-dimensional shape. They are connected to each other by coordination of one of the free OH groups at C-6 of the next binuclear Cu_2L_2 unit (O9d-Cub: 2.442(4) Å). Additional solvent molecules are not coordinated.

In contrast in **9c** (Fig. 7) one copper ion binds two water molecules Cua (O91–Cua: 2.693(3) Å, O92–Cua: 2.858(3) Å). One is orientated into the direction of the furanose rings of the ligands (O92) the other one occupies the opposite coordination place (O91). The angle between the water molecules and Cua is 164.2(2)°. Cub fulfils its coordination sphere with interactions to the free hydroxyl group of its own ligand (O6b–Cub: 2.911(3) Å) and to the one of the next dimeric complex molecule (Cub–O6a: 2.744(2) Å, O6b–Cub–O6a: 147.7(2)°).

In **9e** one methanol molecule is bound directly to Cua into the direction of the furanose rings of the ligands (Cua-O1: 2.465(4) Å, Fig. 8).

Figure 9 shows the projection of the dimeric copper(II) complex **9f**. The compound crystallized from ethanol/water = 2:1 through slow evaporation of the solvents while standing in air. One water is directly bound to Cua (Cua–O1: 2.554(5) Å) and is localized in the opposite direction from the furanose rings of the ligands. The same water molecule is also weakly bound to Cub (Cub–O1: 3.265(5) Å).

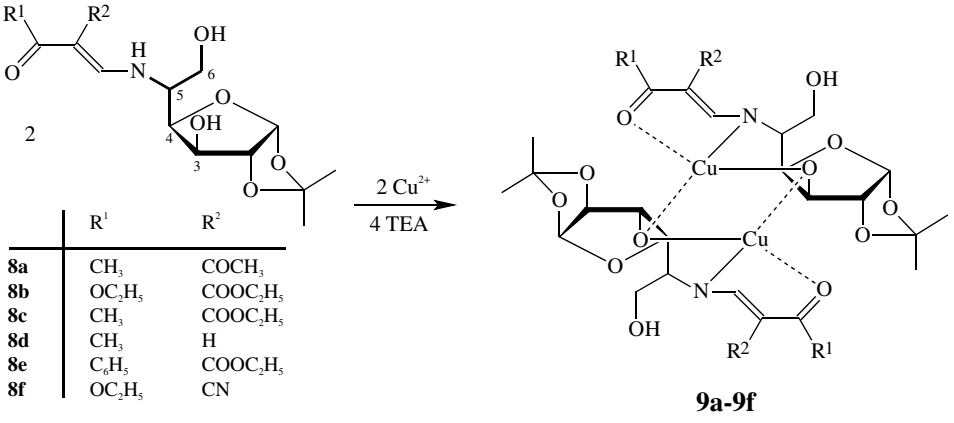
The exact molecular structure of **9d** could not be determined by X-ray single crystal analysis. Decomposition took place in all protic solvent mixtures from which crystallization was tried. Only in toluene under an argon atmosphere could **9d** be dissolved without any disintegration. The electron spray ionization mass spectra shows a peak at $m/z = 720$ with an intensity of 100%. The isotope pattern indicates two copper atoms. So the peak can be assigned to $[Cu_2L_2+Na]^+$. The electronic spectrum showed a d–d band at 562 nm, a LMCT absorption at 353 nm, and a absorption of the ligand at 321 nm. Therefore a dimeric structure of **9d** is plausible.

2.3. Supramolecular structure and puckering in the crystals

A complicated network of H-bridges involving coordinated and additional solvent molecules stabilizes the low symmetry of the complexes. In fact every furanose ring adopts a different conformation (Table 4) and the copper(II) ions exhibit diverse geometries of their coordination spheres.

In the crystals different supramolecular structures were found. In **9a** a two-dimensional and in **9b**, **9c**, and **9e** a chain-like arrangement of the binuclear copper(II) units is realized.

In **9e** also a formation of chains is observed due to the hydrogen bonds between the free 6-OH groups and the oxygen atoms at C-1 (O5a–O4a: 2.904(10) Å, O5b–O4b: 2.864(10) Å). The bound water molecule interacts with a nitrogen atom of a nitrile group of a ligand in a second chain (N2b–O1: 2.830(10) Å und N2a–O1: 2.949(10) Å) which runs in opposite direction (Fig. 10).



	R^1	R^2
8a	CH_3	$COCH_3$
8b	OC_2H_5	$COOC_2H_5$
8c	CH_3	$COOC_2H_5$
8d	CH_3	H
8e	C_6H_5	$COOC_2H_5$
8f	OC_2H_5	CN

Figure 4. Synthesis and basic binuclear structure of the copper(II) complexes **9a**–**f**.

Table 3. Selected interatomic distances, bond lengths [Å], and angels [°] at the copper centres of **9b**, **9c**, **9e**, **9f** (for **9a** see lit. 43)

