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Synthesis and Crystal Structure of a Heptanuclear and an Octanuclear Copper(II) Complex Derived from α-D-Glucofuranoses

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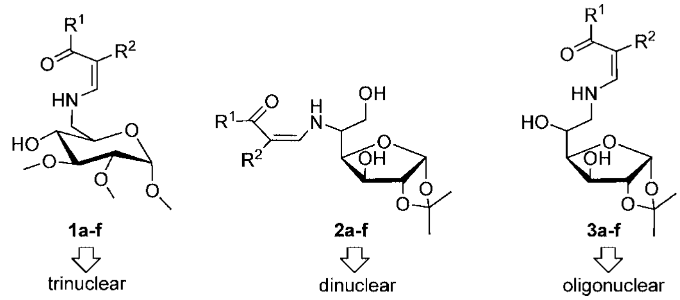
Cu^{II} complexes of different 6-(β-keto-enamino)-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoses **3a**–**f** have a high tendency to build up oligonuclear clusters. Two new oligonuclear copper(II) complexes could be synthesised, crystallised and their structures determined. The complex **Cu(3a)** was found to consist of a heptanuclear cluster in which two β-cubane like substructures share one copper ion. The structure is highly asymmetric and in the cluster every Cu^{II} ion has a different coordination geometry. Variation of the residues of the β-ketoenaminic unit leads to the formation of the octanuclear copper(II) complex **Cu(3e)**. Similarly, this has two β-cubane subunits consisting of a heptanuclear structure with an additionally attached copper ion. In the crystal, two Cu_8 cluster molecules are found differing in their geometries due to intermolecular interactions responsible for the formation of a supramolecular network.

Introduction

While there are a number of structurally characterised octanuclear copper clusters, examples of heptanuclear species rarely feature in the literature although recently a few compounds were synthesised and their properties determined. By complexation of 2,4,6-triallyloxy-1,3,5-triazin with CuCl or $CuCl_2$, Cu_7 and Cu_8 clusters could be isolated.[1] A dimeric tetradecanuclear copper macrocyclic complex with a heptanuclear core structure derived from 2,6-diaminomethyl-4-methylphenol and copper acetate could be synthesised and structurally characterised.[2] Heptanuclear copper subunits have been found in metal-organic frameworks comprised of 1,2,4-triazoles.[3] Addition of ethylenediamine to a D-mannopyranose containing Fehling's solution leads to a heptanuclear Cu^{II} complex.[4] Further, linear "tritopic" ligands have been found to assemble copper complexes with higher orders of oligomerisation[5] such as ferromagnetic Cu_8 pinwheel clusters.[6] Copper(II) salts form with *N*-(2-pyridylmethyl)acetamide,[7] *N*-propyamine[8] or dipyridyl ketone and 2-hydroxypyridine[9] Cu_8-clusters. Octanuclear metallamacrocyclic complexes have been synthesised from the pentadentate trianionic Schiff base ligand *N*,*N*′-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine)[10] or ditopic thiocarbohydrazones.[11] Efficient cleavage of supercoiled DNA in the presence of H_2O_2 was observed for an octanuclear copper(II) complex.[12] Derived from cytidine,[13] dithiocarbamates,[14] bis(diphenylphosphanyl)amide and



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

⇨ complexed with Cu^{II} ions

Scheme 1. Influence of the sugar backbone on the oligomerisation of copper(II) complexes.

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$(Me_3Si)_2Se$[15] and methylsiloxane[16] different supramolecular arrangements of Cu_8 clusters have been be obtained. As a building block for the synthesis of heterobimetallic complexes, an octanuclear cubic copper(I) complex, exhibiting six free peripheral coordinating sites, was synthesised from 4,5-diazafluorene.[17]

Our attempts to build up oligonuclear copper complexes of β-ketoenaminic ligands based on amino carbohydrates led to very effective catalysts for the oxidation of 3,5-di-*tert*-butylcatechol.[18] Depending on the amino carbohydrate used, different types of oligomerisation could be observed. Compounds derived from 6-amino-6-deoxy-1,2,3-tri-*O*-methyl-α-D-glucopyranosides **1a**–**f** form trinuclear copper(II) complexes[19] and with 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoses of type **2a**–**f** as the sugar backbone very stable dinuclear complexes could be obtained.[20] However, simply changing the position of the amino group starting from 6-amino-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoses **3a**–**f** lead to the formation of oligonuclear Cu^{II} complexes (Scheme 1). The structures of these complexes from **3a**–**f** were very difficult to assign because of their size and their lack of suitability for NMR spectroscopy. They differ depending on the residues R^1 and R^2, the copper(II) salt used for complexation and the reaction conditions.

