[1] Review: J. M. Seddon, R. H. Templer in *Handbook of Biological Physics, Vol. 1* (Eds.: R. Lipowsky, E. Sackmann), Elsevier, Amsterdam, **1995**, p. 97.

[2] I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, Oxford, **1998**, p. 24.

[3] a) K. Borisch, S. Diele, P. Göring, C. Tschierske, *J. Chem. Soc. Chem. Commun.* **1996**, 237; b) K. Borisch, S. Diele, P. Göring, H. Müller, C. Tschierske, *Liq. Cryst.* **1997**, *22*, 427; c) K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *Angew. Chem.* **1997**, *109*, 2188; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2087; d) K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 529.

[4] a) V. S. K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, *J. Am. Chem. Soc.* **1997**, *119*, 1539; b) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449; c) V. Percec, C.-H. Ahn, W.-D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 8619.

[5] a) A. Pegenau, P. Göring, C. Tschierske, *J. Chem. Soc. Chem. Commun.* **1996**, 2563; b) A. Pegenau, P. Göring, S. Diele, C. Tschierske, *Eur. J. Chem.* **1999**, *5*, 1643.

[6] Other liquid crystalline pentaerythritol derivatives have been reported, but their mesogenity was provided by extended anisometric (calamitic, disclike, or taper-shaped) rigid cores fixed to the pentaerythritol unit; calamitic units: R. Eidenschink, F.-H. Kreuzer, W. H. de Jeu, *Liq. Cryst.* **1990**, *8*, 879; K. Zab, D. Joachimi, O. Agert, B. Neumann, C. Tschierske, *Liq. Cryst.* **1995**, *18*, 489; J. Andersch, S. Diele, D. Lose, C. Tschierske, *Liq. Cryst.* **1996**, *21*, 103; K. Praefcke, P. Psaras, A. Eckert, *Liq. Cryst.* **1993**, *13*, 551; disclike units: J. L. Schulte, S. Laschat, V. Vill, E. Nishikawa, H. Finkelmann, M. Nimtz, *Eur. J. Org. Chem.* **1998**, 2499; extended taper-shaped units: J. Malthête, *New J. Chem.* **1996**, *20*, 925.

[7] Linear oligoalkylene amides without the possibility to form hydrogen bonds show columnar or smectic phases: U. Stebani, G. Lattermann, M. Wittenberg, J. H. Wendorff, *J. Mater. Chem.* **1997**, *7*, 607.

[8] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485.

[9] a) C. Viney, R. J. Twieg, T. P. Russell, L. E. Depero, *Liq. Cryst.* **1989**, *5*, 1783; b) T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabashi, Y. Nishihata, H. Terauchi, *J. Mater. Chem.* **1991**, *1*, 169; c) H. T. Nguyen, G. Sigaud, M. F. Achard, F. Hardouin, R. J. Twieg, K. Betterton, *Liq. Cryst.* **1991**, *10*, 389; d) S. Pensec, F.-G. Tournilhac, P. Bassoul, *J. Phys. II France* **1996**, *6*, 1597; e) S. V. Arehart, C. Pugh, *J. Am. Chem. Soc.* **1997**, *119*, 3027; f) S. Takenaka, *J. Chem. Soc. Chem. Commun.* **1992**, 1748; g) G. Johansson, V. Percec, G. Ungar, K. Smith, *Chem. Mater.* **1997**, *9*, 164; h) U. Dahn, C. Erdelen, H. Ringsdorf, R. Festag, J. H. Wendorff, P. A. Heiney, N. C. Maliszewskyj, *Liq. Cryst.* **1995**, *19*, 759; i) V. Percec, D. Schlüter, Y. K. Kwon, J. Blackwell, M. Möller, P. J. Slangen, *Macromolecules* **1995**, *28*, 8807; j) V. Percec, G. Johansson, G. Ungar, J. Zhou, *J. Am. Chem. Soc.* **1996**, *118*, 9855.

[10] A. Pegenau, X. H. Cheng, C. Tschierske, P. Göring, S. Diele, *New J. Chem.* **1999**, *23*, 465.

[11] In only one case a transition from a thermotropic *Pm*3*n* phase to another micellar cubic phases was mentioned, see ref. [4c].

[12] Aproximately 61 % of the molecular volume of compound **3F** consits of the perfluoralkyl groups (calculated using volume increments, see: A. Immrizi, B. Perini *Acta Crystallogr. Sect. A* **1977**, *33*, 216). For this part of the calculation the density of perfluorohexane ($\rho = 1.682\,\mathrm{g\,cm^{-3}}$) was assumed. The remaining 39 % was assumed to have a density of $1.0\,\mathrm{g\,cm^{-3}}$ which gave the average value of $\rho = 1.4\,\mathrm{g\,cm^{-3}}$.

[13] a) J. Charvolin, J. F. Sadoc, *J. Phys. (Paris)* **1988**, *49*, 521; b) K. Fontell, K. K. Fox, E. Hansson, *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *1*, 9; c) R. Vargas, P. Mariani, A. Gulik, V. Luzzati, *J. Mol. Biol.* **1992**, *225*, 137; d) H. Delacroix, T. Gulik-Krzywicki, P. Mariani, V. Luzzati, *J. Mol. Biol.* **1993**, *229*, 526; e) P. Sakya, J. M. Seddon, R. H. Templer, R. J. Mirkin, G. J. T. Tiddy, *Langmuir* **1997**, *13*, 3706.

