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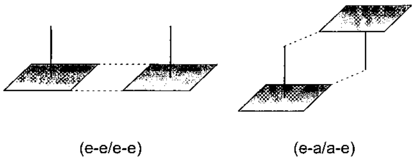
Magnetic Interactions as Supramolecular Function: Structure and Magnetic Properties of Hydrogen-Bridged Dinuclear Copper(II) Complexes**

Winfried Plass,* Axel Pohlmann, and
Jens Rautengarten

*Dedicated to Professor Ernst-Gottfried Jäger
on the occasion of his 65th birthday*

Hydrogen bonds play a key role in interactions in biological structures, supramolecular chemistry, and crystal engineering.[1] As such they are also important to understand the properties of relevant magnetic materials.[2] In particular for some copper(II)-containing coordination compounds it has been shown that the variation of possible supramolecular interactions can substantially influence the magnetic properties of related coordination polymers.[3]

Although copper(II) complexes have been widely studied, only two basic patterns of hydrogen bonding have been observed for dinuclear units (Scheme 1). In accord with the preferred square-planar coordination environment for copper(II) ions with the option of one or two additional apical ligands, these hydrogen bonds can be denoted as either equatorial–equatorial (e–e) or equatorial–apical (e–a) with regard to the position of the involved donor and acceptor atoms. If one considers that the magnetic orbital at each copper(II) ion is defined by the short equatorial bonds, that is basically an orbital of $d_{x^2-y^2}$ type with some possible admixture of d_{z^2} character, a qualitative magneto-structural correlation would predict antiferromagnetic coupling for (e–e/e–e) bridging patterns and weak interactions, which should be of ferromagnetic nature, for (e–a/a–e) bridging patterns. In addition, the magnitude of the magnetic coupling should also be related to the strength of the involved hydrogen bonds. This basic concept is in agreement with the observed structural and magnetic data of relevant systems.[4]



Scheme 1. Schematic representation for the hydrogen bonding patterns observed for dinuclear copper(II) complexes with square-pyramidal coordination geometry at the copper(II) centers (e: equatorial position, a: apical position).

To probe this qualitative magneto-structural relationship we synthesized the copper(II) complex with the trivalent, pentadentate Schiff base ligand *N*-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine (H_3sabhea). The resulting self-complementary complex cation [Cu(H_2sabhea)]$^+$ can be isolated as hydrogen-bridged dinuclear complex **1**. Complex **1** can be reversibly deprotonated in aqueous solution yielding **2**, the first triply hydrogen-bridged dinuclear copper(II) complex.

[{Cu(H_2sabhea)}$_2$](BF_4)$_2$ **1**

[{Cu(H_2sabhea)}{Cu(Hsabhea)}]BF_4 **2**

The X-ray crystal structure analyses[5] of the isolated compounds **1**·0.5 EtOH·0.25 H_2O (**1a**) and **2**·H_2O (**2a**) reveal the dimeric hydrogen-bridged structure of the cationic copper(II) complexes (Figure 1). The prearranged coplanar configuration for three donor sets of the H_3sabhea ligand (O1, N1, and N2; see Figure 1) defines the orientation of the equatorial plane of the distorted square-pyramidal coordination environment of the copper(II) centers.[6] This is consistent with the observed elongation of the apical Cu–O bonds by about 25–30 pm as compared to the relevant equatorial bonds (see Figure 1). The two hydrogen bonds in **1** involve the equatorially coordinated alcohol group as donor and the phenolate oxygen as acceptor; this leads to a (e–e/e–e) bridging pattern (see Scheme 1). The observed O···O distance of 260 pm is within the range of strong O–H···O hydrogen bonds.[1f] In **1** both apical coordinated alcohol groups are oriented *cis* with respect to the hydrogen bonding

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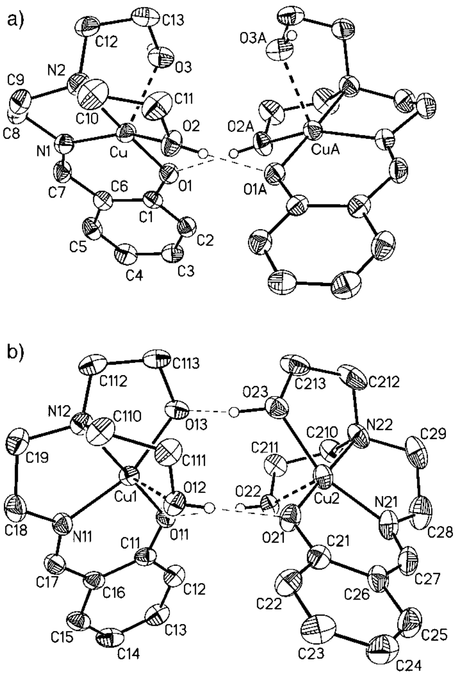