Results and Discussion

By variation of the reaction conditions and after continual attempts at crystallisation, we were able to obtain crystals of the Cu^{II} complexes derived from the ligands **3a** and **3e** which were suitable for single crystal X-ray structure analysis (Figure 1).

Synthesis and Crystal Structure of Cu(3a)

Reaction of **3a** with $Cu(OAc)_2$ in a toluene/methanol mixture with an excess of triethylamine leads to the formation of **Cu(3a)**. The dark green powder obtained could be crystallised from benzene/methanol to give green crystals suitable for single-crystal X-ray structure analysis (Table 1). In the heptanuclear complex, two doubly deprotonated ligand molecules one of which acts as a tridentate ligand (D), one as a tetradentate ligand (A) and three triply deprotonated ligand molecules acting as tetradentate ligands (B, C, E) are enclosed (Figure 1, a). The Cu atom labeled Cuc is further coordinated by a 2,4-pentandionate ion which is formed from a ligand molecule during synthesis. The composition of the compound is therefore $[Cu_7(\eta^4\text{-}\mathbf{3a})_3(\eta^4\text{-}H\mathbf{3a})(\eta^3\text{-}H\mathbf{3a})(acac)]$. The elemental unit contains additional solvent molecules. The structure can be described as consisting of two β-type cubane-like cluster which share the copper atom labeled Cug. The bridging ligand atoms between the copper centres are the alkoxido oxygen atoms O2a–O2e, O6b, O6c and O6e. The triply deprotonated ligands B, C and E are coordinated to the copper atoms Cub, Cud and Cuf, while the doubly deprotonated ligands A and