[14] The formation of the $\mathrm{Cub_{V2}}$ phase from the $\mathrm{S_A}$ phase and from the M phase is kinetically hindered. Therefore the M phase can be cooled down to room temperature and the cubic phase only develops slowly. Once formed it can be heated to 54–56 °C where the transition to the M phase occurs.

[15] It could be a 2D-modulated variant of the $\mathrm{S_A}$ phase (ribbon phase) or a noncubic 3D phase as, for example, a tetragonal phase: A. M. Levelut, B. Donnio, D. W. Bruce, *Liq. Cryst.* **1997**, *22*, 753; M. C. Holmes, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 485. However, because of the rather low viscosity a ribbon phase seems to be more likely. Here the smectic layers are interrupted in regular intervals with formation of ribbonlike segments. These segments are arranged in a 2D lattice.

[16] B. E. Smart in *Organofluorine Chemistry, Principles and Commercial Applications* (Eds.: R. E. Banks, B. E. Smart, J. C. Tatlow), Plenum, New York, **1994**, p. 57.

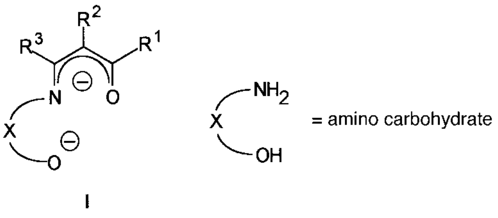
[17] Compounds **1H**–**3H** and **1F**–**3F** are also amphiphilic in a wider sense, because they are built up of two incompatible units, but in contrast to classical amphiphiles, the mesophases of compounds **1F**–**3F** could not be changed by the addition of protic solvents.

New Building Blocks for the Design of Oligonuclear Copper Complexes Based on Amino Carbohydrates[**]

Rainer Wegner, Michael Gottschaldt, Helmer Görls, Ernst-G. Jäger,[*] and Dieter Klemm[*]

Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

Next to iron, copper is the most important biological element for binding, transport, and activation of molecular oxygen. Copper-containing oxidases for the four-electron reduction of oxygen often display dinuclear (e.g. catechol oxidase)[1] or oligonuclear active centers (e.g. ascorbate oxidase).[2] The great biological importance of such copper complexes has induced intensive studies on oligonuclear model compounds.[3] Our concept for the design of oligonuclear complexes is to use structurally modified amino derivatives of carbohydrates instead of the proteins that are the "backbones" of the natural systems and to bind the metal through tridentate, anionic ligand structures of type **I**.



I

---

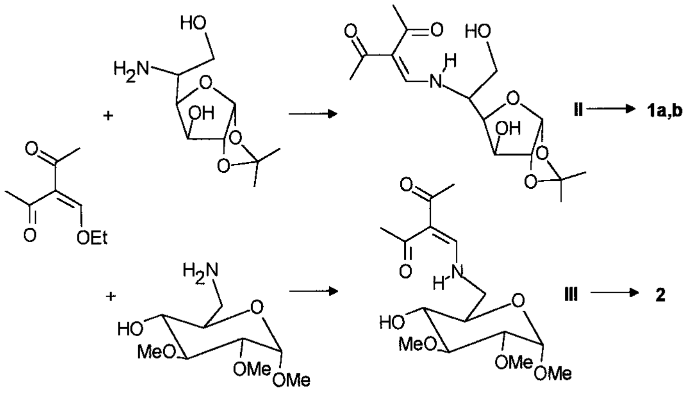
[*] Prof. Dr. E.-G. Jäger, Dr. R. Wegner, Dr. H. Görls
Institut für Anorganische und Analytische Chemie der Universität
August-Bebel-Strasse 2, 07743 Jena (Germany)
Fax: (+49) 3641-948102
E-mail: cej@rz.uni-jena.de

Prof. Dr. D. Klemm, M. Gottschaldt
Institut für Organische und Makromolekulare Chemie der Universität
Humboldtstrasse 10, 07743 Jena (Germany)
Fax: (+49) 3641-948202
E-mail: c5koan@rz.uni-jena.de

[**] We thank the Deutsche Forschungsgemeinschaft (collaborative research project SFB 436 "metal-mediated reactions modeled after nature"), the Fonds der Chemischen Industrie, and the Thuringian Ministry for Science, Research and Culture for financial support.

The protonated forms of such chelating ligands **I** are easily accessible by condensation of hydroxyalkylamines with 1,3-dicarbonyl compounds. Even with the first prototypes[4] a high tendency of the metal complexes to reach coordinative saturation by the formation of di- or tetranuclear complexes was found.[5] Much interest has been shown for the copper complexes[5–16] because of the ligand-dependant magnetic interaction between the metal centers. The substituents R^1-R^3 as well as the bridging groups X[17] are useful for tuning properties such as redox potential and Lewis acidity of the central atom, which are important for catalytic reactions.

