An Unprecedented, Copper-Mediated, In-Situ Multi-Step Ligand Formation – Synthesis, Structure, and Magnetism of Bis(μ-methoxo)bis[nitrato(2-methoxymethylamino-3-methylpyridine)copper(II)]☆

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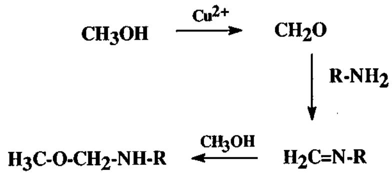
A novel chelating ligand, synthesized in situ within the coordination sphere of Cu^{II} from 2-amino-3-methylpyridine, MeOH, and dioxygen from the air, is found to form a strongly coupled, dinuclear methoxo-bridged Cu^{II} compound with the formula $[Cu(L)(CH_3O)(NO_3)]_2$ (L = 2-methoxymethylamino-3-methylpyridine). The geometry around the copper atom is square pyramidal and the Cu–Cu distance within the dinuclear unit is 3.011(2) Å with an Cu–O–Cu angle of 103.13(8)°. Synthesis, X-ray crystal structure, and magnetism are reported.

In situ ligand formations in the presence of metal ions are not uncommon[1][2][3], and several cases are known of such reactions, like Schiff-base couplings and the formation of phthalocyanins[1][2][3]. The metal ion in these cases acts as a template, to facilitate the ring closure or the addition. Cases where a multi-step ligand reaction occurs are relatively rare. Our recent studies towards the formation of formamidines[4] have prompted us to further investigations of such reactions with aminopyridine ligands. We now wish to report a most unusual case of a three-step reaction (see Scheme 1) in which 2-amino-3-methylpyridine first forms a Schiff base with formaldehyde – in situ formed gradually by MeOH oxidation – which subsequently reacts with Cu-coordinated methanol to a 2-methoxymethylamino-3-methylpyridine chelating ligand. Copper(II) is known to be a catalyst for the air oxidation of methanol to formaldehyde[5]. The Schiff-base reaction is followed by the third step in which a methanol molecule inserts into the imine double bond[6a], resulting in the dinuclear compound: $[Cu(L)(CH_3O)(NO_3)]_2$ (in which L = 2-methoxymethylamino-3-methylpyridine). The first oxidation must originate from dioxygen from the air, as the reaction does not occur under argon. In fact deliberate addition of CH_2O accellerates the reaction. Under argon only a methoxo-bridged dinuclear Cu^{II} compound with the starting ligand, 2-amino-3-methyl-pyridine, is formed (see Experimental Section).

Structural analysis of the title compound reveals a dinuclear methoxo-bridged dinuclear unit with a centre of symmetry located between two copper ions (see Figure 1). The Cu atom has a square-pyramidal geometry with a basal plane formed by a nitrogen atom of the ligand, two oxygen atoms of the bridging methoxo molecules and an oxygen atom of the coordinating nitrate anion. The Cu–N distance and the Cu–O distances are in the normal range of ca. 2.00 Å[7]. The angles of the basal plane are almost linear [O1a–Cu1–O11 168.71(6), O1–Cu1–N11 170.61(7)°]. The apical site is occupied by the ether oxygen atom (O20) of the ligand with a distance of 2.318(2) Å and with the angle O20–Cu1–N11 of 93.09(9)°. The most striking feature of the structure is the presence of the newly synthesized ligand 2-methoxymethylamino-3-methylpyridine. Synthesis of methoxomethylamino compounds is known[6], however, in some cases they are unstable[6c]. In fact the present ligand might quite well be stabilized by the Cu chelation.

Scheme 1. Proposed reaction scheme (R = 3-methylpyridin-2-yl)



The Cu–Cu distance within the dinuclear unit is 3.011(2) Å with an Cu–O–Cu angle of 103.13(8)°. These distances and angles can be compared with some methoxo-bridged Cu^{II} dinuclear compounds which have also distances of ca. 3.0 Å and an angle of about 103°[8]. The lattice structure is stabilized by stacking between the pyridine rings of different units (ring–ring distance of 3.613 Å) and by a relatively strong hydrogen-bonding of an amino-nitrogen atom and an oxygen atom of the nitrate anion [N17···O13 = 2.939(9) Å].

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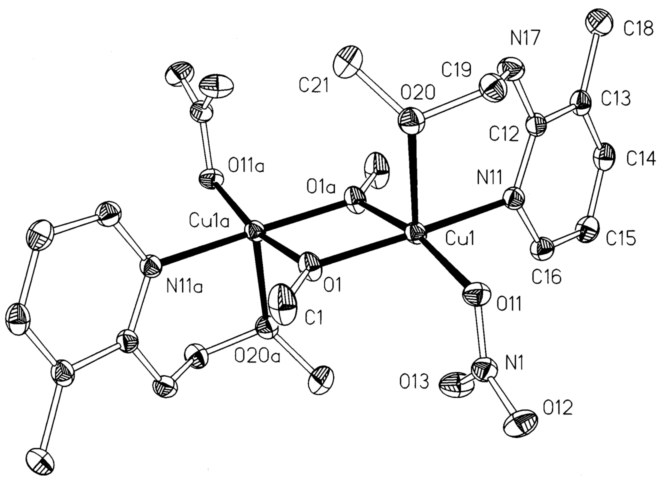
Figure 1. Plot of the structure with atom-labelling scheme; H atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: Cu1−O1 1.917(2), Cu1−O1a 1.9270(17), Cu1−N11 1.998(2), Cu1−O11 2.0267(18), Cu1−O20 2.318(2), Cu1−Cu1a 3.011(2); O1−Cu1−O1a 76.87(8), O1−Cu1−N11 170.61(7), O1a−Cu1−N11 94.22(8), O1−Cu1−O11 96.50(8), O1a−Cu1−O11 168.71(6), N11−Cu1−O11 91.81(8), O1−Cu1−O20 91.85(9), O1a−Cu1−O20 103.27(9), N11−Cu1−O20 93.09(9), O11−Cu1−O20 85.91(8), Cu1−O1−Cu1a 103.13(8) ($a = -x, -y, -z$).