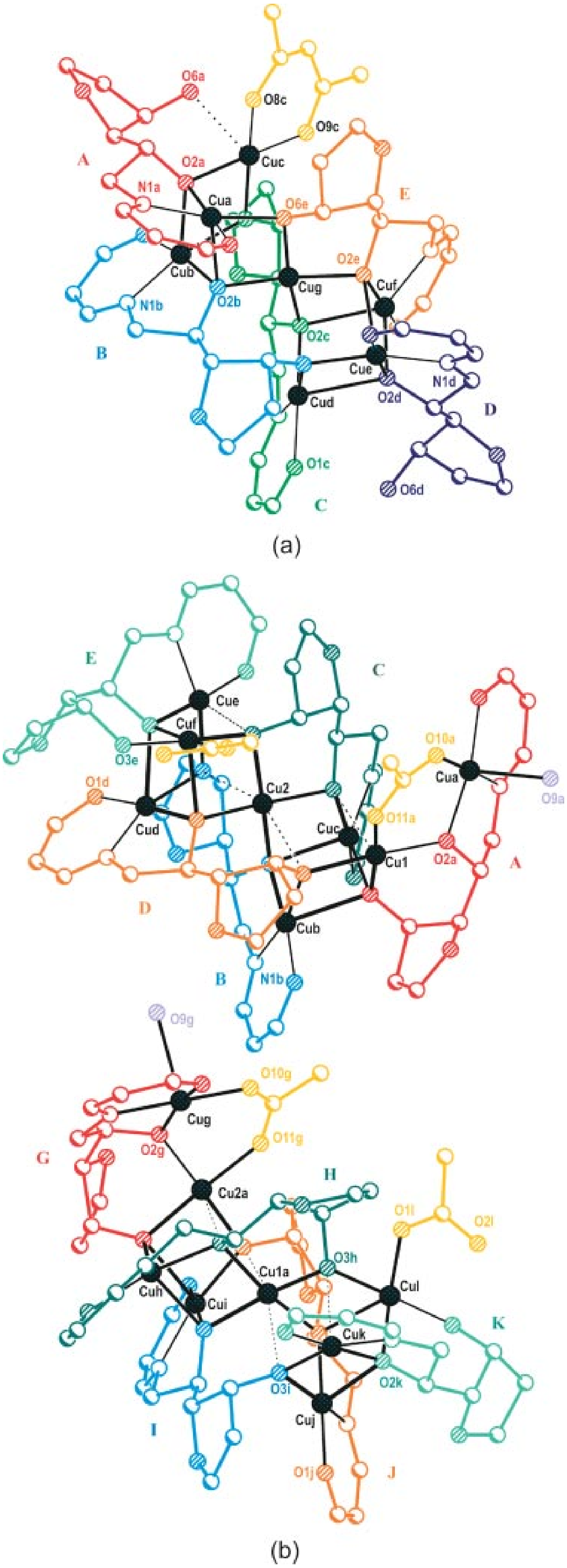

Figure 1. Representation of a) the structure of **Cu(3a)** and b) the structure of the two clusters in the crystal of **Cu(3e)**. Only the inner core, the connecting C-chain and the furanose rings are shown; for clarity all other atoms are omitted and the ligand fragments are coloured differently.

D are coordinated to the copper atoms Cua and Cue (Figure 2). The central copper atom Cug is surrounded by the alkoxido oxygen atoms in the 3-position of the tetradentate ligands and the corresponding alkoxido groups in the 5-position. The coordination geometry is therefore octahedral. Cuc bears the acetylacetonate ligand and is incorporated into the cubane structure by the oxygen atoms O2a (5-position of ligand A), O6c and O6e (3-position of ligands C and E). Its distorted octahedral coordination sphere is completed by the hydroxido oxygen atom O6a (3-position of ligand A). All other copper atoms are five-coordinate. Cua, Cub, Cud and Cue are surrounded by the carbonyl (O1) and 5-alkoxido oxygen (O2) atoms and the enaminic nitrogen atom of their own ligands (A, B, C and D). The fourth coordination position in the plane of the square-pyramidal geometry is occupied by one of the 3-alkoxido oxygen atoms belonging to one of the tetradentate ligands in the neighbouring cubane subunit (Cua–O6e; Cub–O6c; CuD–O6b, Cue–O6b). The 5-alkoxido oxygen atom of the neighbouring ligand in the same cubane subunit is located in the axial position. The last copper atom Cuf bears the 5-alkoxido oxygen atom O2d instead of the 3-alkoxido oxygen atom. Its coordination geometry is much more distorted than the coordination spheres of the other five-coordinate copper atoms and can be described both as distorted square-pyramidal and trigonal-bipyramidal. Preliminary studies to determine the magnetic properties of **Cu(3a)** are included in the electronic supporting information.

Table 1. Selected bond lengths [Å] and angles [°] in **Cu(3a)**.