Based on current knowledge, carbohydrates are not typical biological coordination partners for metal atoms. However, as synthetic catalysts they are an interesting alternative to proteins: These chiral, polyfunctional natural substances are accessible in a broad range of molecular sizes, and obey the rules of unit conformation and configuration. They can be functionalized selectively in various ways as mono-, oligo-, or polysaccharides and can be structured supramolecularly (fibers, gels, membranes, mono- and multilayers).[18–20] Hydrophilic and lipophilic properties as well as biological properties such as biocompatibility and biological decomposition and activity can be directed in a broad range. Investigations in recent years on the metallo-organic[21] and complex chemistry[22–27] of N-glycosides, nonmodified carbohydrates, and inosites have shown that carbohydrates have a very interesting potential as complex ligands. We present here the first structurally defined coordination compounds of β-oxoenamine ligands on the basis of amino carbohydrates. Compounds **1a**, **1b** (from ligand **II**), and **2** (from ligand **III**) can be crystallized from methanol/water (**1a**), toluene (**1b**), or methanol/diethyl ether (**2**; Scheme 1).[29] Single-crystal X-ray structures were obtained for **1a** and **2**.



Scheme 1. Synthesis of ligands **II** and **III**.

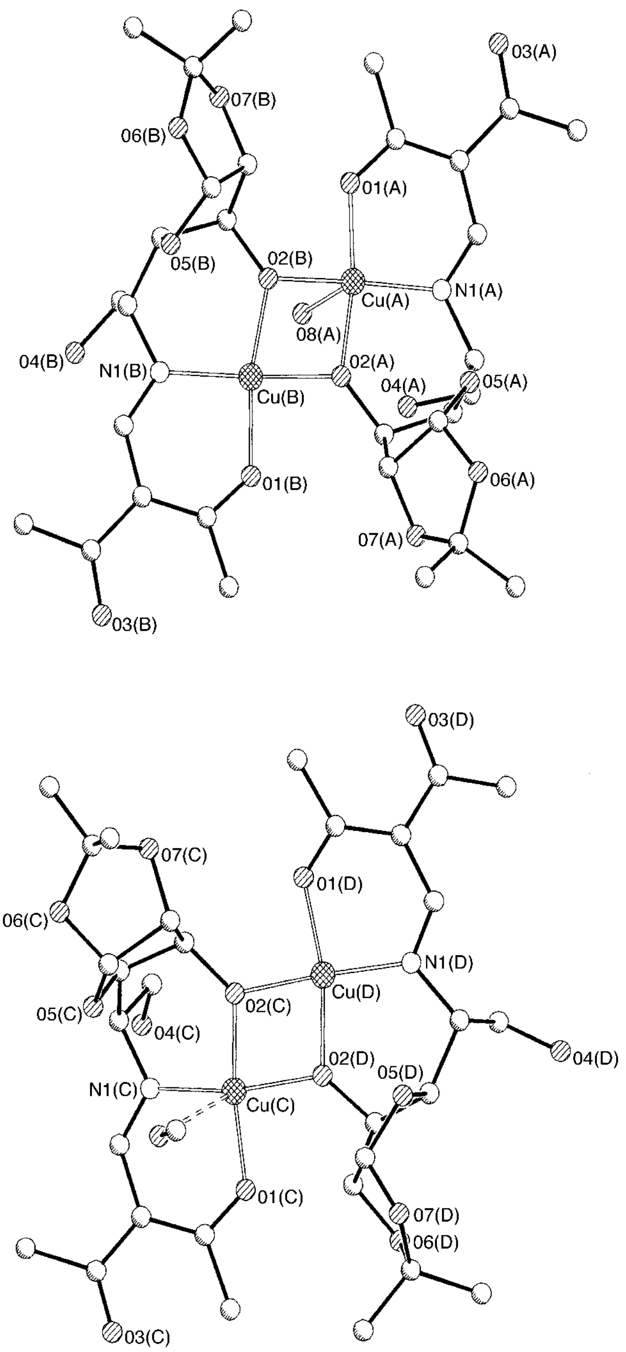


Figure 1. Structure of the two complex molecules in **1a**.

The asymmetric unit of **1a**[30] contains two dinuclear complexes, in which the bridging alcoholate oxygen atoms in the 3-position of the ligand build a Cu_2O_2 four-membered ring with the copper atoms (Figure 1). The distances between the copper atoms are 2.977(1) and 3.020(1) Å, respectively. Striking is the low symmetry of the compound, which is also typical for many natural copper centers. One copper atom is coordinated in a distorted square planar fashion, whereas the other copper atom is in a distorted square pyramidal environment by binding of a water or methanol ligand. The bond lengths and angles in the central coordination unit all show values which could be expected for the named geometries. The different coordination of solvent molecules to the two copper atoms gives a hint that possible substrate molecules might be bound to the copper centers in an unsymmetrical way. Crystals of **1b** were obtained from toluene and are of lower quality, so that only the structural motive could be determined. It shows the presence of symmetric dinuclear complexes without axial ligands.

Investigation of the magnetic properties of **1a** shows diamagnetism over the whole temperature region of 4–300 K, caused by a very strong antiferromagnetic coupling.

