A Unique Copper-Controlled Template Synthesis of Tetradentate N4-Donor Ligands and Their Propeller-Type Linear Trinuclear Cu^{II} Complexes

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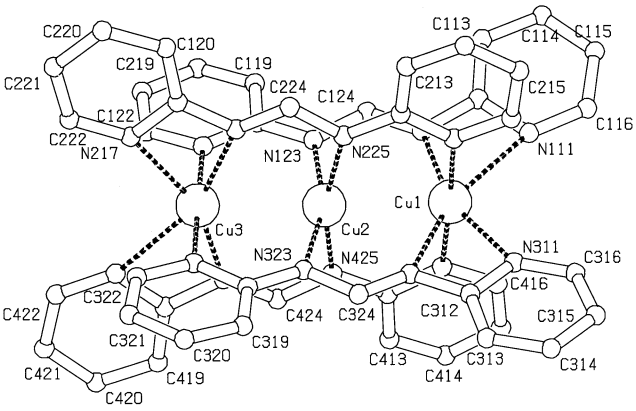
In situ reaction of Cu^{II} triflate with aminopyridine or aminopyrimidine and triethylorthoformate in ethanol results in unique linear trinuclear Cu^{II} complexes with the general formula $[Cu_3(L^-)_4](CF_3SO_3)_2(EtOH)_x$ (L = dehydronated ligand *N,N′*-bis(pyridine-2-yl)formamidine or the new ligand *N,N′*-bis(pyrimidine-2-yl)formamidine). The structure [Cu−Cu−Cu angle 175.19(2)°] consists of four nearly flat molecules of the ligand which contribute to the propeller-type structure around the Cu−Cu−Cu axis. A strong antiferromagnetic interaction between the Cu^{II} ions is observed, resulting in an $S = 1/2$ ground state below 100 K.

Dinuclear and polynuclear exchange-coupled copper(II) complexes are well known, but the number of magnetically as well as structurally investigated trinuclear compounds is quite limited[1]. Also the theory for dinuclear and polynuclear systems is found adequate to describe the exchange parameter of magnetism[1][2], but linear trinuclear compounds are far less discussed. Dinuclear systems are also well documented because their relevance for bioinorganic model systems in copper enzymes[3].

Linear trinuclear Cu^{II} compounds are relatively rare and only few are studied magnetically[4]. A few are known with a CuN_{4-6} chromophore around each Cu^{II} ion[5]. We now wish to report a novel method for in situ synthesis of such trinuclear compounds, which have quite unusual propeller-type structure and a strong magnetic exchange coupling. Compounds $[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}$ (**1**), in which pdf is the dehydronated ligand *N,N′*-bis(pyridine-2-yl)formamidine, and $[Cu_3(pmf)_4](CF_3SO_3)_2(EtOH)_{0.5}$ (**2**), in which pmf is the dehydronated ligand *N,N′*-bis(pyrimidine-2-yl)-formamidine, were synthesized and characterised.

Structural analysis of **1** shows a linear arrangement of 3 Cu^{II} ions surrounded by 4 ligand molecules in a propeller mode, each of which being tetracoordinating to the 3 copper atoms (Figure 1). The central copper atom is distorted square-planar [angles of 163.46(11), 161.11(11)°] and normal Cu−N distances of ca. 2.0 Å. The outer copper ions are six coordinated with distorted square-based geometry, and a slightly different geometry for each copper. The angles of the basal plane of Cu1 (formed by N211−N311−N411−N125) are 176.84(11) and 158.53(11)° and of Cu3 (formed by N117−N217−N317−N423) are 178.50(11) and 156.83(11)°. The short Cu−N distances for Cu(1) and Cu(3) vary from 1.989(3) to 2.191(3) Å. The axial sites of the geometry are occupied by other nitrogens with Cu−N distances that vary from 2.267(4) to 2.543(3) Å. The axial angles slightly differ from linear [N325−Cu1−N111 = 160.81(11)° and N417−Cu3−N223 = 158.18(11)°], as a result of contraints caused by the ligandshape.

Figure 1. Plot of structure **1** with atom-labelling scheme. H- atoms and non-coordinating triflate anions and the ethanol molecules are omitted for clarity[a]



[a] Selected distances [Å] and angles [°]: Cu(1)−Cu(2) 2.6618(8), Cu(2)−Cu(3) 2.6676(8), Cu(1)−N(411) 1.989(3), Cu(1)−N(211) 1.992(3), Cu(1)−N(125) 2.033(3), Cu(1)−N(311) 2.168(3), Cu(1)−N(325) 2.272(3), Cu(1)−N(111) 2.543(3), Cu(2)−N(425) 1.997(3), Cu(2)−N(225) 2.026(3), Cu(2)−N(123) 2.036(3), Cu(2)−N(323) 2.050(3), Cu(3)−N(317) 2.001(3), Cu(3)−N(117) 2.011(3), Cu(3)−N(423) 2.032(3), Cu(3)−N(223) 2.191(3), Cu(3)−N(217) 2.267(4), Cu(3)−N(417) 2.500(3), N(411)−Cu(1)−N(211) 176.84(11), N(125)−Cu(1)−N(311) 158.53(11), N(111)−Cu(1)−N(325) 160.81(11), N(425)−Cu(2)−N(225) 163.46(11), N(123)−Cu(2)−N(323) 161.11(11), Cu(1)−Cu(2)−Cu(3) 175.19(2), N(317)−Cu(3)−N(117) 178.50(11), N(423)−Cu(3)−N(217) 156.83(11), N(223)−Cu(3)−N(417) 158.18(11).