Cua–O1a	1.902(11)	Cua–O2a	2.010(10)
Cua–O2b	2.394(10)	Cua–O6e	2.000(8)
Cua–N1a	1.926(13)	Cub–O1b	1.938(9)
Cub–O2a	2.369(10)	Cub–O2b	2.037(8)
Cub–O6c	1.964(10)	Cub–N1b	1.938(11)
Cuc–O2a	1.966(10)	Cuc–O6c	1.969(10)
Cuc–O8c	1.865(10)	Cuc–O9c	1.952(11)
Cud–O1c	1.964(9)	Cud–O2c	1.980(9)
Cud–N1c	1.898(12)	Cud–O6b	1.961(9)
Cud–N1c	1.898(12)	Cue–O1d	1.929(9)
Cue–O2d	1.995(9)	Cue–N1d	1.880(11)
Cue–O6b	1.939(9)	Cuf–O1e	1.901(9)
Cuf–O2d	2.099(9)	Cuf–O2e	1.958(9)
Cuf–N1e	1.924(12)	Cuf–O2	2.246(9)
Cug–O2c	2.040(9)	Cug–O2e	1.955(8)
Cug–O6e	1.932(9)	Cug–O2b	1.876(9)
O1a–Cua–O2a	173.4(4)	O1a–Cua–O2b	105.7(4)
O1a–Cua–O6e	92.0(4)	O1a–Cua–N1a	89.5(5)
O2a–Cua–O2b	79.9(4)	O2a–Cua–O6e	93.0(5)
O2a–Cua–N1a	84.8(5)	O2b–Cua–O6e	73.7(3)
O2b–Cua–N1a	115.2(5)	O6e–Cua–N1a	170.2(5)
O1b–Cub–O2a	109.2(4)	O1b–Cub–O2b	170.6(4)
O1b–Cub–O6c	97.6(4)	O1b–Cub–N1b	90.7(4)
O2a–Cub–O2b	80.0(4)	O2a–Cub–O6c	72.8(4)
O2a–Cub–N1b	114.1(5)	O2b–Cub–O6c	87.0(4)
O2b–Cub–N1b	83.5(4)	O6c–Cub–N1b	166.9(5)
O2a–Cuc–O9c	93.0(5)	O2a–Cuc–O6c	82.4(4)
O6c–Cuc–O8c	91.4(4)	O2a–Cuc–O8c	172.1(4)
O6c–Cuc–O9c	170.6(5)	O8c–Cuc–O9c	93.9(5)
O6b–Cud–N1c	166.1(4)	O1c–Cud–O2c	174.1(4)
O1c–Cud–O2d	101.9(4)	O1c–Cud–O6b	98.0(4)
O1c–Cud–N1c	89.7(5)	O2c–Cud–O2d	79.5(3)
O2c–Cud–O6b	87.9(4)	O2c–Cud–N1c	84.5(5)
O2d–Cud–O6b	77.4(3)	O2d–Cud–N1c	112.5(4)
O6b–Cue–N1d	166.5(5)	O1d–Cue–O2d	176.2(4)
O1d–Cue–O2e	103.4(4)	O1d–Cue–O6b	95.2(4)
O1d–Cue–N1d	90.3(4)	O2d–Cue–O2e	78.9(3)
O2d–Cue–O6b	88.0(4)	O2d–Cue–N1d	86.1(4)
O2e–Cue–O6b	84.3(3)	O2e–Cue–N1d	106.4(4)
O2e–Cuf–N1e	84.3(4)	O1e–Cuf–O2c	98.4(4)
O1e–Cuf–O2d	101.8(4)	O1e–Cuf–O2e	168.4(4)
O1e–Cuf–N1e	92.2(4)	O2c–Cuf–O2d	80.3(3)
O2c–Cuf–O2e	77.9(3)	O2c–Cuf–N1e	141.0(4)
O2d–Cuf–O2e	88.5(4)	O2d–Cuf–N1e	134.0(4)
O2e–Cug–O6e	91.6(4)	O2b–Cug–O2c	99.4(4)
O2b–Cug–O2e	169.9(4)	O2c–Cug–O6e	164.5(4)
O2c–Cug–O2e	83.2(4)	O2b–Cug–O6e	88.3(4)

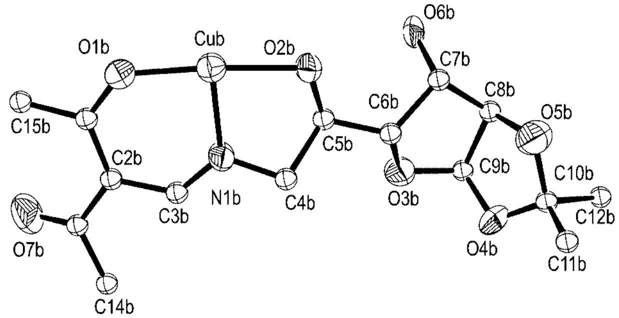

Figure 2. View of ligand B coordinated to the copper atom "Cub" in the structure of **Cu(3a)** with the crystallographic numbering and displacement ellipsoids shown at the 50% probability level; H-atoms are omitted for clarity.