9b			
Cua–Cub	3.0038(4)	Cuc–Cud	3.0030(5)
Cua–N1a	1.903(2)	Cuc–N1c	1.907(2)
Cub–N1b	1.931(2)	Cud–N1d	1.921(2)
Cua–O1a	1.921(2)	Cuc–O1c	1.9184(19)
Cub–O1b	1.9297(19)	Cud–O1d	1.9335(19)
Cua–O2a	1.9238(19)	Cuc–O2c	1.9081(19)
Cub–O2b	1.9188(19)	Cud–O2d	1.9245(18)
Cua–O2b	1.926(2)	Cuc–O2d	1.9316(19)
Cub–O2a	1.960(2)	Cud–O2c	1.9470(19)
CubO9d	2.442(2)	O6b–O9c	2.730(5)
N1a–Cua–O1a	92.69(9)	N1c–Cuc–O1c	92.85(9)
N1a–Cua–O2a	96.68(9)	N1c–Cuc–O2c	96.66(9)
O2a–Cua–O2b	78.31(8)	O2c–Cuc–O2d	77.91(8)
N1b–Cub–O1b	92.14(9)	N1d–Cud–O1d	92.26(9)
N1b–Cub–O2b	96.76(9)	N1d–Cud–O2d	96.47(9)
O2b–Cub–O2a	77.60(8)	O2d–Cud–O2c	77.16(8)
9c			
Cua–Cub	3.0134(5)	Cub–O6b	2.911(3)
Cua–N5a	1.912(3)	Cub–N5b	1.902(3)
Cua–O3a	1.927(3)	Cub–O3b	1.932(3)
Cua–O7a	1.906(3)	Cub–O7b	1.924(3)
Cua–O3b	1.938(3)	Cub–O3a	1.937(3)
Cua–O91	2.693(3)	Cua–O92	2.858(3)
O7a–Cua–N5a	93.02(14)	O7b–Cub–N5b	91.52(13)
N5a–Cua–O3a	96.38(13)	N5b–Cub–O3b	96.08(13)
O3a–Cua–O3b	77.43(12)	O3b–Cub–O3a	77.33(12)
9e			
Cua–Cub	2.9802(8)	Cua–O1	2.465(4)
Cua–N1a	1.925(4)	Cub–N1b	1.931(4)
Cua–O2a	1.922(3)	Cub–O2b	1.928(3)
Cua–O1a	1.903(3)	Cub–O1b	1.934(3)
Cua–O2b	1.949(3)	Cub–O2a	1.920(3)
O1a–Cua–N1a	92.36(15)	O1b–Cub–N1b	92.89(16)
N1a–Cua–O2a	96.42(14)	N1b–Cub–O2b	96.06(15)
O2a–Cua–O2b	77.35(12)	O2b–Cub–O2a	77.92(12)
9f			
Cua–Cub	2.9332(9)	Cua–O1	2.554(5)
Cua–N1a	1.925(4)	Cub–N1b	1.928(5)
Cua–O7a	1.902(4)	Cub–O7b	1.895(4)
Cua–O1a	1.912(4)	Cub–O1b	1.919(4)
Cua–O7b	1.924(4)	Cub–O7a	1.932(4)
O1a–Cua–N1a	93.61(19)	O1b–Cub–N1b	94.7(2)
N1a–Cua–O7a	98.13(19)	N1b–Cub–O7b	97.31(18)
O7a–Cua–O7b	77.09(16)	O7b–Cub–O7a	77.07(17)

2.4. Catecholoxidase-like activity

The synthesized copper(II) complexes were used as catalysts for the oxidation of di-*tert*-butylchatechol to the corresponding quinone under the already published conditions.[42–44] Only **9a** and **9d** show a significant activity (**9a**: $k_{cat.} = 2.8(3)\,h^{-1}$, $K_M = 7.08(50)\times10^{-3}$ mol/L, $k_{obs} = 4.0(2)\,h^{-1}$ and **9d**: $k_{cat.} = 30.8(29)\,h^{-1}$, $K_M = 3.97(7)\times10^{-3}$ mol/L, $k_{obs} = 6.99(29)\,h^{-1}$). Compounds **9b**, **9c**, **9e**, and **9f** were found to be not more active as catalysts in this reaction than the copper(II) acetate used for the synthesis of the compounds.

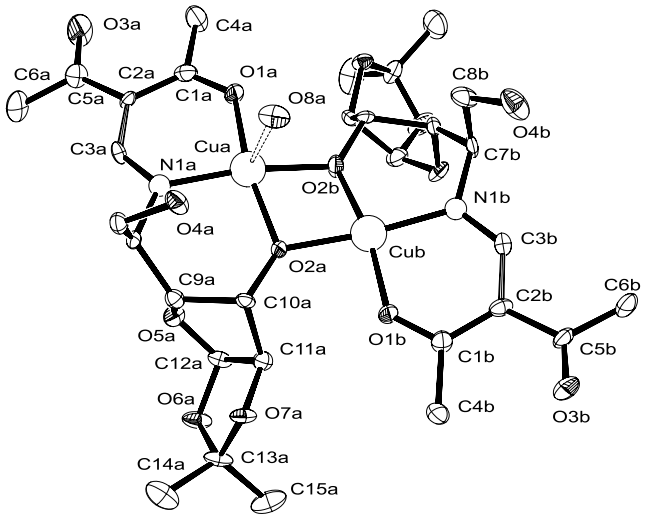


Figure 5. Structure of one subunit in **9a** (without hydrogen atoms).

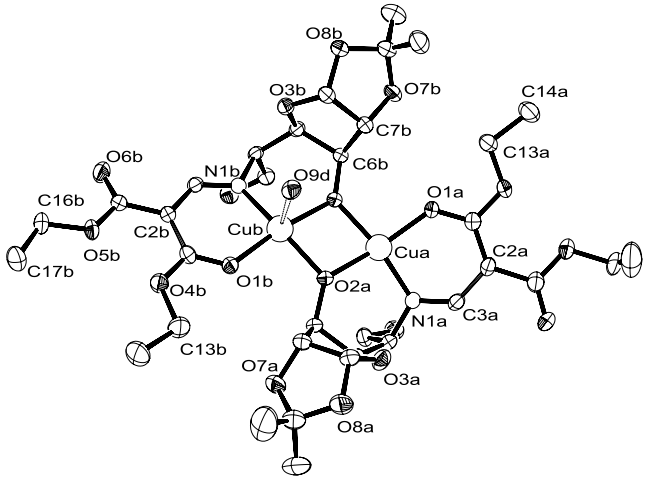


Figure 6. Structure of one subunit in **9b** (without hydrogen atoms).