This coupling is less strong in **1b**. At room temperature the remaining paramagnetism and the diamagnetism of the sample compensate, so that no resulting susceptibility can be measured. Compound **1b** is EPR-silent but, as a result of the remaining paramagnetism, shows no NMR spectrum which can be interpreted, except for the signals of the peripheral methyl groups. Such strong antiferromagnetic coupling is also characteristic of copper complexes of Schiff bases of 3-aminopropanol.[5–7] This is in contrast to the weak or even lacking coupling in complexes derived from Schiff bases of 2-aminoethanol[5, 8–16] or 2-aminoglucose.[28]

Complex **2**[31] shows a trinuclear structure (Figure 2) which can formally be interpreted by an insertion of a copper acetate monomer in a dinuclear compound similar to **1a**. At a first glance, a distorted square planar environment is found for all three copper atoms in the trimer. By intermolecular, chain-type binding of the peripheral oxygen atoms of neighboring molecules with Cu(A), a square-pyramidal coordination of Cu(A) results, in which the central atom is moved 0.046(3) Å out of the base plane. At the two other copper atoms the methoxy oxygen atoms in the 3-position of the ligand serve as axial ligands; Cu(B) (with O2(A)) reaches a distorted square pyramidal geometry, and Cu(C) (with O2(A) and O2(B)) a distorted octahedral geometry. The additional donor atoms allow, by addition of a third copper atom to two building blocks of type **I**, a rarely observed trinuclear structure. With all three copper atoms having different axial ligands, **2** shows—like **1a**—a strikingly low symmetry. Even the copper–copper distances between Cu(C) and its neighbors differ significantly (3.248(3) and 3.207(3) Å). Nevertheless, both values are within a range known for such complexes, in which two metal atoms are bridged by a catechol ligand. This is a remarkable parallel to the oxidases named above.

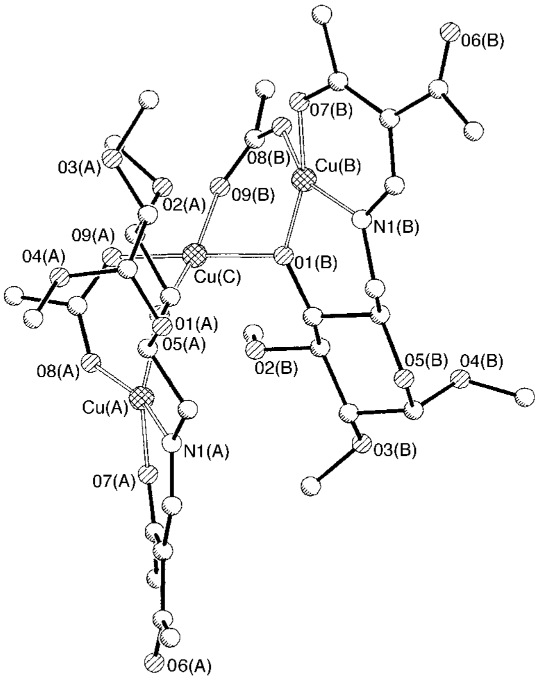


Figure 2. Structure of the copper complex **2**.

The effective magnetic moment of **2** at room temperature is 2.71 μ_B (Figure 3). The temperature-dependant measurement showed an antiferromagnetic coupling, by which the paramagnetism at 2 K is decreased to 1.64 μ_B. This is close to the spin-only value of a $S=\frac{1}{2}$ ground state. The EPR spectrum can be described as a signal for $S=\frac{1}{2}$ at $g=2.04$ and two signals of a paramagnet with $S=1$ at $g=1.47$ and 5.87. Whereas the latter signals decrease in intensity with decreasing temperature, the signal for the doublet state grows stronger and obeys a Boltzmann distribution. Therefore, it can be assumed that two copper atoms in **2** are coupled antiferromagnetically, while the third one is not involved in coupling interactions. Taking this into regard, fitting of the measured data results in a coupling constant J of $-309\,\mathrm{cm}^{-1}$, which underlines the observed strong coupling.[5–7]

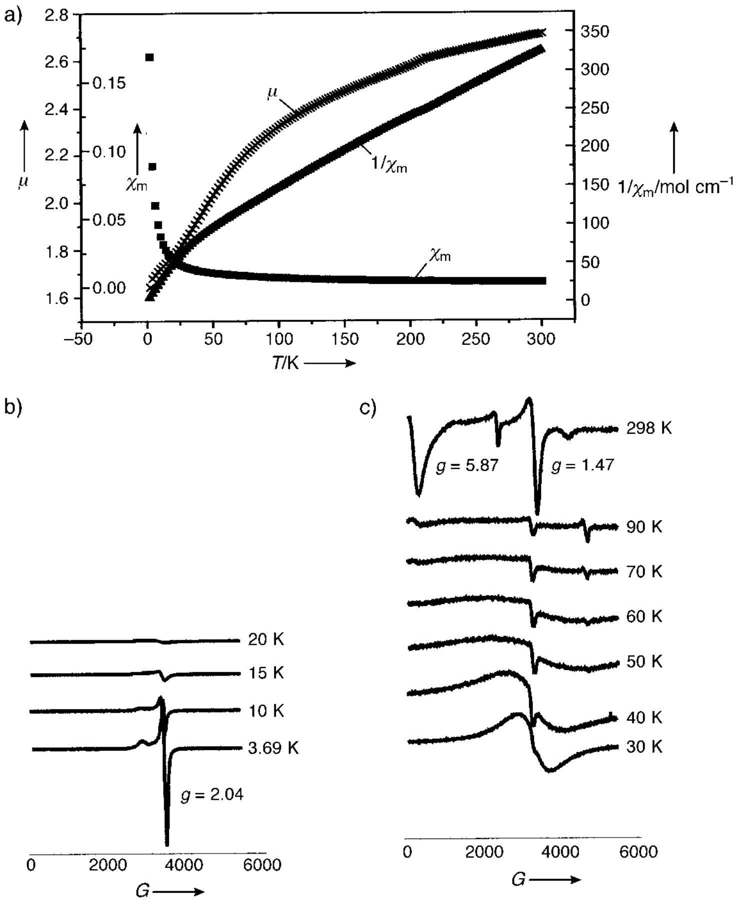
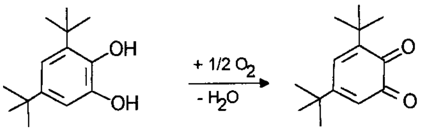


Figure 3. a) Magnetic behavior (χ_m vs. T (■), χ_m^{-1} vs. T (▲), and magnetic moment μ vs. T (×)) and b), c) EPR spectra (right: ×20 for $T>30$ K) of **2**.

