An Unusual Metal-Mediated Formation of an Asymmetrical Carboxylate-Bridged Dinuclear Copper(II) Complex

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Introduction

Oligonuclear copper complexes have been object of intensive studies because of their remarkable magnetic coupling properties and redox behavior.[1] They possess great potential as models for bioinorganic systems,[2] as catalysts,[3] and as new materials[4] such as molecular magnets.

In order to synthesize trinuclear copper complexes, we used a 1:2 reaction of a metal cation with metal-containing precursors H-**2**(M). The syntheses described in this paper are based on the derivatives **1**(M) with M = Co, Ni, Cu[5] and follow the synthesis path of similar nickel derivatives[6] (Chart 1).

Recent investigations show that the analogous trinuclear copper complex Cu[**2**(Cu)]$_2$ can be transformed into the dinuclear compound **3**(Cu,Cu). Its new octadentate ligand is formed by a copper-mediated rearrangement and ester hydrolysis.

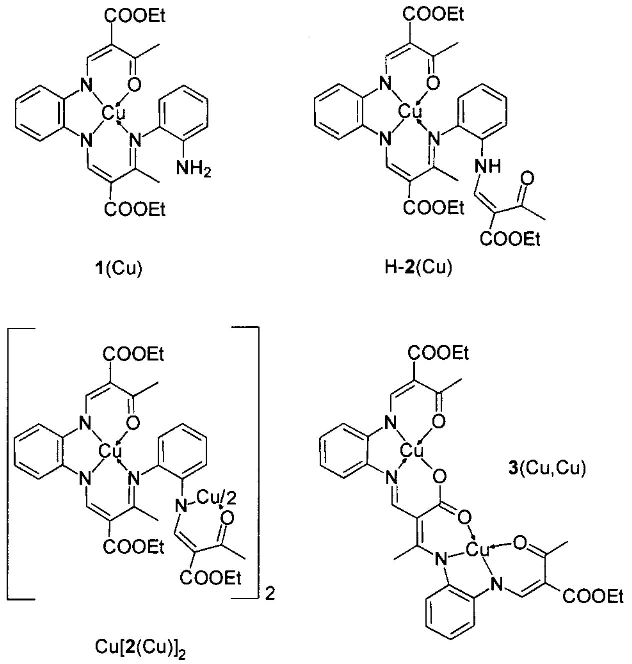
Results and Discussion

The precursor H-**2**(Cu) was obtained via the condensation of the copper chelate **1**(Cu)[5] with 3-ethoxy-2-acetylacrylic acid ethyl ester. The 2:1 reaction of H-**2**(Cu) and anhydrous Cu(ac)$_2$ leads to the trinuclear complex Cu[**2**(Cu)]$_2$.

In moist solvents (toluene, dioxane, pyridine) Cu[**2**(Cu)]$_2$ forms the dinuclear compound **3**(Cu,Cu). Additionally, H-**2**(Cu) was found in the reaction mixture. Using moist dioxane as solvent, **3**(Cu,Cu) may also be obtained by the reaction of H-**2**(Cu) and Cu(ac)$_2$.

The compounds H-**2**(Cu), Cu[**2**(Cu)]$_2$, and **3**(Cu,Cu) have been characterized by X-ray crystallography[7] (cf. Figures 1−3), and temperature dependent magnetic susceptibility measurements down to 2 K have been obtained.

Chart 1



1(Cu)

H-**2**(Cu)

Cu[**2**(Cu)]$_2$

3(Cu,Cu)