The ligand-field spectrum reveals a broad band with a centre around $14.6{\cdot}10^3$ cm^{-1}, which is common for a square pyramidal geometry[9]. A typical infrared vibration is found at 3349 cm^{-1} as a strong sharp peak, attributed to the N−H vibration. The anion vibrations of the nitrate are found at 1453 and 1299 cm^{-1} (a splitting of 154 cm^{-1}) which is in the range for didentate coordinating nitrate[10]. In the present case one of the oxygen atoms of the nitrate anion has a strong bonding to the Cu^{II} ion and the second oxygen atom (O13) is involved in a strong intermolecular hydrogen bonding (see above).

The powder EPR spectrum at 77 K only shows a very weak signal with a $g_{\perp}$ of 2.06, a resolved $g_{\parallel}$ of 2.32, with $A_{\parallel}$ of 14.2 mT, typical for a $CuNO_3(O)$ chromophore[9]. Given the dinuclear nature, this weak signal must originate from a mononuclear impurity. Even a nitrogen superhyperfine structure is observed with 3 lines, which also agrees with one nitrogen donor atom per Cu. In frozen solution (DMF) at 77 K a similar spectrum is obtained, indicative of monomerisation in solution. Low-temperature solid-state powder magnetic susceptibility recorded in the region 250−5 K, shows an almost diamagnetic species below 200 K. A preliminary fit with $g = 2.10$ results in a $-2J$ value over 500 cm^{-1}.

Summarizing, it is concluded that an MeOH oxidation reaction occurs initiated by the Cu^{II} ion. However, other factors, like the strength of the anion, must contribute as well, since weaker coordinating anions like perchlorate and triflate under identical conditions, do not yield such a reaction product.

Further work will deal with related ligands yielding this structure and with oxidation reaction studies to obtain more information about the reaction process.

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Experimental Section

General: Ligand-field spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained with 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[11].

Synthesis: 2-Amino-3-methylpyridine was obtained from Acros Organics; 0.6 mmol of $Cu(NO_3)_2 \cdot 3\,H_2O$ and 1.2 mmol of 2-amino-3-methylpyridine were each dissolved in ca. 10 ml of methanol. The copper solution was added carefully to the ligand solution and filtered to remove any undissolved material. The blue solution was kept at room temp., and after a few days blue crystalline material was obtained from the solution which turned green. The product was filtered and air-dried. Adding a little sodium hydroxide or heating the solution yields the same blue compound. Yield ca. 80%. − $C_{18}H_{30}Cu_2N_6O_{10}$ (617.56): calcd. C 35.01, H 4.90, Cu 20.50, N 13.61; found 35.07 C, 5.12 H, 20.12 Cu, 13.85 N.

Using a higher L/M ratio (L/M = 4:1 or 6:1) a violet methoxo-bridged dinuclear Cu^{II} compound with the formula $[Cu_2(\text{2-amino-3-methylpyridine})_4(CH_3O)_2](NO_3)_2$ was obtained. This structure is confirmed by elemental and X-ray crystal structure analysis[13]. The same compound is derived when the present reaction (L/M ratio 2:1) is carried out under argon.

X-ray Crystal Structure Analysis: Crystal data for $[Cu(C_8H_{12}N_2O)(CH_3O)(NO_3)]_2$: $C_{18}H_{30}Cu_2N_6O_{10}$, $M = 617.56$, triclinic, space group $P\bar{1}$ (no.2), $a = 8.336(5)$, $b = 8.734(5)$, $c = 10.357(5)$ Å, $\alpha = 109.24(5)$, $\beta = 91.99(5)$, $\gamma = 113.13(4)°$, $V = 642.9(6)$ Å^3, $Z = 1$, $D_c = 1.595$ g cm^{-3}, $T = 193$ K, $\mu(\text{Mo-}K_{\alpha}) = 1.715$ mm^{-1}, $F(000) = 318$, $R1 = 0.0299$, $wR2 = 0.0804$ with $I > 2\sigma(I)$, $S = 1.084$, 3982 data collected, 2627 data used, 163 parameters. A blue crystal with dimensions of 0.48 × 0.45 × 0.27 mm was selected, mounted to the glass fiber using the oil-drop method[12a]. Rigaku AFC-7S diffractometer, graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å), ω-2θ scans. Data reduction using the TEXSAN[12b] 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)[12c]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0457{\cdot}P)^2 + 0.3867{\cdot}P]$, where $P = (F_o^2 + 2{\cdot}F_c^2)/3$ was adopted. Full-matrix least-squares refinement method on F^2 was applied, using the SHELXL-93[12d] package.

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-102597. 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].

☆ Dedicated to Professor *Bernt Krebs* on the occasion of his 60th birthday.

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