The structures of **1a**, **b** and **2** contain elements which are found in different metalloenzymes, for example the 1,3-bridging of two metal atoms by an acetate and by an alcoholate, as in **2**. The double alcoholate bridge in **1a**,**b** is reminiscent of catechol oxidase[1] and other oxidases and oxygenases with copper centers. Owing to their low symmetry, the oligonuclear building blocks in **1a** and **2** might be of some importance for catalytic reactions.

Indeed, both compounds catalyze the oxidation of 3,5-di-*tert*-butylcatechol (dtbc) with oxygen [Eq. (1)].[32] Figure 4 shows the time-dependent difference spectra for the reaction of a 10^{-4}M solution of **1a** with 50 equivalents of dtbc. The



(1)

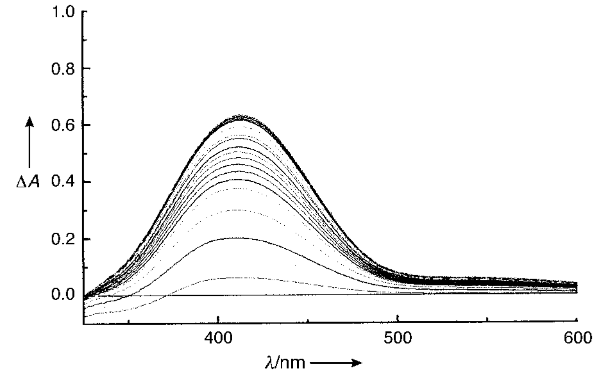


Figure 4. Difference spectrophotometric analysis of the oxidation of dtcb catalyzed by **1a**.

kinetic investigations were carried out as described in the literature.[32] With regard to the catalyst, a first-order reaction was determined for each reaction; with regard to the substrate, saturation kinetics was observed in both cases. Interpretation of the data with the Michaelis–Menten model leads to rate constants k_{cat} of 2.8(3) and 135(5) h^{-1} for **1a** and **2**, respectively. Therefore, especially **2** is an efficient catalyst.

Experimental Section

General synthesis of bis[1,2-*O*-isopropylidene-5-deoxy-5-*N*-(3-acetylbut-3-en-2-on-4-yl)aminoglucofuranosidatoaquadicopper(II)-bis[1,2-*O*-isopropylidene-5-deoxy-5-*N*-(3-acetylbut-3-en-2-on-4-yl)aminoglucofuranosidatomethanolato]dicopper(II) $\cdot$ 4 H_2O (**1a**), bis[1,2-*O*-isopropylidene-5-deoxy-5-*N*-(3-acetylbut-3-en-2-on-4-yl)aminoglucofuranosidato]dicopper(II) $\cdot$ $n\,C_7H_8$ (**1b**), and bis[1,2,3-*O*-trimethyl-6-deoxy-6-*N*-(3-acetylbut-3-en-2-on-4-yl)aminoglucosidato]bis(μ-acetato)tricopper(II) (**2**): 5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoside[29] or 6-amino-6-deoxy-1,2,3-*O*-trimethyl-α-D-glucopyranoside[29] (0.5 mmol) was dissolved in methanol (**1a**, **b**: 15 mL; **2**: 10 mL). Triethylamine (202 mg, 2 mmol) and 3-ethoxymethylene-2,4-pentandione (78 mg, 0.5 mmol) were added dropwise. This leads to the ligands **II** and **III**. After the mixture was stirred for 1 h, copper acetate monohydrate (**1a**, **b**: 91 mg, 0.5 mmol; **2**: 136 mg, 0.75 mmol) was added. The reaction mixture was left to stand overnight, and then the solvent was evaporated.

Isolation of **1a**, **b:** The residue was taken up in toluene. Upon slow evaporation of the solvent, crystallization of **1b** occurs. Recrystallization of **1b** from water/methanol (1/1) leads to the precipitation of **1a**.

Isolation of **2**: The residue was taken up in diethyl ether. Upon slow evaporation of the solvent, blue crystals of **2** can be obtained.

Received: July 12, 1999 [Z13708]

---

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

[2] A. Messerschmidt, *Metal Sites Proteins Models* **1998**, *90*, 37–68.

[3] R. Than, A. A. Feldmann, B. Krebs, *Coord. Chem. Rev.* **1999**, *182*, 211–241.

[4] a) E.-G. Jäger, *Z. Chem.* **1966**, *6*, 111–112; b) H. Elias, D. Hess, H. Paulus, E.-G. Jäger, F. Gräfe, *Z. Anorg. Allg. Chem.* **1990**, *589*, 101–114.