Figure 1. Molecular structure of the hydrogen-bridged cationic complexes **1** (a) and **2** (b) in crystals of **1a** and **2a**, respectively. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. All hydrogen atoms not bound to alcoholic oxygen atoms are omitted for clarity. Solid broken lines indicate bonds to atoms in the apical position of the coordination polyhedron. Hydrogen bonds (thin broken lines) and interatomic distances [pm] and bond angles [°]: **1a**: Cu-O1 189.5(2), Cu-O2 200.5(2), Cu-O3 225.4(2), Cu-N1 192.5(2), Cu-N2 201.9(2); O1 ··· O2A 259.6(3), O3 ··· O3A 353.4(3), Cu ··· CuA 473.6(2); O1-Cu-N2 178.36(9), O2-Cu-N1 151.49(9), O2-Cu-O3 98.26(8), O3-Cu-N1 107.36(9). **2a**: Cu1-O11 192.7(2), Cu1-O12 226.0(2), Cu1-O13 196.3(2), Cu1-N11 193.8(2), Cu1-N12 204.4(2), Cu2-O21 191.8(2), Cu2-O22 227.9(2), Cu2-O23 198.5(2), Cu2-N21 193.1(3), Cu2-N22 203.8(2); O11 ··· O22 266.4(3), O12 ··· O21 265.8(3), O13 ··· O23 244.2(3), Cu1 ··· Cu2 461.4(2); O11-Cu1-N12 174.50(8), O12-Cu1-N11 101.49(9), O12-Cu1-O13 94.35(8), O13-Cu1-N11 160.36(9), O21-Cu2-N22 176.50(9), O22-Cu2-N21 105.11(9), O22-Cu2-O23 90.44(8), O23-Cu2-N21 159.81(10).

plane, yielding an arrangement that is prepositioned for a third hydrogen bond (interatomic distance between O3 and O3A is 353 pm).

The deprotonation of one of the two apical alcohol groups, as observed in **2**, increases the hydrogen bond acceptor ability of the corresponding oxygen atom and, therefore, enables the formation of the third hydrogen bond between the two copper(II) units. This is accompanied with a conformational alternation of the ethylenediamine chelate ring (N1-C8-C9-N2: δ in **1** and λ in **2**, see Figure 1), which enables the rearrangement of the copper(II) coordination environments in such a way that the equatorial planes now include the newly hydrogen-bonded oxygen atoms O13 and O23 (cf. Figure 1b). The hereby established unique (e–e/e–a/a–e) bridging pattern contains a very short O ··· O distance of 244 pm (O13 ··· O23), which is within the range of very strong hydrogen bonds,[1f] whereas the two other hydrogen bonds (O12 ··· O21 and O11 ··· O22: 266 pm) are slightly longer than in the protonated complex **1**.

The X-band ESR spectra of microcrystalline powders of **1a** and **2a** recorded at 50 K show broad unstructured bands with no detectable hyperfine structure at $g = 2.09$ (peak to peak separation: 10 mT) and $g = 2.10$ (peak to peak separation: 13 mT), respectively, and a band at half-field from the forbidden $\Delta m_S = 2$ transition at approximately 150 mT. Moreover the temperature dependence of the half-field resonances is consistent with an antiferromagnetic coupling between the two magnetic copper(II) centers. Similar behavior is found for X-band ESR spectra of frozen aqueous solutions of **1** and **2**. In particular the band at half-field transition expected for an exchange-coupled system is observed.

The magnetic susceptibility χ of polycrystalline samples of **1a** and **2a** was measured in a temperature range of 2–295 K using a SQUID susceptometer with an applied field of $H = 10$ kOe. The temperature dependence of the product $\chi_M T$ is shown in Figure 2. At higher temperatures the susceptibility data obeys the Curie–Weiss law and $\chi_M T$ is close to the expected spin-only value for two independent copper(II) centers per molecule. The observed decrease of $\chi_M T$ upon cooling is in accord with the presence of intramolecular antiferromagnetic interactions between the hydrogen-bridged copper(II) centers of **1** and **2**. A quantitative analysis of the magnetic data (corrected for diamagnetic contributions using Pascal constants) assuming an isotropic interaction using the Heisenberg–Dirac–Van Vleck Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$ was used to describe the temperature dependence of the product $\chi_M T$. As shown in Figure 2, good fits to the experimental data were attained for the magnetic parameters $g = 2.07$ and $J = -21$ cm^{-1} for **1a** and $g = 2.12$ and $J = -7$ cm^{-1} for **2a**.