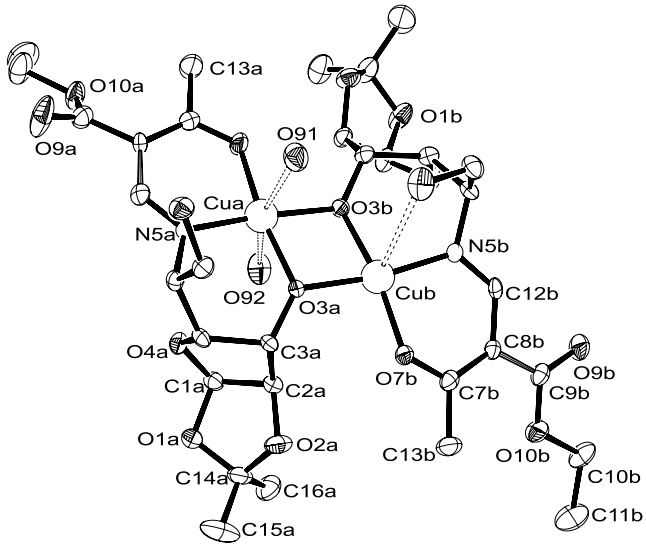


Figure 7. Structure of **9c** (without hydrogen atoms).

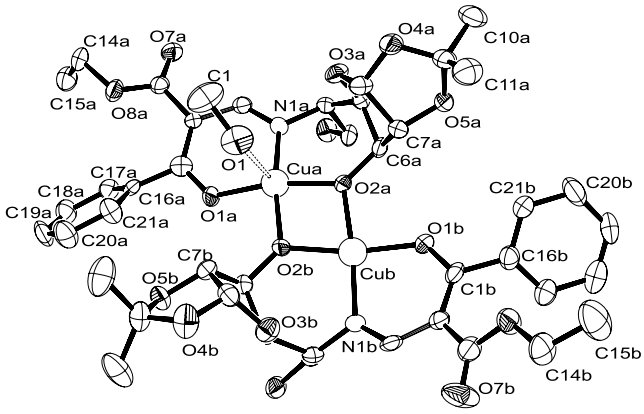


Figure 8. Structure of **9e** (without hydrogen atoms).

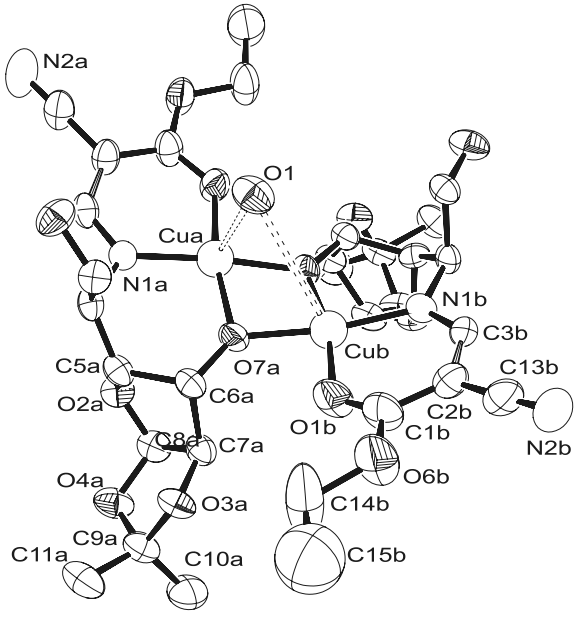


Figure 9. Structure of **9f** (without hydrogen atoms).

2.5. Conclusions

In contrast to complexes derived from 3-aminopropanol, which form stable and highly symmetric binuclear copper(II) complexes, carbohydrate derived compounds lead to structures of low symmetry and supramolecular architecture. The furanose rings induce a 'strain' on the metal centres. The copper ions are forced to saturate their coordination sphere by complexation of additional donor atoms originating in solvent molecules, free hydroxyl groups of the same ligand, or interactions to oxygen atoms of the next complex molecule. For **9a** and **9d**, this results in a catalytic activity in the catecholoxidase-like reaction.

3. Experimental section

3.1. General methods

Electronic spectra were recorded with a Varian Cary 1 or Cary 5E spectrophotometer at room temperature. IR spectra were measured on a Perkin–Elmer 2000 spectrometer; NMR spectra on a Bruker AC-200, mass spectra on a Finnigan MAT SSQ 710 or a Finnigan MAT 95XL TRAP and elemental analyses on a Leco CHNS 932.

3.2. Procedure A (synthesis of 8a–f)

To a solution of 3.2 mmol (700 mg) 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**8**) in 50 mL dry MeOH 3.5 mmol (355 mg) Et_3N and 3.5 mmol of the corresponding compound **a**–**f** were added. The solution was stirred 1–24 h until the starting material was not longer detected by TLC. The solvent was evaporated and the samples were dried. Cleaning was carried out by column chromatography over silica gel 60 (0.063–0.2 mm) in the specified solvents.

Table 4. Conformation and puckering parameter of the furanose rings in **9a**–**f** (except **9d**)[59]

Compound	Ring	Sequence	Conformation	Ratio twist:envelope [%]	Puckering parameter	
					Q [Å]	ϕ [°]
9a	A	O5a–C9a–C10a–C11a–C12a	dist. twist	84:16	0.411	15.16
	B	O5b–C9b–C10b–C11b–C12b	intermediate	52:48	0.418	9.31
	C	O5c–C9c–C10c–C11c–C12c	dist. envelope	9:91	0.367	1.57
	D	O5d–C9d–C10d–C11d–C12d	twist	96:4	0.407	17.23
9b	A	O3a–C5a–C6a–C7a–C8a	dist. twist	90:10	0.364	16.19
	B	O3b–C5b–C6b-C7b–C8b	intermediate	67:33	0.314	5.91
	C	O3c–C5c–C6c–C7c–C8c	dist. twist	86:14	0.345	15.43
	D	O3d–C5d–C6d–C7d–C8d	dist. twist	86:14	0.327	15.56
9c	A	O4a–C1a–C2a–C3a–C4a	dist. envelope	17: 83	0.322	3.05
	B	O4b–C1b–C2b–C3b–C4b	dist. twist	91:9	0.377	16.44
9e	A	O3a–C8a–C7a–C6a–C5a	intermediat	52: 48	0.372	9.33
	B	O3b–C8b–C7b–C6b–C5b	dist. twist	89:11	0.356	16.02
9f	A	O2a–C5a–C6a–C7a–C8a	intermediat	60:40	0.407	10.90
	B	O2b–C5b–C6b–C7b–C8b	dist. twist	88:12	0.415	15.87