[5] a) J. J. Bertrand, J. A. Kelley, C. E. Kirkwood, *Chem. Commun.* **1968**, 1329–1331; b) J. A. Bertrand, J. A. Kelley, *Inorg. Chim. Acta* **1970**, *4*, 203–209; c) J. A. Bertrand, J. A. Kelley, J. L. Breece, *Inorg. Chim. Acta* **1970**, *4*, 247–250; d) J. A. Bertrand, C. Marabella, D. G. Vânderveer, *Inorg. Chim. Acta* **1978**, *26*, 113–119.

[6] a) E. Sinn, *Inorg. Chem.* **1976**, *15*, 358–365; b) J. A. Davis, E. Sinn, *J. Chem. Soc. Dalton Trans.* **1976**, 165–170.

[7] a) N. Matsumoto, T. Tsutsumi, A. Ohyoshi, H. Okawa, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1386–1392; b) N. Matsumoto, I. Ueda, Y. Nishida, S. Kida, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1308–1312; c) N. Matsumoto, T. Kondo, M. Kodera, H. Okawa, S. Kida, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 4041–4043.

[8] F. Wiesemann, B. Krebs, H. Görls, E.-G. Jäger, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1883–1892.

[9] a) W. Haase, *Chem. Ber.* **1973**, *106*, 3132–3148; b) L. Merz, W. Haase, *J. Chem. Soc. Dalton Trans.* **1978**, 1594–1598; c) L. Merz, W. Haase, *J. Chem. Soc. Dalton Trans.* **1980**, 875–879; d) R. Mergehenn, L. Merz, W. Haase, *J. Chem. Soc. Dalton Trans.* **1980**, 1703–1709; e) L. Walz, H. Paulus, W. Haase, H. Langhof, F. Nepveu, *J. Chem. Soc. Dalton Trans.* **1983**, 657–664; f) L. Schwabe, W. Haase, *J. Chem. Soc. Dalton Trans.* **1985**, 1909–1913; g) H. Astheimer, F. Nepveu, L. Walz, W. Haase, *J. Chem. Soc. Dalton Trans.* **1985**, 315–320.

[10] H. Oshio, Y. Saito, T. Ito, *Angew. Chem.* **1997**, *122*, 2789–2791; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2673–2675.

[11] Yu. M. Chumakov, V. N. Biyushkin, T. I. Malinovskii, S. Kulemu, V. I. Tsapkov, M. S. Popov, N. M. Samus, *Koord. Khim.* **1990**, *16*, 945–949.

[12] a) V. Tangoulis, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, C. P. Raptopoulou, A. Terzis, *Chem. Commun.* **1996**, 1297–1298; b) V. Tangoulis, C. P. Raptopoulou, A. Terzis, S. Paschalidou, S. P. Perlepes, E. G. Bakalbassis, *Inorg. Chem.* **1997**, *36*, 3996–4006.

[13] G. A. van Albada, J. Reedijk, R. Hamalainen, U. Turpeinen, A. L. Spek, *Inorg. Chim. Acta* **1989**, *163*, 213–217.

[14] P. L. Dedert, T. Sorrell, T. J. Marks, J. A. Ibers, *Inorg. Chem.* **1982**, *21*, 3506–3517.

[15] a) H. Muhonen, *Acta Chem. Scand. Ser. A* **1980**, *34*, 79; b) H. Muhonen, W. E. Hatfield, J. H. Helms, *Inorg. Chem.* **1986**, *25*, 800–812.

[16] J. Sassmannshausen, H. F. von Schnering, L. Walz, *Z. Kristallogr.* **1997**, *212*, 656–661.

[17] a) E.-G. Jäger, K. Müller, *Z. Anorg. Allg. Chem.* **1981**, *482*, 201–216; b) E.-G. Jäger, K. Schuhmann, H. Görls, *Chem. Ber.* **1997**, *130*, 1643–1646.

[18] D. Klemm, T. Heinze, B. Philipp, W. Wagenknecht, *Acta Polym.* **1977**, *48*, 277–297.

[19] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, *Comprehensive Cellulose Chemistry, Vols. 1 and 2*, Wiley-VCH, Weinheim, **1998**.

[20] J. Tiller, P. Berlin, D. Klemm, *Macromol. Chem. Phys.* **1999**, *200*, 1–9.

[21] D. N. Williams, U. Piarulli, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Chem. Soc. Dalton Trans.* **1994**, 1243–1250.

[22] a) P. Klüfers, H. Piotrowski, J. Uhlendorf, *Chem. Eur. J.* **1997**, *3*, 601–608; b) H. P. Wu, C. Janiak, P. Klüfers, P. Mayer, *Chem. Commun.* **1998**, 2637–2638; c) P. Mayer, P. Klüfers, *Acta Crystallogr. Sect. C* **1998**, *54*, 583–586; d) R. Ahlrichs, B. Ballauf, K. Eichkorn, O. Hanemann, G. Kettenbach, P. Klüfers, *Chem. Eur. J.* **1998**, *4*, 835–844; e) A. Geisselmann, P. Klüfers, B. Pilawa, *Angew. Chem.* **1998**, *123*, 1181–1184; *Angew. Chem. Int. Ed.* **1998**, *37*, 1119–1121; f) J. Bürger, P. Klüfers, *Z. Anorg. Allg. Chem.* **1998**, *624*, 359–360.