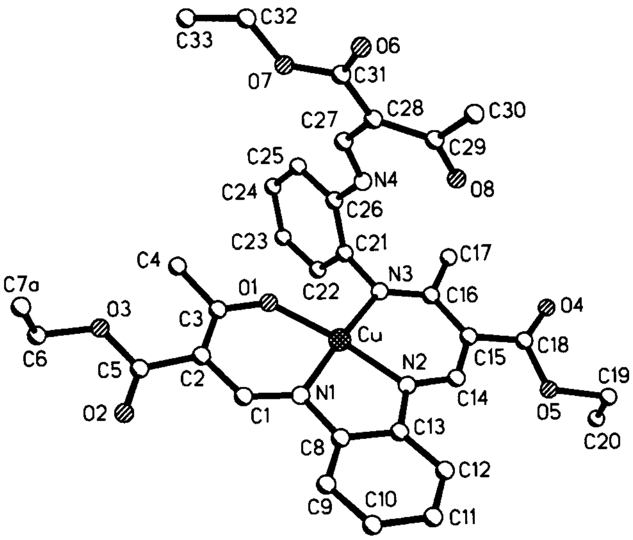


Figure 1. Plot of the structure for H-**2**(Cu) with atom-labeling scheme. H atoms and the acetonitrile molecule are omitted for clarity. Selected distances (Å) and angles (deg): Cu−N(1) 1.931(2), Cu−N(2) 1.912(2), Cu−N(3) 1.977(2), N(4)−O(8) 2.607(2), N(2)−Cu−N(1) 84.72(9), N(2)−Cu−N(3) 92.22(10), N(3)−Cu−O(1) 92.81(9), O(1)−Cu−N(1) 90.09(9). Torsions angle (deg) C(14)−C(15)−C(16)−N(3) 1.3(3). Dihedral angle (deg) O(1)−Cu−N(1)/N(2)−Cu−N(3) 4.3(2).

The structure of H-**2**(Cu) displays a copper chelate part with an additional chelate arm attached, which are arranged approximately perpendicular to each other (88.5°). The copper is coordinated in a nearly square planar fashion (dihedral angle: 4.3(3)°). Due to the steric hindrance on N3 the Cu−N3 distance

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(1) For example: (a) Molenveld, P.; J. F. J. Engbersen, J. F. J.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 6726. (b) Chaudhuri, P.; Winter, M.; Vendova, B. P. D.; Bill, E.; Trautwein, A.; Gehring, S.; Fleischhauer, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 2148. van Albada, G. A.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Eur. J. Inorg. Chem.* **1998**, 547.

(2) (a) Karlin, K. D.; Tyeklar, Z. In *Advances in Inorganic Biochemistry* (*Vol. 9: Models in Inorganic Chemistry*); Eichhorn, G. L., Marzilli, L. G., Eds.; PTR Prentice Hall Inc.: Englewood Cliffs, NJ, 1994. (b) Sträter, N.; Lipscomb, W. N.; Klabunde, T.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *35*, 2024.

(3) *Catalysis by Metal Complexes* (*Vol. 13: Catalytic Activation of Dioxygen by Metal Complexes*); Simandi, L. I., Ed.; Kluwer Academic Publishers: Dordrecht, Boston, London, 1992.

(4) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, 1993.

(5) (a) Jäger, E.-G.; Seidel, D.; Schade, W. *Z. Chem.* **1983**, *23*, 31. (b) Jäger, E.-G.; Seidel, D. *Z. Chem.* **1983**, *23*, 261. (c) Jäger, E.-G.; Seidel, D.; Schade, W. *Z. Chem.* **1983**, *23*, 31.

(6) Seidel, Dietrich. Ph.D. Thesis, Friedrich-Schiller-Universität Jena, 1986.

(7) Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-410488 (H-**2**(Cu), CSD-410489 (Cu[**2**(Cu)]$_2$), and CSD-410490 (**3**(Cu,Cu)), the names of the authors, and the journal citation.