Synthesis and Crystal Structure of Cu(3e)

Heating ligand **3e** to reflux together with $Cu(OAc)_2$ and an excess of triethylamine in a mixture of toluene and hexane for several hours gives **Cu(3e)** as a dark green powder. The product was crystallised from acetone/diethyl ether to give crystals suitable for X-ray structure analysis. The compound crystallises in an orthorhombic space group and, besides several solvent molecules, the asymmetric unit of the unit cell contains two chemically identical clusters with the formula $[Cu_8(\eta^4\text{-}\mathbf{3e})_4(\eta^3\text{-H}\mathbf{3e})(OAc)(\mu\text{-}OAc)(H_2O)]$ shown in part b of Figure 1. There are only small differences in bond lengths and angles between the two cluster molecules (Table 2) so that the following copper atoms (and their ligand molecules) can be regarded as equivalent for the discussion of the structure: Cua–Cug, Cub–Cui, Cuc–Cuh, Cud–Cuj, Cue–Cuk, Cuf–Cul, Cu1–Cu2a and Cu2–Cu1a.

Seven of the eight copper atoms show similar arrangements to that of **Cu(3a)**. They form two heterocubane (Cu_4O_4) subunits which share one corner (Cu2). In contrast to this is the additional copper atom (Cua) which is bound to one of the cubane subunits by a bridging acetate ligand and by the second alkoxido oxygen atom (O3a) of its ligand molecule which binds to three copper atoms of the cubane subunit [O3a–Cu1 1.973(4) Å, O3a–Cub 2.399(4) Å, O3a–Cuc 2.066(4) Å]. The water oxygen atom occupies the axial position with a Cua–O9a bond length of 2.338(5) Å. Five copper atoms of the cluster carry their own ligand molecules (A–E) and the other three copper atoms (Cu1, Cu2

Table 2. Comparison of selected bond lengths [Å] and angles [°] of the two clusters in the crystal structure of **Cu(3e)**.

Cluster 1		Cluster 2	
Cua–N1a	1.929(5)	Cug–N1g	1.927(5)
Cua–O2a	1.939(4)	Cug–O2g	1.944(4)
Cua–O9a	2.327(5)	Cug–O9g	2.408(5)
Cua–O10a	1.938(4)	Cug–O10g	1.927(5)
Cub–O1b	1.937(4)	Cui–O1i	1.940(4)
Cub–N1b	1.907(5)	Cui–N1i	1.911(5)
Cub–O2b	2.005(4)	Cui–O2i	2.006(4)
Cub–O3a	2.400(4)	Cui–O3g	2.451(5)
Cuc–O1c	1.909(4)	Cuh–O1h	1.906(4)
Cuc–N1c	1.927(5)	Cuh–N1h	1.922(5)
Cuc–O2c	1.958(4)	Cuh–O2h	1.949(4)
Cuc–O2b	2.285(4)	Cuh–O2i	2.335(4)
Cud–O3b	2.032(4)	Cuj–O3i	2.018(4)
Cud–O2e	2.293(5)	Cuj–O2k	2.314(5)
Cue–O2e	1.972(4)	Cuk–O2k	1.971(4)
Cuf–O2e	1.958(4)	Cul–O2k	1.963(4)
Cuf–O3c	1.982(4)	Cul–O3h	1.975(4)
Cu2–O3c	1.998(4)	Cu1a–O3h	1.985(4)
Cue–O3c	2.526(4)	Cuk–O3h	2.537(5)
Cu1–O2c	2.549(5)	Cu2a–O2h	2.558(4)
Cu2–O3b	2.446(4)	Cu1a–O3i	2.462(5)
Cu2–O3d	2.533(4)	Cu1a–O3j	2.507(4)
O1a–Cua–O9a	92.24(19)	O1g–Cug–O9g	95.41(19)
O2a–Cua–O9a	101.38(18)	O2g–Cug–O9g	97.89(19)
O3a–Cub–O3d	75.37(12)	O3g–Cui–O3j	74.3(2)
O1b–Cub–N1b	91.80(19)	O1i–Cui–N1i	92.0(2)
O3a–Cuc–N1c	144.67(15)	O3g–Cuh–N1h	149.2(2)
O2b–Cuc–N1c	132.39(16)	O2i–Cuh–N1h	127.49(16)
O2e–Cud–N1d	118.6(2)	O2k–Cuj–N1j	114.8(2)
O3b–Cud–O2e	75.31(12)	O3i–Cuj–O2k	75.55(17)
O2e–Cuf–O3e	88.32(19)	O2k–Cul–O3k	88.31(18)
O3c–Cuf–O3e	176.41(18)	O3h–Cul–O3k	177.28(14)
O3d–Cu2–O2d	168.82(16)	O3j–Cu1a–O2h	169.16(12)
O2d–Cu2–O2b	98.97(13)	O2j–Cu1a–O2i	98.58(18)
O3a–Cu1–O3d	85.18(12)	O3g–Cu2a–O3j	85.97(13)
O2a–Cu1–O3d	176.10(13)	O2g–Cu2a–O3j	176.10(14)
Cu1–O3a–Cub	91.77(15)	Cu2a–O3g–Cui	91.2(3)