[23] a) S. Yano, *Coord. Chem. Rev.* **1988**, *92*, 113–156; b) S. Yano, M. Doi, S. Tamakoshi, W. Mori, M. Mikuriya, A. Ichimura, I. Kinoshita, Y. Yamamoto, T. Tanase, *Chem. Commun.* **1997**, 997–998; c) S. Yano, S. Inoue, R. Nouchi, M. Reiko, S. Kaoru, Y. Yoshie, Y. Yasuda, M. Kato, T. Tanase, T. Kakuchi, Y. Mikata, T. Suzuki, Y. Yamamoto, *J. Inorg. Biochem.* **1998**, *69*, 15–23; d) T. Tanase, T. Onaka, M. Hakagoshi, I. Kinoshita, S. Shibata, M. Doe, J. Fujii, S. Yano, *Chem. Commun.* **1997**, 2115–2116; e) T. Tsubomura, M. Ogawa, S. Yano, K. Kobayashi, T. Sakurai, S. Yoshikawa, *Inorg. Chem.* **1990**, *29*, 2622–2626.

[24] Y. Zhou, B. Wagner, K. Polborn, K. Sunkel, W. Beck, *Z. Naturforsch. B* **1994**, *49*, 1193–1202.

[25] J. M. Harrowfield, M. Mocerino, B. W. Skelton, W. Wei, A. H. White, *J. Chem. Soc. Dalton Trans.* **1995**, 783–797.

[26] a) A. Bernalte-Garcia, M. A. Diaz-Diez, F. J. Garcia-Barros, F. J. Higes-Rolando, C. Valenzuela-Calahorro, *Trans. Met. Chem.* **1996**, *21*,

197–199; b) M. A. Diaz-Diez, F. J. Garcia-Barros, F. J. Higes-Rolando, A. Bernalte-Garcia, C. Valenzuela-Calahorro, *Trans. Met. Chem.* **1995**, *20*, 402–405; c) M. A. Diaz-Diez, F. J. Garcia-Barros, F. J. Higes-Rolando, A. Bernalte-Garcia, C. Valenzuela-Calahorro, *Polyhedron* **1993**, *12*, 2519–2523.

[27] a) K. Hegetschweiler, M. Weber, V. Huch, R. J. Geue, A. D. Rae, A. C. Willis, A. M. Sargeson, *Inorg. Chem.* **1998**, *37*, 6136–6146; b) G. J. Reiss, W. Frank, K. Hegetschweiler, D. Kuppert, *Acta Crystallogr. Sect. C* **1998**, *54*, 614–616; c) L. Hausherr-Primo, K. Hegetschweiler, H. Ruegger, L. Odier, R. D. Hancock, H. W. Schmalle, V. Gramlich, *J. Chem. Soc. Dalton Trans.* **1994**, 1689–1701.

[28] E.-G. Jäger, R. Wegner, H. Görls, D. Klemm, M. Gottschaldt, unpublished results.

[29] Synthesis: K. Dax, B. Gaigg, V. Grassberger, B. Kölbinger, A. E. Stütz, *J. Carbohydr. Chem.* **1990**, *9*, 479–499; B. P. Bashyal, H. F. Chow, L. E. Fellows, G. W. J. Fleet, *Tetrahedron* **1987**, *43*, 415.

[30] Crystal data for **1a**: $C_{30}H_{42}Cu_2N_2O_{14} \cdot 1.75\,H_2O \cdot 0.5\,CH_3OH$, $M_r = 837.79$, blue prisms, crystal size $0.28 \times 0.24 \times 0.20$ 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}, $\mu(Mo_{K\alpha}) = 12.33$ cm^{-1}, $F(000) = 1748$; a total of 15126 reflections up to $h(0/14)$, $k(-19/19)$, $l(-25/27)$ in the range $2.30° \leq \Theta \leq 30.52°$ (completeness of data $\Theta_{max} = 78.2\,\%$), of which 14812 were symmetry-independent ($R_{int} = 0.0410$) and 11657 observed with $F_o > 4\sigma(F_o)$, 933 parameters, 1 restraint, $R1_{obs} = 0.081$, $wR^2_{obs} = 0.141$, $R1_{all} = 0.1106$, $wR^2_{all} = 0.1533$, GOF = 1.095, Flack parameter 0.35(1) (racemic twin), max./min. residual electron density 0.646/ -0.695 e Å^{-3}. Distances [Å] and angles [°]: Cu(A)$\cdots$Cu(B) 2.977(1), Cu(A)/Cu(B)–O/N 1.893(5)–1.956(5), Cu(A)–O8(A) 2.382(5); O/N-Cu-O/N 76.1(2)–102.1(2) and 166.6(2)–173.8(2), Cu(C)$\cdots$Cu(D) 3.020(1), Cu(C)/Cu(D)–O/N 1.918(5), Cu(C)–O(4) 2.674(5), O/N-Cu-O/N 75.9(2)–107.6(2) and 166.7(2)–176.1(2).[31b]