10.1021/ic990374x CCC: $19.00

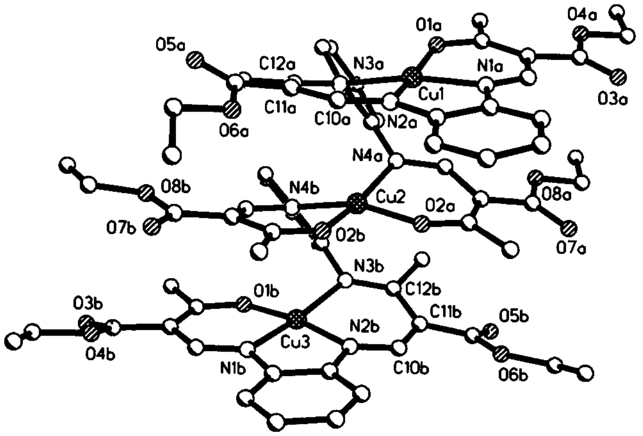


Figure 2. Plot of the structure for Cu[2(Cu)]$_2$ with atom-labeling scheme. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): Cu(1)−N(1a) 1.933(5), Cu(1)−N(2a) 1.905(5), Cu(1)−N(3a) 1.973(5), Cu(1)−O(1a) 1.913(5), Cu(2)−N(4a) 1.953(6), Cu(2)−N(4b) 1.954(4), Cu(2)−O(2a) 1.928(5), Cu(2)−O(2b) 1.914(5), Cu(2)−N(3b) 3.117(5), Cu(3)−N(1b) 1.935(5), Cu(3)−N(2b) 1.918(5), Cu(3)−N(3b) 1.973(5), Cu(3)−O(1b) 1.923(5), Cu(1)−Cu(2) 3.558(5), Cu(2)−Cu(3) 3.631(5), N(2a)−Cu(1)−N(1a) 85.4(2), N(2a)−Cu(1)−N(3a) 92.6(2), N(3a)−Cu(1)−O(1a) 92.7(2), O(1a)−Cu(1)−N(1a) 90.8(2), N(4a)−Cu(2)−O(2a) 90.2(2), O(2b)−Cu(2)−N(4b) 90.6(2), O(2a)−Cu(2)−O(2b) 83.5(2), N(4b)−Cu(2)−N(4a) 100.2(2), N(2b)−Cu(3)−N(1b) 85.7(2), N(2b)−Cu(3)−N(3b) 92.0(2), N(1b)−Cu(3)−O(1b) 91.1(2), O(1b)−Cu(3)−N(3b) 92.8(2). Torsion angles (deg): C(10a)−C(11a)−C(12a)−N(3a) −8.0(2), C(10b)−C(11b)−C(12b)−N(3b) −8.7(2). Dihedral angles (deg): O(1a)−Cu(1)−N(1a)/N(2a)−Cu(1)−N(3a) 13.1(2), N(4a)-Cu(2)−O(2a)/N(4b)−Cu(2)−O(2b) 22.5(2), O(1b)−Cu(3)−N(1b)/N(2b)−Cu(3)−N(3b) 13.1(2).

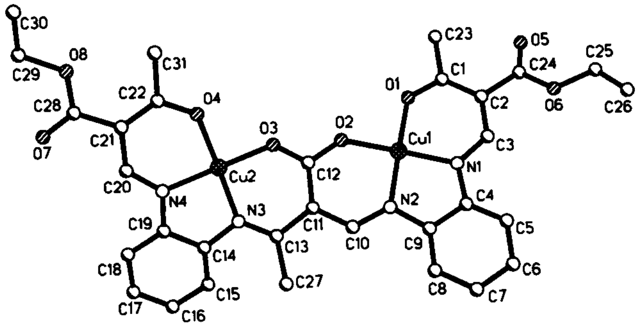
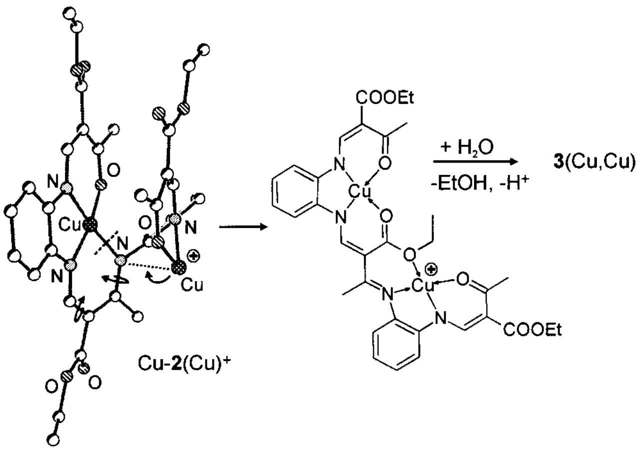