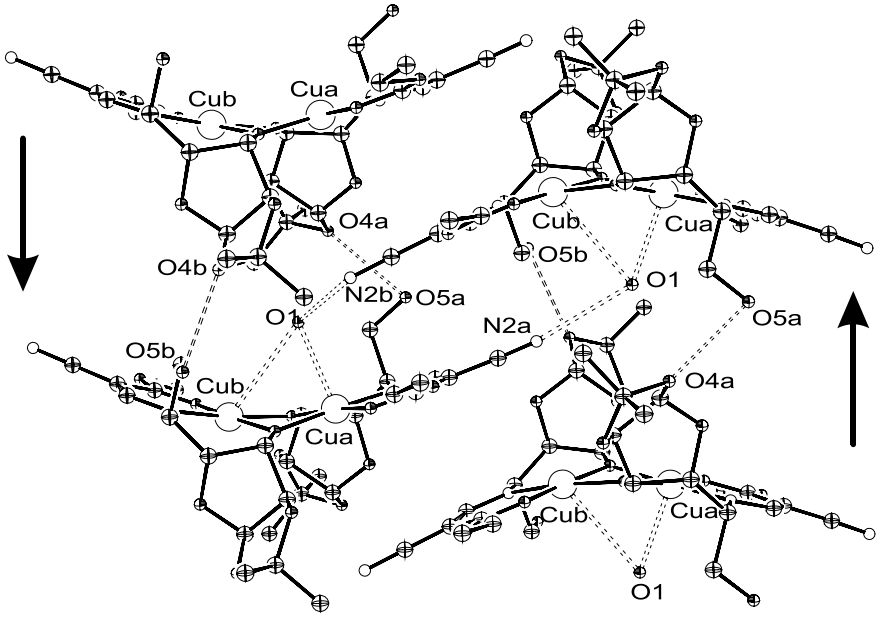


Figure 10. Supramolecular structure in the crystal of **9f**.

3.3. Procedure B

To a solution of 0.3 mmol of the ligand and 0.6 mmol (61 mg) Et_3N in 30 mL MeOH 0.3 mmol (54.3 mg) copper(II) acetate were added and the solution was stirred for at least 24 h. The solvent was evaporated and the sample was dried. The product was extracted with and crystallized from different solvents (see below).

3.4. Procedure C

To a solution of 0.3 mmol of the ligand and 0.6 mmol (61 mg) Et_3N in 30 mL THF 0.3 mmol (40.3 mg) copper(II) chloride were added and the solution was stirred for 24 h at room temperature. The formed precipitate (triethylammonium chloride) was filtered off and the solvent was evaporated.

3.5. 5-Chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (4)[60–62]

Eleven grams (47 mmol) of **3** were diluted in 350 mL dimethoxyethane. The solution was cooled to −10 °C and 5.6 g acetic acid were added drop wise. Then, 7.3 g $NaBH_4$ were added slowly to the cooled solution. The reaction mixture was stirred for at least 8 h (TLC in ethyl acetate/petrol ether 5:1), with the temperature was kept below 0 °C. Excessive acetic acid was neutralized by adding solid $NaHCO_3$ and stirring for 24 h at room temperature. The solution was filtered, evaporated, and poured into ice/sodium chloride. The mixture was extracted with chloroform, dried with Na_2SO_4, and evaporated. Traces of starting material were removed by dissolving the crude product in petrol ether and elution over silica gel until **3** is not longer detected by TLC. Compound **4** was eluted from the silica gel with ethyl acetate. Evaporation yielded 7.5 g (67%) colorless oil: [α] −9.0° (*c*1, $CHCl_3$); IR (ATR); cm^{-1} 3410s, 2988w, 2937w, 2893w, 1633vw, 1457w, 1376s, 1333w, 1295w, 1255w, 1215s, 1163s, 1068vs, 1007vs, 951s, 928s, 882w, 855s, 792w, 705w; DEIMS: *m*/*z* (relative intensity, %) 239 [$(M+1)^+$, 60]; Anal. Calcd for $C_9H_{15}ClO_5$ ($M = 238.67$ g/mol): C, 45.29; H, 6.33; Cl, 14.85. Found: C, 44.68; H, 6.47; Cl, 14.32.

3.6. 5-Chloro-5-deoxy-1,2:3,6-*O*-diisopropylidene-β-L-idofuranose (5)[63]

7.3 g (30.6 mmol) of **4**, 20 mL 2,2-dimethoxypropane, and 20 g molecular sieves (A4) were dissolved in 150 mL acetone. Under stirring 0.4 mL conc. H_2SO_4 was added drop wise. The solution was stirred at room temperature until the starting material is no longer detected by TLC (2 h, TLC: solvent ethyl acetate/petrol ether 1:1, RF-value of **5**: 0.91). CaO was added for neutralization and the suspension is stirred overnight. The solution was filtered and evaporated. The crude product filtered over silica gel, yielded 6.6 g (75%) colorless oil: bp 102–105 °C/0.15mmHg; [α] +46.0° (*c*1, $CHCl_3$); lit.[62] oil; [α] +48.8° (*c*1, $CHCl_3$); DEIMS: *m*/*z* (relative intensity, %) 279 [$(M+1)^+$, 30]; Anal. Calcd for $C_{12}H_{19}ClO_5$ ($M = 278.73$ g/mol): C, 51.88; H, 6.91; Cl, 12.76. Found: C, 51.99; H, 6.79; Cl, 12.28.