[31] a) Crystal data for **2**: $C_{34}H_{52}Cu_3N_2O_{18}$, $M_r = 967.40$, blue prisms, crystal size $0.32 \times 0.30 \times 0.20$ mm^3, monoclinic, space group $P2_1$, $a = 10.0735(3)$, $b = 21.3865(7)$, $c = 10.4135(2)$ Å, $\beta = 110.789(1)°$, $V = 2097.4(1)$ Å^3 , $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.532$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 15.82$ cm^{-1}, $F(000) = 1002$; a total of 6973 reflections up to $h(-12/12)$, $k(-20/26)$, $l(-12/13)$ in the region $5.19 \leq \Theta \leq 26.37°$ (completeness of data $\Theta_{max} = 98.7\,\%$), of which 6973 were symmetry-independent ($R_{int} = 0.035$) and 6127 observed with $F_o > 4\sigma(F_o)$; 514 parameters, 1 restraint, $R1_{obs} = 0.039$, $wR^2_{obs} = 0.087$, $R1_{all} = 0.050$, $wR^2_{all} = 0.094$, GOF = 1.029, Flack parameter 0.01(1), max./min. residual electron density 0.257/ -0.355 e Å^{-3}. Distances [Å] and angles [°]: Cu(A)$\cdots$Cu(B) 5.735(3), Cu(A)$\cdots$Cu(C) 3.248(3), Cu(B)$\cdots$Cu(C) 3.207(3), Cu–O/N 1.940(4), Cu(A)$\cdots$O6(B) (symmetry operation for equivalent atoms: $-x$, $0.5 + y$, $-z$) 2.753(4), Cu(B)$\cdots$O2(A) 2.898(4), Cu(C)–O2(A) 2.586(4), Cu(C)–O2(B) 2.572(4); O1(A)-Cu(A)-N1(A) 95.6(1), O/N-Cu-O/N 73.6(1)–106.9(1) and 152.0(1)–172.3(1). b) Crystallographic Data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-129253 (**1a**) and -129254 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[32] General remarks on the kinetic investigations: The measurements were carried out as described in J. Reim, B. Krebs, *J. Chem. Soc. Dalton Trans.* **1997**, 3793–3804. For qualitative testing of the catalytic activities, 10^{-4} M solutions of the copper complexes in methanol were mixed with 50 equivalents of dtcb. The reaction with oxygen was monitored by observing the absorption of the quinone at 400 nm against a solution of the pure complex with the same concentration by means of UV/Vis spectroscopy (VARIAN-Spectrophotometer Cary 5). As reference for the catalytic reaction, a 10^{-4} M solution of copper acetate monohydrate was used, which shows a significant lower activity ($k < 1.5$ h^{-1}). The given rate constants are mean values of three measurements with a discrepancy value of the Lineweaver–Burk plot of $r \geq 0.992$.

Simple Synthesis of a Chlorin–Fullerene Dyad with a Novel Ring-Closure Reaction[**]

Franz-Peter Montforts* and Olaf Kutzki

Amongst the covalent functionalizations of buckminster fullerene C_{60},[1] the linkage to porphyrins has opened the possibility of constructing artificial photosynthetic systems[2] in which there is light-induced transfer of electrons or energy from a porphyrin donor to a fullerene acceptor. Apart from one example in which a derivative of naturally occurring chlorophyll was attached to a fullerene by [2+3] cycloaddition,[3] all known fullerene-based photosynthetic models contain completely unsaturated porphyrins and phthalocyanines as the donor unit;[4] they are usually linked to C_{60} by long ether or ester bridges.[5] We report here on the total synthesis of a dyad that contains fullerene C_{60} bound to a chlorin by two methylene bridges and thus at a very small distance. The dyad, which is synthesized in an unusual one-pot reaction with concomitant formation of the chlorin macrocycle and linkage to the fullerene, is the first of this type that contains a chlorin moiety which is the chromophore in naturally occurring photosynthetic systems.

The starting point for the synthesis was the tripyrrolenickel complex *rac*-**3** (Scheme 1); we have already employed this complex in the synthesis of chlorins[6] and corrins.[7] After hydrolysis of the ester group in *rac*-**3**, the pyrrole aldehyde **2** was linked to tricyclic *rac*-**3** by decarboxylation and decomplexation. Subsequent recomplexation with zinc(II) or nickel(II) acetate gave the tetrapyrrolemetal complexes *rac*-**5a**, **b** and *rac*-**6a**, **b**. The robust nickel complex *rac*-**6a**, **b** was produced in order to characterize the tetracyclic compound. It was obtained as a separable binary mixture of diastereomers on account of the chiral center at C-1 and because of the helicity of the chromophore in the complex. The labile linear tetrapyrrolezinc complex *rac*-**5a**, **b** was cyclized upon heating in the presence of C_{60} to give the chlorin–fullerene dyad **7** along with the 15-cyano-substituted dyadic system **8** as a side product. This one-pot reaction is a complex cascade of single steps, the exact sequence of which has not yet been determined; however, it involves 1) loss of cyanide and formation of an enamine double bond at C-1, 2) cyclization between C-19 and the enaminoid double bond under the templating influence of the central zinc ion, 3) decarbobenzoxylation, 4) oxidation of the initially formed dihydrochlorin with atmospheric oxygen, 5) extrusion of sulfur dioxide, and finally 6) a Diels–Alder reaction between the diene formed and C_{60} as the dienophile to yield dyad **7**. The 15-cyano-

---

[*] Prof. Dr. F.-P. Montforts, Dipl.-Chem. O. Kutzki
Institut für Organische Chemie der Universität
FB2 Biologie/Chemie
Postfach 330440, 28334 Bremen (Germany)
Fax: (+49) 421-218-3720
E-mail: mont@chemie.uni-bremen.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds des Verbandes der Chemischen Industrie in the form of a doctoral grant for O.K. We thank Dr. Mayer-Posner, Bruker-Daltonik GmbH, for recording the MALDI-TOF mass spectra and the Hoechst AG for their donation of fullerene.

0570-0833/00/3903-0599 $ 17.50+.50/0