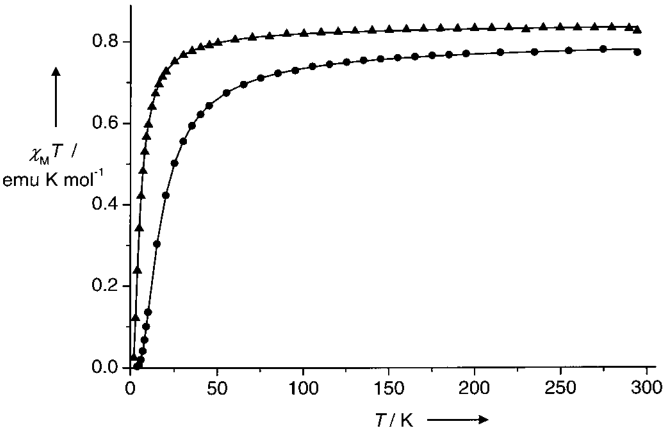

Figure 2. Experimentally determined temperature dependence of $\chi_M T$ for **1a** (●) and **2a** (▲). The solid lines represent the calculated values (see text).

Density functional theory (DFT) calculations were performed to elucidate the electronic structure of the cationic complexes of **1** and **2**.[7] In all calculations split-valence basis sets were used that have been augmented by diffuse functions for the oxygen atoms to enable a proper description of the hydrogen bonds.[8] The geometry optimization was performed with the generalized gradient approximation functional Becke88/Perdew91 (B88/PW91).[9] The calculated structural parameters are in good agreement with the values obtained from the X-ray structure analysis. In particular this holds for the coordination environment of the copper(II) centers (calculated structure data for **1**: $\tau = 0.43$; for **2**: Cu1 $\tau = 0.28$, Cu2 $\tau = 0.33$; for X-ray structures see reference [6]) as well as the hydrogen bonding scheme (calculated structure data for **1**: O1 ··· O2A 259, O3 ··· O3A 355; for **2**: O11 ··· O22 265, O12 ··· O21 265, O13 ··· O23 242 pm; for X-ray structures see. Figure 1).

If the broken-symmetry formalism is utilized, it is possible to express the singlet–triplet gap of exchange-coupled systems with one unpaired electron per center as $J = E_B - E(S=1)$,[10] where E_B is the energy of the broken-symmetry state. This procedure is in keeping with the proposal of Perdew, Savin, and co-workers,[11] who suggested that the broken-symmetry single determinant is the correct solution of the Kohn–Sham equations for the singlet state. The exchange coupling constants calculated with the B88/PW91 functional (**1**: -68 and **2**: $-31\,\text{cm}^{-1}$) are too large as compared to the experimental values. This is consistent with the generally observed overestimation of the stabilization of the singlet state relative to the triplet state by DFT methods. The inclusion of Hartree–Fock(HF)-type contributions, which are known to usually overestimate the relative stability of the triplet state, can improve the accuracy of the calculated values.[10] Consequently, calculations with the hybrid method b3lyp[12] yield exchange-coupling constants of -17 and $-6\,\text{cm}^{-1}$ for **1** and **2**, respectively, which are in excellent agreement with the experimental values.

The magnetic orbitals as derived from the broken-symmetry calculations have basically $d_{x^2-y^2}$ character with contributions from the equatorial oxygen and nitrogen atoms. This is consistent with the observed distorted square-pyramidal coordination geometry at the copper(II) centers. The reduced exchange-coupling constant for **2** as compared to that for **1** indicates that only hydrogen bonds of the (e–e) type are effectively transmitting exchange interactions between the copper(II) centers, that is both the hydrogen donor and the hydrogen acceptor must have contributions to the respective magnetic orbital. Moreover, according to a magneto-structural correlation based on the O ··· O distance of hydrogen-bridged copper(II) complexes that was derived from a theoretical study on the model system $[\{Cu(OH)(NH_3)_2(H_2O)\}_2]$,[13] complexes **1** and **2** should exhibit much larger exchange-coupling constants in the range of -80 to $-100\,\text{cm}^{-1}$. This is indicative for the importance of the relative orientation of the magnetic orbitals with respect to each other, which for **1** and **2** is unfavorable as compared to the coplanar orientation of the model system $[\{Cu(OH)(NH_3)_2(H_2O)\}_2]$ used for the theoretical study.[13]