and Cuf) are surrounded by the bridging alkoxido groups of the ligands and by an acetate oxygen atom. Except for the central copper atom (Cu2) which has a distorted octahedral environment, each copper atom has five binding partners in a more or less distorted square-planar geometry. Cub and Cuc are bound directly to each other by the alkoxido oxygen atom O2b which occupies the axial position in the environment of Cuc with a (for this position) remarkably short bond length of 2.285(4) Å. The fourth equatorial position in the ligand sphere of Cuc is occupied by one alkoxido group (O3d) of the ligand D from the other cubane subunit. The same position can be found for this atom in the ligand sphere of Cub, whereas the axial position is occupied by O3a. Cu1 is one of the atoms without its own ligand molecule. It is surrounded by the oxygen of the bridging acetate ion (O11a) and four alkoxido oxygen atoms, O3a, O3d, O2c and O2b with each pair being in the 3- and in 5-positons of their ligands. The axial ligand is the alkoxido oxygen O2c [2.549(4) Å] which makes the cubane subunit of the so-called β-type with two parallel longer Cu–O bonds perpendicular to each other. The central copper atom Cu2 is surrounded by the six alkoxido oxygen atoms of the ligands B, C and D. In the second subunit of the cluster there are two copper atoms, Cud and Cue, with their own ligands. As for Cub and Cuc, the Cu–ligand monomers are bridged by the alkoxido atom O2e which originates from the axial ligand of Cud at a relatively short distance of 2.293(5) Å. The ligand sphere of Cuc is completed by the alkoxido oxygen atoms in the 3-positions of the ligands B and C from the other subunit, with O3c in the axial position [2.526(5) Å]. O3b is the last binding partner of Cud in the fourth equatorial position. The last copper atom of the cluster Cuf is surrounded by the two alkoxido groups in the 5-positons of the neighbouring ligand molecules D and E, O3c from ligand C of the other subunit and by the oxygen atom O3e of the neighbouring ligand E. This is the only hydroxido group which is not deprotonated in the complex since it is the only one not acting as a bridging ligand and forming a hydrogen bond with the carbohydrate ring oxygen atom O4e [O···O distance 2.883(5) Å].

The copper-bound water molecule containing O9a forms a hydrogen bond with the carboxylate oxygen atom O7k of the other octanuclear cluster [O9a···O7k 2.784(5) Å; *x*, *y* + 1, *z* – 1] and the diethyl ether oxygen atom O1 [O9a···O1 2.773(6) Å; *x*, *y* + 1, *z*]. The water molecule of the other cluster (O9g) forms a corresponding hydrogen bond with the next neighbouring complex [O9g···O7e 2.827(6) Å; *x*, *y* – 1, *z*] and one ethanol oxygen atom [O9g···O4 2.827 Å; *x*, *y* – 1, *z*]. These hydrogen bonds establish chains. The next step towards a 3D network results from the water molecule containing O6 which is found at a distance of 2.896(8) Å from O9g and the next symmetry equivalent O9g at –*x* – 1, –*y* – *z*, *z*.