3.7. 5-Amino-5-deoxy-1,2:3,6-*O*-diisopropylidene-α-D-glucofuranose (7)

10.2 g (36.5 mmol) of **5** was dissolved in 200 mL *N*,*N*-dimethylformamide and stirred together with 14.2 g NaN_3 for 72 h at 120 °C. TLC control of the reaction is difficult as **5** and the formed 5-azido-5-deoxy-1,2:3,6-*O*-diisopropylidene-α-D-glucofuranose (**6**) have the same RF value (e.g., 0.6 for ethyl acetate/petrol ether 1:5). The reaction mixture was evaporated to dryness, dissolved in water, and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and evaporated. The ratio of **5** to **6** is about 1:4 (NMR). 10.1 g (ca. 35.4 mmol) of this mixture and 4.4 g (88.6 mmol) hydrazine hydrate were dissolved in 200 mL MeOH and heated to 40 °C. Freshly prepared Raney-Nickel suspension was added portion wise under stirring until there was no longer development of gas. The suspension is heated under reflux for 1 h, filtered and evaporated. To regain the unreacted chloride **5** the mixture is eluted over silica gel with ethyl acetate/petrol ether 3.5:1 until negative detection of **5** by TLC. The product than is eluted with MeOH. The solution is evaporated, the product is tried, and recrystallized from ethyl acetate/heptane yielded 6.1 g (65%) of colorless needles: mp 68–69 °C; DEIMS: m/z (relative intensity, %) 260 [$(M+1)^+$, 80]; Anal. Calcd for $C_{12}H_{21}NO_5$ ($M = 259.30$ g/mol): C, 55.60; H, 8.11; N, 5.41. Found: C, 54.14; H, 7.77; N, 4.50.

3.8. 5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8)[64]

4.4 g (17 mmol) of **7** are dissolved in 30 mL MeOH. Then, a solution of 1.2 g conc. H_2SO_4 in 20 mL water is added dropwise and the solution stirred for 72 h at room temperature. A large excess of $BaCO_3$ is added and the suspension is stirred overnight and heated under reflux for again 3 h. The barium salts are filtered off and the product is cleaned by elution over silica gel (solvent MeOH), yielded 3.1 g (80%) colorless needles: mp 175 °C, lit.[64] 178 °C; [α] −13.3° (*c*1, MeOH); IR (ATR); cm^{-1} 3316s, 3216s, 2923w, 2861w, 1664w, 1609vs, 1486s, 1426s, 1377vs, 1278s, 1221s, 1164s, 1132s, 1066vs, 999vs, 955vs, 868vs, 785vs, 689s, 624s; DEIMS: m/z (relative intensity, %) 220 [$(M+1)^+$, 90]; Anal. Calcd for $C_9H_{17}NO_5$ ($M = 219.11$ g/mol): C, 49.32; H, 7.76; N, 6.39. Found: C, 49.48; H, 8.34; N, 6.34.

3.9. 5-*N*-(2′,2′-Diacetylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8a)

Procedure A. Chromatography (ethyl acetate) yielded 880 mg (83%) colorless needles: mp 177 °C; [α] −59.6° (*c*1, MeOH); R_f 0.30 (ethyl acetate); IR (ATR); cm^{-1} 3372s, 3287s, 2985w, 2962w, 2934w, 1609vs, 1557vs, 1407s, 1384s, 1351s, 1314s, 1298s, 1243vs, 1218vs, 1164w, 1095w, 1064vs, 1014vs, 983s, 943s, 893w, 854s, 820w, 668w, 636w. DCIMS: m/z (relative intensity, %) 330 [$(M+1)^+$, 60]; UV/vis (MeOH); λ_{max} 290 nm ($\lg\varepsilon = 4.3087$), 255 nm ($\lg\varepsilon = 4.2164$); 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, 54.72; H, 7.30; N, 4.29.

3.10. 5-*N*-(2′,2′-Diethoxycarbonylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8b)

Procedure A. Chromatography (ethyl acetate) and recrystallization from ethanol/petrol ether yielded 770 mg (62%) colorless needles suitable for X-ray structure analysis: mp 157 °C, [α] −34.1° (*c*1, MeOH); R_f 0.38 (ethyl acetate); IR (ATR); cm^{-1} 3338s, 3171w, 2979s, 2935s, 2878s, 1689vs, 1657vs, 1614vs, 1466w, 1425s, 1376s, 1322s, 1269s, 1211vs, 1164s, 1147w, 1122w, 1071vs, 1008vs, 886s, 858w, 798s, 747w, 625w; DCIMS: m/z (relative intensity, %) 390 [$(M+1)^+$, 70]; UV/vis (MeOH); λ_{max} 278 nm ($\lg\varepsilon = 4.3454$), 222 nm ($\lg\varepsilon = 4.0746$); 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, 52.44; H, 7.11; N, 3.60.

3.11. 5-*N*-(2′-Acetyl-2′-ethoxycarbonylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8c)

Procedure A. Chromatography (ethyl acetate/MeOH 3:1) yielded 817 mg (71%) colorless oil: [α] −34.6° (*c*1, MeOH); R_f 0.18 (ethyl acetate/hexane 2:1); IR (ATR); cm^{-1} 3372s, 2984w, 2935w, 1737vw, 1671s, 1631vs, 1562s, 1415s, 1374s, 1303s, 1237s, 1214s, 1164w, 1066vs, 1009vs, 956w, 882w, 854s, 790s, 644w, 617w; DCIMS: m/z (relative intensity, %) 360 [$(M+1)^+$, 70]; UV/vis (dioxane); λ_{max} 293 nm ($\lg\varepsilon = 4.1715$), 233 nm ($\lg\varepsilon = 4.1740$); 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, 51.62; H, 7.34; N, 3.65.

3.12. 5-*N*-(2′-acetylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8d)

Procedure A. Chromatography (ethyl acetate/MeOH 3:1) yielded 505 mg (55%) yellow oil: [α] −83.2° (*c*1, MeOH); R_f 0.18 (ethyl acetate); IR (ATR); cm^{-1} 3309s, 2986w, 2937w, 2885vw, 1735w, 1635vs, 1551s, 1493s, 1375s, 1257s, 1213s, 1164s, 1067vs, 1009vs, 958s, 882w, 858w, 790s, 746w, 669w, 618w; DCIMS: m/z (relative intensity, %) 288 [$(M+1)^+$, 80]; UV/vis (dioxane); λ_{max} 296 nm ($\lg\varepsilon = 4.2085$); 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, 52.73; H, 7.49; N, 4.44.