In conclusion, we have shown that by utilizing a self-complementary copper(II) coordination unit the first triply hydrogen-bridged dinuclear transition metal complex has been synthesized. This system can be reversibly switched between its triple (**2**) and double hydrogen-bridged (**1**) forms by proton transfer. Their structural and magnetic properties show that a simple magneto-structural correlation based on a hydrogen bond length criterion is not sufficient. On the contrary the key factor is given by the hydrogen bonding pattern. In contrast, the fine tuning of the magnetic properties is related to the hydrogen bonding distances and the relative orientation of the magnetic orbitals of both copper units with respect to the hydrogen bonding pattern.

Experimental Section

The ligand H_3sabhea was synthesized as described in reference [14].

1a: H_3sabhea (0.25 g, 1 mmol) dissolved in ethanol (10 mL) was added to a solution of $Cu(BF_4)_2 \cdot 6H_2O$ (0.34 g, 1 mmol) in ethanol (10 mL) at room temperature. The resulting deep green solution was stirred for 30 min and allowed to stand at room temperature. After a few days green crystals of **1a** formed which were isolated by filtration and washed with ethanol (0.25 g, 61 %). Elemental analysis (%) calcd for $C_{27}H_{41.5}B_2Cu_2F_8N_4O_{6.75}$: C 39.04, H 5.04, N 6.74; found: C 38.93, H 5.06, N 6.81.

2a: A 2N aqueous solution of NaOH (2 mL) was added to H_3sabhea (0.50 g, 2 mmol) dissolved in water (10 mL). To this solution $Cu(BF_4)_2 \cdot 6H_2O$ (0.69 g, 2 mmol) dissolved in water (10 mL) was added. After stirring for 30 min the solution was allowed to stand at room temperature. Within a few days blue crystals of **2a** formed (0.42 g; 57 %). Elemental analysis (%) calcd for $C_{26}H_{39}BCu_2F_4N_4O_7$: C 42.57, H 5.36, N 7.64; found: C 42.57, H 5.16, N 7.41.

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[5] Crystal structure analyses data: **1a**: $C_{27}H_{41.5}B_2Cu_2F_8N_4O_{6.75}$, $M_r = 830.8$, crystal dimensions $0.1 \times 0.2 \times 0.4$ mm, tetragonal, $P\bar{4}2_1c$, $a = 1580.50(7)$, $c = 1350.70(9)$ pm, $V = 3.3740(3)\,\text{nm}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.636\,\text{g cm}^{-3}$, $F(000) = 1702$, $T = 183$ K, $\lambda = 71.073$ pm, $\mu(\text{Mo}_{K\alpha}) = 1.354\,\text{mm}^{-1}$, θ range 1.82–27.01°, 19045 measured, 3683 independent reflections ($R_{\text{int}} = 0.056$), 237 parameters, $wR_2 = 0.070$, $R_1 = 0.032$ for 2722 reflections with $F > 4\sigma(F)$, Flack parameter $x = 0.52(2)$, max./min. residual electron density in the final difference Fourier map $0.3/-0.3 \times 10^{-6}\,\text{e pm}^{-3}$. **2a**: $C_{26}H_{39}BCu_2F_4N_4O_7$, $M_r = 733.5$, crystal dimensions $0.05 \times 0.1 \times 0.5$ mm, monoclinic, $P2_1/c$, $a = 1426.35(7)$, $b = 1838.00(9)$, $c = 1160.78(6)$ pm, $\beta = 94.1310(10)°$, $V = 3.0352(3)\,\text{nm}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.605\,\text{g cm}^{-3}$, $F(000) = 1512$, $T = 183$ K, $\lambda = 71.073$ pm, $\mu(\text{Mo}_{K\alpha}) = 1.476\,\text{mm}^{-1}$, θ range 1.43–26.99°, 16338 measured, 6419 independent reflections ($R_{\text{int}} = 0.030$), 461 parameters, $wR_2 = 0.085$, $R_1 = 0.039$ for 5015 reflections with $F > 4\sigma(F)$, max./min. residual electron density in the final difference Fourier map $0.4/-0.4 \times 10^{-6}\,\text{e pm}^{-3}$. The crystallographic data were collected on a Bruker AXS SMART. Lorentz and polarization corrections as well as an empirical absorption correction were performed. The structures were solved by direct methods (SHELXTL) and subsequent full-matrix least-squares refinement against F^2 (G. M. Sheldrick, *SHELXL97*, Universität Göttingen, **1997**). For **1a** the observed systematic absences suggest either of the tetragonal space groups $P\bar{4}2_1c$ and $P4/mnc$. Attempts to solve the structure in the centrosymmetric space group $P4/mnc$ were unsuccessful. This led in agreement with intensity statistics to the noncentrosymmetric tetragonal space group $P\bar{4}2_1c$ as the final choice. The refinement afforded a Flack parameter (H. D.

Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876 – 881) of about 0.5, which could not be reduced upon inversion of the parameter set. Therefore the final structure refinement was performed by assuming racemic twinning. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to alcoholic oxygen atoms were refined isotropically, whereas all other hydrogen atoms were treated by using the appropriate riding model. 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-161491 (**1a**) and CCDC-161490 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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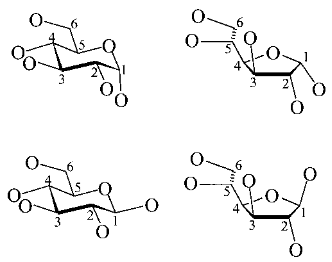
A Transition Metal Complex of D-Glucose**

Peter Klüfers* and Thomas Kunte

Special attention is paid to the carbohydrates as the most abundant biogenic raw materials when establishing benign chemical syntheses as a part of sustainable development. In order to overcome the "overfuctionalization" of the carbohydrates, which bear a number of very similar functionalities rather than a large number of functionalities, classical carbohydrate chemistry often uses multistep reaction sequences. Due to by-products and an extensive use of auxiliary agents, carbohydrate chemistry is by no means "green", despite the usage of biogenic raw materials.[1] One approach to solve this problem is reaction steering by metal catalysis. To plan catalysis in a rational way, basic information is needed; in particular, how the substrate reacts with a metal in a specified oxidation state.[2] To what extend the fundamentals are lacking in that area is illustrated by the statement that, to the best of our knowledge, up to now not a single transition-metal complex of D-glucose, as the most important monosaccharide, has been characterized structurally. One of the reasons for this might be the high reactivity of the reducing sugars. Not only the ease of oxidation and their instability in alkaline solution must be accounted for, even the monosaccharides themselves are mixtures in solution. When a coordinating metal moiety is exposed to glucose, for example, it is not predictable whether the sugar will react through its α- or β-furanose, α- or β-pyranose, or a less stable form (Scheme 1; neither open-chain nor septanose forms are considered). For the epimeric D-mannose, it was demonstrated that coordination to a metal can establish β-D-mannofuranose as the main species, although this isomer is unimportant in the normal solution equilibrium of the aldose.[3]



Scheme 1. Oxygen atom pattern of the common α- (top) and β-D-glucose isomers (bottom): Pyranoses with $^4C_1$ conformation (left) and furanoses (right).

Herein, we report on the characterization of a transition metal complex of D-glucose in solution and the solid state. The metal is the good oxidant palladium(II)—oxidation of the aldose, however, could be avoided to such an extent that even crystallization became possible. The starting point of the experiments was the unexpected behaviour of "Pd-en", an aqueous solution of $[(en)Pd(OH)_2]$ (en = ethylenediamine), towards cellulose. Pd-en is a coordinating cellulose solvent, which dissolves the polysaccharide with formation of a metal complex.[4] On investigating largely hydrolyzed cellulose (degree of polymerization approximately 30, compared with about 3000 for native cellulose), our attention was attracted since even with these short chained and hence end-group rich celluloses, there was no enhanced precipitation of palladium(0) due to oxidation of the reducing end groups. Hence monosaccharides—the "pure" reducing end groups—were dissolved in Pd-en and it became apparent that simply cooling the mixtures to about 5 °C suffices to obtain stable solutions without metal precipitation (as expected, no *N*-glycoside formation of the en ligands was observed at the low temperatures applied[5]). Since palladium(II) complexes with an N_2O_2 ligand set are sufficiently inert and diamagnetic, the mixture of isomers can be investigated by NMR spectroscopy in solution. Figure 1 shows the spectrum of a solution with a 3:1 molar ratio of palladium and the sugar. The signals, assigned by $^1H/^{13}C$ correlated spectra, indicated an anomeric mixture made up of two parts α- and one part β-pyranose

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