Though the bond lengths and angles in the two cluster molecules are very similar (Table 2), least-squares plane calculations on the coordinate planes show further differences – not so much in the mean deviation from planarity and in the copper distance from the plane but in the angles between them. It is striking that the highest differences between the two cluster molecules is found for the Cuc and Cuh coordinate planes [angles with Cu1 and Cu2a 33.0(2)° and 78.6(2)°, Cua/Cug 21.2(2)° and 28.2(2)°, Cud/Cuj 111.5(2)° and 80.2(2)°, Cue/Cuk 26.4(2)° and 37.2(2)° and Cuf/Cul 112.2(2)° and 98.8(2)°, respectively]. This is coincidental with the fact that the peripheral carboxylate oxygen atom of the ligand of Cuh is involved in hydrogen bonding, whereas the corresponding oxygen atom belonging to the ligand of Cuc shows no intermolecular interaction. The angles between the two cubane subunits in each cluster, at 103.8(2)° and 105.8(2)°, differ from the ideal 90(2)° but much less so than in **Cu(3a)**.

Conclusions

In summary, the use of β-ketoenaminic ligands derived from 6-amino-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose provides access to polynuclear copper(II) complexes with highly asymmetric structures. Complexation of 6-[(2,2-diacetylvinyl)amino]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**3a**) gives a heptanuclear cluster whereas 6-[(2-ethoxycarbonyl-2-phenylcarbonylvinyl)amino]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**3e**) leads to the formation of an octanuclear compound. The resultant structures provide insight into the coordination behaviour of this class of carbohydrate-based ligand.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. Electronic spectra were recorded with a Varian Cary 1 or Cary 5E spectrophotometer at room temperature. IR spectra were recorded on a Perkin–Elmer 2000 spectrometer; NMR spectra on a Bruker AC-200 instrument and mass spectra on a Finnigan MAT SSQ 710 or a Finnigan MAT 95XL TRAP machine. Elemental analyses were performed on a Leco CHNS 932.

Heptacopper(II) Complex Cu(3a): The ligand **3a** (0.5 mmol) and triethylamine (2 mmol) were heated to reflux together with copper(II) acetate monohydrate (0.6 mmol) in a 4:1 mixture of toluene/methanol (50 mL) for 4 h. The solution was filtered and the solvent evaporated. The residue was recrystallised from benzene/methanol to give dark green crystals suitable for X-ray structure analysis. IR (ATR): $\tilde{\nu}$ = 3372 (w), 2985 (w), 2936 (w), 2881 (w), 2845 (vw), 1645 (w), 1596 (vs), 1521 (s), 1442 (s), 1384 (vs), 1280 (s), 1214 (s), 1164 (w), 1066 (s), 1010 (s), 940 (s), 872 (s), 793 (w), 646 (s), 615 (w) cm^{-1}. UV/Vis (methanol): λ_{max} = 269 (lgε = 4.8063), 304 (lgε = 4.5201), 654 nm (lgε = 2.8552). MS (ESI in methanol): *m/z* (%) = 2100 (3), [7 Cu] $[Cu_7L_5 + Na]^+$, 1648 (15), [5 Cu] $[Cu_5L_4 + Na]^+$, 1256 (100), [4 Cu] $[Cu_4L_3 + Na]^+$. $C_{80}H_{111}Cu_7N_5O_{37}$ $[Cu_7L_5Acac]$ (2174.20): calcd. C 44.19, H 5.15, N 3.22; found C 44.26, H 5.54, N 3.39.