3.13. 5-*N*-(2′-Ethoxycarbonyl-2′-phenylcarbonyl-vinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-gluco-furanose (8e)

Procedure A. Chromatography (ethyl acetate) yielded 1050 mg (78%) colorless oil: [α] −23.9° (*c*1, MeOH); R_f 0.45 (ethyl acetate); IR (ATR); cm^{-1} 3367s, 3286s, 3060w, 2984s, 2936s, 2901w, 1666vs, 1619vs, 1560s, 1446w, 1376s, 1307s, 1214vs, 1163s, 1067s, 1009vs, 853w, 785s, 724w, 698s, 669s, 616w; DCIMS: *m*/*z* (relative intensity, %) 422 [(M+1)$^+$, 50]; UV/vis (MeOH); λ_{max} 246 nm (lgε = 4.2735), 302 nm (lgε = 4.3076); Anal. Calcd for $C_{21}H_{27}NO_8$ (*M* = 421.45 g/mol): C, 59.89; H, 6.46; N, 3.33. Found: C, 59.40; H, 6.33; N, 3.20.

3.14. 5-*N*-(2′-Ethoxycarbonyl-2′-nitrilvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8f)

Procedure A. Chromatography (ethyl acetate) yielded 710 mg (65%) colorless oil: [α] −33.0° (*c*1, MeOH); R_f 0.55 (ethyl acetate); IR (ATR); cm^{-1} 3373s, 3294s, 2984w, 2936w, 2210vs, 1677vs, 1615vs, 1436w, 1378s, 1332w, 1240vs, 1163s, 1067vs 1009vs, 955w, 860w, 782s, 676w, 617w; DCIMS: *m*/*z* (relative intensity, %) 343 [(M+1)$^+$, 70]; UV/vis (MeOH); λ_{max} 281 nm (lgε = 4.3603), 205 nm (lgε = 4.0816); 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, 51.76; H, 6.82; N, 7.76.

3.15. Bis-(5-*N*-(2′,2′-diacetylvinyl)amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-aquo-dicopper(II)-bis-(5-*N*-(2′,2′-diacetylvinyl)amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-methanolo-dicopper(II) (9a)

Procedure B. The residue was dissolved in toluene. During the slow evaporation of the solvent a violet toluene containing compound crystallizes. Recrystallization from water/MeOH = 1:1 leads to the precipitation of 28 mg (24.00%) deep blue crystals of **9a** in a quality suitable for X-ray crystal structure determination: IR (KBr); cm^{-1} 3331w, 2984s, 2928s, 1719vw, 1649w, 1584vs, 1457s, 1395vs, 1357s, 1283s, 1257s, 1213s, 1165s, 1125s, 1059vs, 1008vs, 946s, 882s, 844s, 732s, 696w, 638s; UV/vis (MeOH); λ_{max} 651 nm (lgε = 2.2201), 373 nm (lgε = 3.1284); ESIMS: *m*/*z* 1585 (Cu_4L_4+Na)$^+$, 1173 (Cu_3L_3+H)$^+$, 804 (Cu_2L_2+Na)$^+$, 783 ($Cu_2L_2H_2$)$^+$, 423 (CuL(MeOH))$^+$, 391 (CuL)$^+$; Anal. Calcd for $C_{61}H_{96}N_4O_{33}Cu_4[Cu_4L_4H_2OCH_3OH]$ (*M* = 1667.62 g/mol): C, 43.94; H, 5.80; N, 3.36. Found: C, 44.05; H, 5.87; N, 3.31.

3.16. Bis-(5-*N*-(2′,2′-Diethoxycarbonylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-dicopper(II) (9b)

Procedure C. The residue was extracted with toluene to give a blue solid, which can be recrystallized from MeOH/water to give 66 mg (49%) of deep-blue crystals suitable for X-ray crystal structure analysis: IR (KBr); cm^{-1} 3426vw, 2955s, 2923vs, 2854vs, 1733vw, 1675w, 1604s, 1461s, 1412w, 1377s, 1347w, 1259s, 1215w, 1166w, 1068vs, 1013vs, 868w, 796vs, 727w, 642w; UV/vis (MeOH); λ_{max} 583 nm (lgε = 2.6685), 352 nm (lgε = 3.4462), 292 nm (lgε = 3.9691), 225 nm (lgε = 4.5733); ESIMS: *m*/*z* 2728 (Cu_6L_6+Na)$^+$, 1827 (Cu_4L_4+Na)$^+$, 1353 (Cu_3L_3)$^+$, 925 (Cu_2L_2+Na)$^+$; 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.

3.17. Bis-(5-*N*-(2′-acetyl-2′-ethoxycarbonylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-diaquo-dicopper(II) (9c)

Procedure B with 150 mg (0.42 mmol) **8c**. The residue was extracted with toluene to give a blue solid, which can be recrystallized from MeOH/water to give 77 mg (42%) of deep-blue crystals suitable for X-ray crystal structure analysis: IR (ATR); cm^{-1} 3519w, 2981w, 2936w, 2897w, 1662s, 1604vs, 1442s, 1410s, 1373s, 1279s, 1207w, 1167w, 1133w, 1062s, 998s, 956w, 885w, 843w, 822w, 778w, 729w; UV/vis (ethanol); λ_{max} 350.4 nm (lgε = 4.0003),302 nm (lgε = 4.3407), 244 nm (lgε = 4.6613); ESIMS: *m*/*z* 863 (Cu_2L_2+Na)$^+$; Anal. Calcd for $C_{33}H_{54}N_2O_{19}Cu_2$-[$Cu_2L_2$2$H_2OCH_3OH$] (*M* = 908.22 g/mol): C, 43.64; H, 5.99; N, 3.08. Found: C, 45.75; H, 5.99; N, 2.99.