Figure 3. Plot of the structure for **3**(Cu,Cu) with atom-labeling scheme. H atoms are omitted for clarity. Selected distances (Å) and angles [deg]: Cu(1)−O(1) 1.933(5), Cu(1)−O(2) 1.905(5), Cu(1)−N(1) 1.973(5), Cu(1)−N(2) 1.913(5), Cu(2)−N(3) 1.973(5), Cu(2)−N(4) 1.923(5), Cu(2)−O(4) 1.918(5), Cu(2)−O(3) 1.935(5), C1(2)−O(2) 1.294(9), C(12)−O(3) 1.247(9), Cu(1)−Cu(2) 5.730(5), O(1)−Cu(1)−N(1) 85.4(2), N(1)−Cu(1)−N(2) 92.6(2), N(2)−Cu(1)−O(2) 92.7(2), O(2)−Cu(1)−O(1) 90.8(2), O(3)−Cu(2)−N(3) 85.7(2), N(3)−Cu(2)−N(4) 92.0(2), N(4)−Cu(2)−O(4) 91.1(2), O(4)−Cu(2)−O(3) 92.8(2). Dihedral angle (deg): O(1)−Cu(1)−N(1)/N(2)−Cu(1)−O(2a) 7.1(2), O(3)−Cu(2)−N(3)/N(4)−Cu(2)−O(4) 8.0(2).

is significantly stretched. A fifth bond to the carbonyl oxygen of the chelate arm of a neighboring molecule (2.825(4) Å) pulls the copper slightly out of the chelate plane (0.05 Å). The magnetic behavior observed for H-**2**(Cu) is typical for a $S = {}^1/_2$ system ($\mu_{\mathrm{eff}} = 1.80\ \mu_{\mathrm{B}}$, $1/\chi_{\mathrm{Mol}}$ vs T is linear down to 2 K with $C = 0.411$ K cm^3 mol^{-1} and $\Theta = -1.704$ K).

The trinuclear Cu[**2**(Cu)]$_2$ is the bis-precursor copper complex.[7] It is characterized by a nearly symmetric and planar arrangement of the three chelate units with Cu−Cu distances of 3.558(5) and 3.631(5) Å. The central copper atom is coordinated by the free chelate arms of two precursors H-**2**(Cu) in a highly distorted tetrahedral coordination (dihedral angle: 22.5(2)°). Upon complex formation, the precursor geometry undergoes a significant distortion: (i) The terminal copper atoms have a more distorted square planar geometry (dihedral angles: −8.0(2)° and −8.7(2)°). (ii) The chelate arms are strongly deformed in comparison to the free precursor. The magnetic susceptibility measurements for Cu[**2**(Cu)]$_2$ show a magnetic moment per trimer of 2.93 μ_{B} at 295 K, which decreases to 1.86 μ_{B} at 5 K. This indicates an antiferromagnetic coupling between the copper(II) ions within the trinuclear unit, resulting in a $S = {}^1/_2$ ground state below 5 K. The fit on the Hamiltonian $\mathbf{H} = -J\,[(\mathbf{S}_{\mathrm{A1}}\cdot\mathbf{S}_{\mathrm{B}}) + (\mathbf{S}_{\mathrm{A2}}\cdot\mathbf{S}_{\mathrm{B}})] - J'(\mathbf{S}_{\mathrm{A1}}\cdot\mathbf{S}_{\mathrm{A2}})$ leads to $J = -20$ cm^{-1} assuming that $J' = 0$.