Octacopper(II) Complex Cu(3e): Ligand **3e** (290 mg, 0.69 mmol) together with $Cu(OAc)_2$ (125 mg, 0.69 mmol) and triethylamine (200 µL, 2.76 mmol) in 50 mL toluene/hexane, 4:1 were refluxed for 5 h. After cooling to room temperature the mixture was filtered, the solvent evaporated and the dark green powder dried. After several attempts the product could be crystallised from acetone/ether to give 105 mg (32%) of dark green crystals suitable for X-ray structure analysis. IR (ATR): $\tilde{\nu}$ = 3429 (vw), 2982 (w), 2937 (w), 1708 (vw), 1669 (s), 1620 (vs), 1568 (vs), 1554 (s), 1449 (s), 1415 (vs), 1382 (s), 1283 (s), 1262 (s), 1213 (s), 1164 (w), 1068 (s), 1010 (s), 732 (w), 699 (w), 642 (w), 617 (vw) cm^{-1}. UV/Vis (toluene): λ_{max} = 299 (lgε = 4.4810), 320 (lgε = 4.4517), 615 nm (lgε = 2.6894). MS (ESI in Methanol): *m/z* (%) = 2618 (0.5) [8 Cu] $[Cu_8L_5 + Na]^+$, 2499 (1) [6 Cu] $[Cu_6L_5 + Na]^+$, 1994 (3) [5 Cu] $[Cu_5L_4]^+$, 1532 (20) [4 Cu] $[Cu_4L_3 + Na]^+$, 444 (100) [0 Cu] $[L + Na]^+$. $C_{109}H_{126}Cu_8N_5O_{44}$ $[Cu_8L_5(OAc)_2]$ (2718.59): calcd. C 48.16, H 4.67, N 2.58; found C, 48.54; H 4.69; N, 2.64.

X-ray Crystallographic Study: 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 polarisation effects but not for absorption.[21,22] The structures were solved by direct methods (SHELXS[23]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[24]). The hydrogen atoms of the structures were included in calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[16] XP (SIEMENS Analytical X-ray Instruments, Inc.) or ORTEP was used for structure representations.

CCDC-188438 (for **Cu(3a)**) and -188437 (for **Cu(3e)**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for Cu(3a): $C_{94}H_{129}Cu_7N_5O_{39}$, M_r = 2397.80 $g\,mol^{-1}$, pink prisms, size 0.12 × 0.10 × 0.10 mm, orthorhombic, space group $P2_12_12_1$, a = 19.12230(10), b = 23.912(2), c = 28.021(2) Å, V = 12812.7(14) Å^3, T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.243 $g\,cm^{-3}$, μ (Mo-K_α) = 12.11 cm^{-1}, F(000) = 4972, 20404 reflections in h(–17/22), k(–24/24), l(–32/31), measured in the range 1.29° ≤ θ ≤ 24.44°, completeness θ_{max} = 72.1% (due to crystal decomposition), 13374 independent reflections, R_{int} = 0.0707, 8979 reflections with $F_o > 4\sigma(F_o)$, 1232 parameters, 0 restraints, R_{1obs} = 0.0854, wR_{2obs} = 0.2178, R_{1all} = 0.1184, wR_{2all} = 0.2376, GOOF = 1.010, Flack parameter 0.02(2), largest difference peak and hole: 1.051 / –0.745 e Å^{-3}.

Crystal Data for Cu(3e): $C_{114.75}H_{144.5}Cu_8N_5O_{47.5}$, M_r = 2862.17 $g\,mol^{-1}$, blue prisms, size 0.12 × 0.10 × 0.10 mm, orthorhombic, space group $P2_12_12$, a = 28.205(6), b = 45.281(9), c = 21.342(4) Å, V = 27257(9) Å^3, T = –90 °C, Z = 8, $\rho_{calcd.}$ = 1.395 $g\,cm^{-3}$, μ (Mo-K_α) = 13.06 cm^{-1}, F(000) = 11840, 70163 reflections in h(–36/33), k(–58/20), l(–25/24), measured in the range 1.31° ≤ θ ≤ 27.47°, completeness θ_{max} = 89.7%, 47879 independent reflections, R_{int} = 0.0347, 37010 reflections with $F_o > 4\sigma(F_o)$, 3152 parameters, 0 restraints, R_{1obs} = 0.0593, wR_{2obs} = 0.1437, R_{1all} = 0.0870, wR_{2all} = 0.1610, GOOF = 1.048, Flack parameter 0.006(8), largest difference peak and hole: 1.049/–0.514 e Å^{-3}.

Supporting Information (see also the footnote on the first page of this article): Analytical data of **3a**, **3e**, selected crystal data for copper complexes, preliminary results of magnetic measurements for **Cu(3a)**.

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