3.18. Bis-(5-*N*-(2′-acetylvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-dicopper(II) (9d)

Procedure B. The residue was extracted with toluene and the solvent was evaporated to give 86 mg (82%) violet solid. The substance could not be crystallized from any solvent we tried: IR (ATR): cm^{-1} 3358s, 2985s, 2917s, 1667w, 1600vs, 1515vs, 1455w, 1398vs, 1381vs, 1258w, 1213s, 1164w, 1125w, 1062vs, 1006vs, 955s, 883s, 843s, 822s, 750w, 647w, 619w; ESIMS: *m*/*z* 719 (Cu_2L_2+Na)$^+$, 372 (CuL+Na)$^+$; UV/vis (MeOH); λ_{max} 321 nm (lgε = 4.3217), 353 nm (lgε = 4.0174), 562 nm (lgε = 3.3363); Anal. Calcd for $C_{26}H_{38}Cu_2N_2O_{12}$ [Cu_2L_2] (*M* = 697.69 g/mol): C, 44.86; H, 5.50; N, 4.02. Found: C, 43.30; H, 6.17; N, 3.59.

3.19. Bis-(5-*N*-(2′-ethoxycarbonyl-2′-phenylcarbonyl-vinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-gluco-furanoso)-methanolo-dicopper(II) (9e)

Procedure B. The crude product was extracted with toluene, evaporated, and recrystallized from MeOH/water to give 75 mg (52%) of violet crystals suitable for

X-ray crystal structure analysis: IR (ATR); cm^{-1} 3460w, 3060vw, 2984w, 2937w, 2897w, 1661s, 1600vs, 1497w, 1453vs, 1409vs, 1369vs, 1281vs, 1217s, 1166s, 1126s, 1050s, 1007s, 872w, 778s, 738s, 701vs, 646s, 619s; ESIMS: m/z 989 $(Cu_2L_2+Na)^+$; UV/vis (MeOH); λ_{max} 205 nm ($lg\varepsilon = 4.6255$), 252 nm ($lg\varepsilon = 4.6587$), 327 nm ($lg\varepsilon = 4.3677$); Anal. Calcd for $C_{42}H_{50}Cu_2N_2O_{16}$ $[Cu_2L_2]$ ($M = 965.95$ g/mol): C, 52.32; H, 5.23; N, 2.91. Found: C, 52.34; H, 4.99; N, 2.92.

3.20. Bis-(5-*N*-(2′-ethoxycarbonyl-2′-nitrilvinyl)amino-5-desoxy-1,2-*O*-isopropylidene-α-D-glucofuranoso)-aquo-dicopper(II) (9f)

Procedure C with 450 mg (1.3 mmol) of **8f**. The residual was recrystallized from toluene/MeOH to give 223 mg (42%) of violet crystals suitable for X-ray crystal structure analysis: IR (ATR); cm^{-1} 3496s, 2986w, 2935w, 2900w, 2206vs, 1682vw, 1630vs, 1515s, 1471w, 1438s, 1414s, 1378s, 1351s, 1299w, 1257s, 1207s, 1165w, 1120w, 1060s, 995s, 885w, 870w, 843w, 831w, 758w, 645w, 611vw; ESIMS: m/z 830 $(Cu_2L_2+Na)^+$; UV/vis (MeOH); λ_{max} 342 nm ($lg\varepsilon = 3.8503$), 294 nm ($lg\varepsilon = 4.4347$), 259 nm ($lg\varepsilon = 4.1853$), 225 nm ($lg\varepsilon = 4.5733$). Anal. Calcd for $C_{30}H_{40}Cu_2N_4O_{14}$ $[Cu_2L_2]$ ($M = 807.76$ g/mol): C, 44.61; H, 4.99; N, 6.94. Found: C, 44.66; H, 5.10; N, 6.89.

4. Crystal structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[65,66]

The structures were solved by direct methods (SHELXS[67]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97[68]). For compound **8b** (FO997)the hydrogen atoms of the amin-, the hydroxyl group and the ring-atoms were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of the other structures were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically.[65] ORTEP32 was used for structure representations.

Further details of the crystal structure investigations are available on request from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1 EZ, on quoting the depository number CCSD-185925 (**8b**, fo977), CCDC-129253 (**9a**, fo1063), CCSD-185924 (**9b**, fo1556), CCSD-192874 (**9c**, fo1714), CCSD-185923 (**9e**, fo1495), and CCSD-185922 (**9f**, fo1468) and the names of the authors, and the journal citation.

4.1. Crystal data for 8b (FO977)

$C_{17}H_{27}NO_9$, $M_r = 389.40$ g mol^{-1}, colorless prism, size $0.30\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1$, $a = 11.6522(6)$, $b = 7.3797(4)$, $c = 12.5751(7)$ Å, $\beta = 107.677(3)°$, $V = 1030.3(1)$ Å^3, $T = 20$ °C, $Z = 2$, $\rho_{calcd.} = 1.255$ g cm^{-3}, μ (Mo-K_α) = 1.02 cm^{-1}, $F(000) = 416$, 4089 reflections in $h(-14/14)$, $k(-9/9)$, $l(-15/15)$, measured in the range $3.24° \leqslant \Theta \leqslant 26.48°$, completeness $\Theta_{max} = 99\%$, 4078 independent reflections, $R_{int} = 0.042$, 3140 reflections with $F_o > 4\sigma(F_o)$, 281 parameters, 1 restraints, $R1_{obs} = 0.056$, $wR2_{obs} = 0.119$, $R1_{all} = 0.079$, $wR2_{all} = 0.131$, GOOF = 1.074, Flack-parameter 0.7(13), largest difference peak and hole: 0.351/−0.192 e Å^{-3}.

4.2. Crystal data for 9a (FO1063)

$C_{30}H_{42}Cu_2N_2O_{14}$*1/2$CH_3OH$*21/4$H_2O$, $M_r = 837.79$ g mol^{-1}, blue prism, size $0.28\times0.24\times 0.20$ mm^3, monoclinic, space group $P2_1$, $a = 10.3923(3)$, $b = 13.8859(5)$, $c = 25.9903(8)$ Å, $\beta = 101.517(2)°$, $V = 3675.1(2)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.514$ g cm^{-3}, μ (Mo-K_α) = 12.33 cm^{-1}, $F(000) = 1748$, 15126 reflections in $h(0/14)$, $k(-19/19)$, $l(-25/27)$, measured in the range $2.30° \leqslant \Theta \leqslant 30.52°$, completeness $\Theta_{max} = 78.2\%$, 14812 independent reflections, $R_{int} = 0.041$, 11657 reflections with $F_o > 4\sigma(F_o)$, 933 parameters, 1 restraints, $R1_{obs} = 0.080$, $wR2_{obs} = 0.141$, $R1_{all} = 0.110$, $wR2_{all} = 0.153$, GOOF = 1.095, Flack-parameter 0.35(1), largest difference peak and hole: 0.646/−0.695 e Å^{-3}.