The Cu−Cu distances of 2.6618(8) and 2.6676(8) Å, are only slightly longer than in the two other comparable

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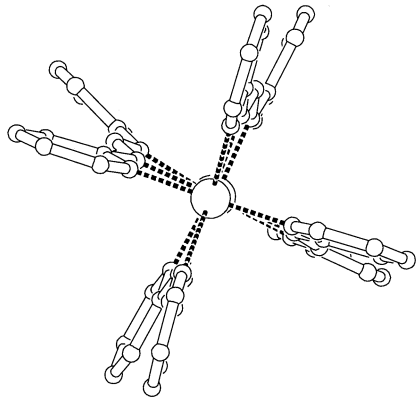
CuN_x-bridged linear copper(II) compounds[5a][5c], but shorter than in the azido-bridged trinuclear compounds[4][5b][5d].

The linear angle Cu1−Cu2−Cu3 is 175.19(2)°. Viewing along the Cu−Cu−Cu axis (Figure 2) a propeller type arrangement is visible in which the ligands are almost perpendicular to the axis with angles between the two rings of each ligand which vary from 27.73 to only 8.19°. Hydrogen bonds between the oxygens of the lattice ethanol and the triflate molecules (O···O 2.82 and 3.02 Å) stabilize the lattice.

Figure 2. View along the Cu−Cu−Cu axis of structure (**1**)



The ligand field spectrum of both compounds show a broad band with a double maximum at 16.3 and $20.8 \cdot 10^3$ cm^{-1} for **1** and at 16.9 and $20.9 \cdot 10^3$ cm^{-1} for **2**. These two absorptions are both d-d transitions[6a][6b], and it is tempting to assume that the highest energy is from the central Cu atom, although Cu2 is not perfectly square planar, and the lowest energy from the outer six-coordinated Cu atoms[5c][6c].

The EPR spectra at room temperature shows a broad absorption centered around g = 2.11 and a weaker broad absorption at ca. g = 3.6, which disappear upon cooling to 77 K. The EPR signal sharpens upon cooling and a very weak $g_{//}$ at ca. 2.3 is observed (no $A_{//}$ resolved). No structural conclusions can be drawn from these spectra. Preliminary temperature dependent magnetic susceptibility measurements down to 5 K, shows a magnetic moment of ca. 1.50 B.M. per copper(II) ion at 270 K, which decreases to ca. 1.0 B.M. at 20 K, which indicates an antiferromagnetic coupling between the copper(II) ions within the trinuclear units[6d][5c]. In the area 70−5 K $1/\chi$ vs. T is linear with $\Theta = 0$ and agrees with $\mu = 1.05$ (or 1.8 B.M./Cu_3) which agrees with a ground state only one unpaired electron per 3 Cu^{II}. A preliminary fit on the hamiltonian $H = -2J[(\mathbf{S}_A \cdot \mathbf{S}_B) + (\mathbf{S}_B \cdot \mathbf{S}_C)]$ shows that $J = -100$ cm^{-1} and assumes $J' = 0$.

Further work will deal with related ligands yielding this structure and with a full magnetic study. In summary, we have shown that copper ions can control the template synthesis of tetradentate formamidine ligands, simultanously resulting in linear trinuclear Cu^{II} complexes.

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Experimental Section

General: Ligand field spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. − X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer, using DPPH (g = 2.0036) as a standard. − Magnetic susceptibilities were measured in the temperature range 5−300 K with a Manics DSM-8 susceptometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants[8].

Synthesis: 2-Aminopyridine and 2-aminopyrimidine are obtained from Acros Organics; metal salts and solvents were commercially available and used without further purification. 1.2 mmol of $Cu(CF_3SO_3)_2$ and 1.2 mmol of 2-aminopyridine or 2-aminopyrimidine were each dissolved in ca. 10 ml of ethanol. To each solution ca. 5 ml of triethylorthoformate was added. The copper solution was added carefully to the amino compound solution and filtered to remove any un-dissolved material. After a few days black crystalline material was obtained, filtered, and air-dried.

Compound **1** $\{[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}\}$ can also be synthesized directly from the copper(II)triflate salt and the ligand Hpdf (which was synthesized in the literature[7]) in ethanol plus triethylorthoformate to remove the water from the ethanol. Satisfactory elemental analysis were obtained.

X-ray Crystal Structure Analysis: Crystal data for $[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}$: $C_{49}H_{45}Cu_3F_6N_{16}O_{7.5}S_2$, M = 1346.75, monoclinic, space group $P2_1/c$ (no. 14), a = 12.974(3), b = 17.769(4), c = 24.227(5) Å, β = 92.73(3)°, V = 5579(2) $Å^3$, Z = 4, D_c = 1.603 g cm^{-3}, T = 193 K, μ(Mo-K_α) = 1.295 mm^{-1}, $F(000)$ = 2736, 11365 reflections measured, 10881 independent, R_{int} = 0.0317, (2.52 < θ < 26.54°), a black crystal with dimensions of 0.30 × 0.30 × 0.25 mm was selected, mounted to the glass fiber using the oil drop method[9a]. Rigaku AFC-7S diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), ω-2θ scans. Data reduction using the TEXSAN[9b] package. The intensity data were corrected for Lorentz and polarization effects and for absorption and extinction. All non H atoms were refined anisotropically. H atoms were situated from difference Fourier map and refined isotropically. The structure was solved using direct methods SHELXS-86[9c]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0970 P)^2 + 09.6067 P]$, where $P = (F_o^2 + 2 F_c^2)/3$ was adopted. Refinement method full-matrix least-squares on F^2 using SHELXL-93[9d] package converged to $R1$ [$I > 2\sigma(I)$] = 0.0475, $wR2$ = 0.1478 (all data) for 751 parameters, S = 0.892, largest difference peak and hole 1.080 and −0.437 e·$Å^{-3}$.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101041. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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