Scheme 1



The dinuclear copper complex **3**(Cu,Cu) is an approximately planar chelate complex of an $[\mathrm{N_4O_4}]^{4-}$ octadentate ligand. The copper atoms are bridged by a carboxylate and a diaminotrimethyne unit with a Cu−Cu distance of 5.730(5) Å. The copper atoms are each $[\mathrm{N_2O_2}]^{2-}$ coordinated and display a nearly square planar geometry (dihedral angles: 7.1(2) and 8.0(2)°). The copper units are twisted by 37° caused by steric interactions of the peripheral methyl group on C(13). This distortion results in the chirality of the molecule. The exclusive crystallization of one isomer is reflected in the chiral space group $Pna2_1$ (Flack parameter: 0.05(3)). The magnetic behavior observed for **3**(Cu,Cu) is typical for a symmetrical copper(II) dimer with an antiferromagnetic coupling, resulting in a $S = 0$ ground state below 20 K. The fit on the Hamiltonian $\mathbf{H} = -J\,(\mathbf{S}_{\mathrm{A}}\cdot\mathbf{S}_{\mathrm{B}})$ shows that $J = 120$ cm^{-1}.

The structure of Cu[**2**(Cu)]$_2$ gives some clues for the driving forces of the formation of the dinuclear complex **3**(Cu,Cu). The copper atoms in the precursor and **3**(Cu,Cu) and the terminal copper atoms of Cu[**2**(Cu)]$_2$ form a square planar coordination geometry, which is the most preferred geometry in such chelate complexes.[8a] In contrast to this, the central copper atom of the trinuclear complex is distorted tetrahedrally coordinated. The distance Cu2−N3a (3.12 Å) is comparatively short. This suggests that the formation of the more stabilized dinuclear complex could have occurred by additional coordination of the N3 from the coordination sphere of the terminal copper atom to the central copper atom, followed by the bond breakage between this nitrogen and the terminal copper atom, two conformational changes on double bonds, and an ester hydrolysis (cf. Scheme 1).

Although copper(II) is generally known to be a good catalyst for hydrolysis reactions on its own ligands[8b] and in phosphatase

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(8) Martell, A. E.; Calvin, M. *Chemistry of the Metal Chelate Compounds*; Prentice Hall, Inc.: New York, 1952; (a) pp 253−257, (b) pp 355−362.

analogous systems,[1a,9] such a finding is nevertheless remarkable, because related complexes containing peripheral ester groups, e.g., open-chain Schiff base complexes and tetraazaannulene derivatives, are characterized by an extreme stability against bases as well as acids.[10] Although the complexes **1**(Cu) and H-**2**(Cu) are sensitive to hydrolysis, they are hydrolyzed exclusively on the imine bond and not on the ester group.

In summary, we have shown that the dinuclear copper complex **3**(Cu,Cu) can be synthesized directly via the precursor H-**2**(Cu) with Cu(ac)$_2$ or alternatively via the trinuclear complex Cu[2(Cu)]$_2$. The formation of **3**(Cu,Cu) is a copper-mediated rearrangement and ester hydrolysis. We are currently completing a full magnetic study of these complexes as well as an investigation of the mechanism of the copper-mediated reaction. We are also interested in ligand systems with different substitution patterns and the possibility of forming analogous heteronuclear complexes.

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Supporting Information Available: Listings of syntheses, crystal data, and information about structure solution and refinement and data and plots of magnetic susceptibility measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Kövári, E.; Krämer, R. *J. Am. Chem. Soc.* **1996**, *118*, 12704. Hegg, E. L.; Mortimore, S. H.; Cheung, C. L.; Huyett, J. E.; Powell, D. R.; Burstyn, J. N. *Inorg. Chem.* **1999**, *38*, 2961.

(10) Cf. synthesis methods of macrocyclic ligands: (a) Jäger, E.-G.; Keutel, H.; Rudolph, M.; Krebs, B.; Wiesemann, F. *Chem. Ber.* **1995**, *128*, 503. (b) Müller, K.; Jäger, E.-G. *Z. Anorg. Allg. Chem.* **1989**, *577*, 195. (c) Jäger, E.-G. *Z. Chem.* **1968**, *8*, 30.