4.3. Crystal data for 9b (FO1556)

$C_{34}H_{52}Cu_2N_2O_{19}$*1/2 H_2O, $M_r = 928.86$ g mol^{-1}, blue prism, size $0.12\times0.10\times0.08$ mm^3, monoclinic, space group $P2_1$, $a = 10.4383(1)$, $b = 25.9592(3)$, $c = 15.8939(2)$ Å, $\beta = 102.435(1)°$, $V = 4205.74(8)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.467$ g cm^{-3}, μ (Mo-K_α) = 10.9 cm^{-1}, $F(000) = 1940$, 18571 reflections in $h(-13/13)$, $k(-33/33)$, $l(-20/20)$, measured in the range $2.05° \leqslant \Theta \leqslant 27.47°$, completeness $\Theta_{max} = 99.7\%$, 18542 independent reflections, $R_{int} = 0.028$, 16847 reflections with $F_o > 4\sigma(F_o)$, 1056 parameters, 1 restraints, $R1_{obs} = 0.035$, $wR2_{obs} = 0.082$, $R1_{all} = 0.043$, $wR2_{all} = 0.087$, GOOF = 1.010, Flack-parameter 0.004(6), largest difference peak and hole: 0.874/−0.455 e Å^{-3}.

4.4. Crystal data for 9c (FO1714)

$C_{32}H_{46}Cu_2N_2O_{16}$*2 H_2O, $M_r = 877.82$ g mol^{-1}, blue prism, size $0.10\times0.08\times0.06$ mm^3, triclinic, space group P1, $a = 7.8448(2)$, $b = 9.0849(3)$, $c = 14.2672(4)$ Å, $\alpha = 97.892(1)$, $\beta = 100.267(1)$, $\gamma = 97.698(1)$ °, $V = 977.87(5)$ Å^3, $T = -90$ °C, $Z = 1$, $\rho_{calcd.} = 1.491$ g cm^{-3}, μ

(Mo-K_α) = 11.64 cm^{-1}, $F(000) = 458$, 7081 reflections in $h(-9/10)$, $k(-11/9)$, $l(-17/18)$, measured in the range $2.51° \leqslant \Theta \leqslant 27.46°$, completeness $\Theta_{max} = 99.2\%$, 7074 independent reflections, $R_{int} = 0.050$, 5945 reflections with $F_o > 4\sigma(F_o)$, 503 parameters, 3 restraints, $R1_{obs} = 0.038$, $wR2_{obs} = 0.079$, $R1_{all} = 0.054$, $wR2_{all} = 0.085$, GOOF = 0.994, Flack-parameter −0.008(9), largest difference peak and hole: 0.318/−0.363 e $Å^{-3}$.

4.5. Crystal data for 9e (FO1495)

$C_{42}H_{48}Cu_2N_2O_{16}$*3/2$CH_3OH$*1/2 H_2O, $M_r = 1020.98$ g mol^{-1}, colorless prism, size 0.12×0.12×0.08 mm^3, orthorhombic, space group $P2_12_12_1$, $a = 11.0545(4)$, $b = 16.1507(3)$, $c = 27.4101(9)$ Å, $V = 4893.7(3)$ $Å^3$, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.386$ g cm^{-3}, μ (Mo-K_α) = 9.42 cm^{-1}, $F(000) = 2128$, 10612 reflections in $h(-14/14)$, $k(-19/18)$, $l(-35/35)$, measured in the range $2.37° \leqslant \Theta \leqslant 27.47°$, completeness $\Theta_{max} = 96.9\%$, 10581 independent reflections, $R_{int} = 0.071$, 6259 reflections with $F_o > 4\sigma(F_o)$, 589 parameters, 0 restraints, $R1_{obs} = 0.051$, $wR2_{obs} = 0.118$, $R1_{all} = 0.086$, $wR2_{all} = 0.123$, GOOF = 0.964, Flack-parameter 0.024(13), largest difference peak and hole: 1.364/−0.386 e $Å^{-3}$.

4.6. Crystal data for 9f (FO1468)

$C_{30}H_{40}Cu_2N_4O_{15}$*1/2$C_4H_8O$, $M_r = 859.79$ g mol^{-1}, purpur prism, size 0.12×0.12×0.10 mm^3, orthorhombic, space group $P2_12_12_1$, $a = 17.8764(4)$, $b = 26.6582(6)$, $c = 7.9868(2)$ Å, $V = 3806.13(15)$ $Å^3$, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.500$ g cm^{-3}, μ (Mo-K_α) = 11.92 cm^{-1}, $F(000) = 1784$, 8201 reflections in $h(-22/22)$, $k(-34/34)$, $l(-10/10)$, measured in the range $2.28° \leqslant \Theta \leqslant 27.49°$, completeness $\Theta_{max} = 98.1\%$, 8167 independent reflections, $R_{int} = 0.065$, 6091 reflections with $F_o > 4\sigma(F_o)$, 465 parameters, 1 restraints, $R1_{obs} = 0.069$, $wR2_{obs} = 0.190$, $R1_{all} = 0.086$, $wR2_{all} = 0.198$, GOOF = 1.066, Flack-parameter 0.05(2), largest difference peak and hole: 1.721/−0.779 e $Å^{-3}$.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (Collaborative Research Center 436, Jena, Germany), the Fonds der Chemischen Industrie (Germany) and by the Thueringer Ministerium für Wissenschaft, Forschung und Kultur (Erfurt, Germany) is gratefully acknowledged.

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