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CO_2 fixation by dicopper(II) complexes in hypodentate framework of N_8O_2†

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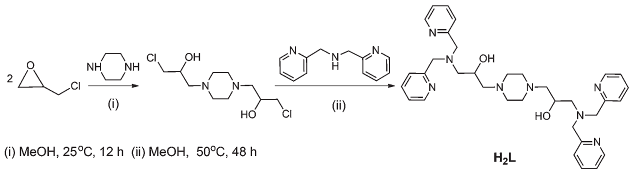
A new ligand with N_8O_2 donors containing three potential metal-binding sites (H_2L) and its tricopper(II) complex 1 are synthesized. The tricopper species is found to be formed from a hypodentate dicopper(II) complex 2 in basic solutions. Complex 2 may be isolated from the reaction of H_2L with a copper source under acidic conditions. Complex 2 can undergo CO_2-abstraction to yield an octacopper(II) complex 3. The single crystal structures of complexes 2 and 3 are characterized by X-ray crystallography.

Polydentate ligands containing multi-metal coordination sites are interesting research targets either in metalloproteins or for designing novel structure–reactivity relationships. Investigation into *p*-MMO metalloenzymes has disclosed a tricopper(II) complex with a rarely known triangular subunit in a cyclic skeleton of $(CuO)_3$.[1] The constitution of the ligand in this tricopper(II) complex is composed of three tetradentate components of N_2O_2 donors with the assistance of two alkoxides and one oxide ion. All three copper centers are in a square planar configuration, although two kinds of coordination sites are involved.[1]

Although trinuclear copper(II) complexes with multidentate ligands in other configurations have been previously reported, the detailed coordination chemistry of such triangular tricopper(II) species remain elusive.[2,3] In order to understand the fundamental properties of coordination in such compounds, we introduced bipyridinyl amine which provides a tridentate coordinating mode and is supposed to offer better coordinating power into the ligand.[4]

In addition, CO_2 fixation has recently been becoming a more important topic in coordination chemistry.[5] Using copper complexes, particularly with a Cu(II)–O(H)–Cu(II) component, for such a purpose has been reported.[6] Herein, we report a new polydentate ligand with N_8O_2 donors that exhibits a hypodentate dinuclear complex without a hydroxide-bridging moiety, and can show reactivity towards CO_2 fixation.



Scheme 1 Synthesis of the N_8O_2 polydentate ligand.

The synthesis of $[(2\text{-}Py_2CH_2)_2NCH_2CH(OH)CH_2]_2(c\text{-}C_4H_8N_2)$ (**H_2L**) was succeeded first by the reaction of piperazine with epichlorohydrin in double molar amounts to form the alcohol derivative, and was then followed by the reactions with bis((pyridine-2-yl)methyl)amine to yield the desired product in 33% yields (Scheme 1).[2]

The reaction of **H_2L** and three molar amounts of hexaaquocopper(II) perchlorate in acetonitrile with the addition of four molar amounts of triethylamine readily results in the formation of a deep green complex **1**. The electronic spectra show λ_{max} appearing at 697 nm (ε, 196 M^{-1} cm^{-1}) and a shoulder at *ca.* 860 nm (ε, ~180 M^{-1} cm^{-1}). Such spectral data imply that complex **1** may consist of copper(II) centers in both square planar and five-coordinate trigonal bipyramidal configurations.[7]

The measurement of the molar conductivity for **1** in acetonitrile (5×10^{-4} M) at 25 °C was 353 Ω^{-1} cm^2 mol^{-1}, supporting that the complex salt is a trivalent perchlorate.[8] A peak at 998.0325 *m/z* found by HR-ESI-MS matches with a tricopper cation in the form of $[LCu_3(OH)(ClO_4)_2]^+$, in which a hydroxide presumably bridges two copper ions. In the infrared spectra, the uncoordinated perchlorate anions were evidenced at 1088 and 624 cm^{-1}.

The half-wave potential ($E_{1/2}$) of complex **1** was measured by cyclic voltammetry in deoxygenated acetonitrile at 25 °C. Two cathodic waves at −0.58 V and −0.80 V correspond to the

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† Electronic supplementary information (ESI) available: The characterization and synthetic procedure of the new compounds; UV, CV and EPR spectral data; crystallographic data of **2** and **3** in CIF format; magnetic properties of **1** and **3**; ESI titration spectrum of the ligand mixing with copper. CCDC 976265–976266. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53497a

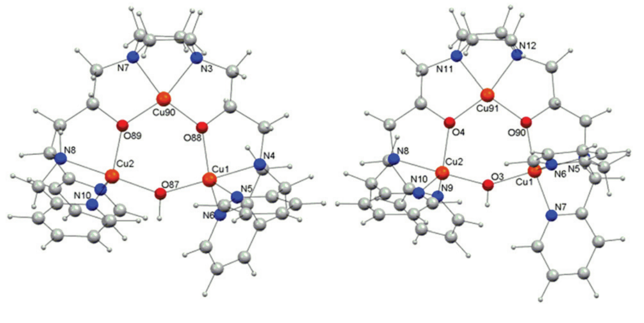
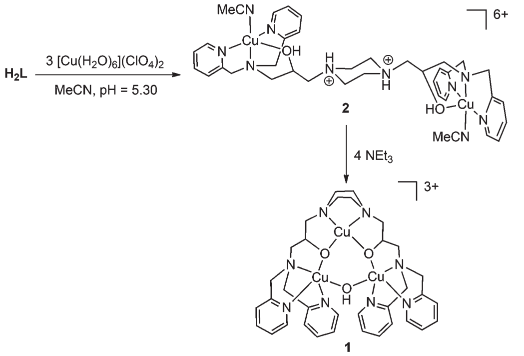


Fig. 1 Optimized DFT structures for complex **1** (*R*,*S*-, left; *R*,*R*-, right).



Scheme 2 Synthesis of the N_8O_2 hypodentate dicopper(II) complex and tricopper(II) complex.

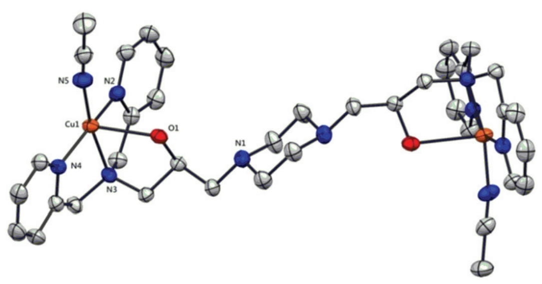


Fig. 2 ORTEP plot and selected atom-labeling scheme of the cationic part of **2** at 150 K, shown with 50% probability displacement ellipsoids. H-atoms and counteranions have been omitted for clarity.

reduction of three Cu(II) atoms.[9] The smaller reversible signal at −0.80 V may be assigned to the central component with N_2O_2 coordination and the larger irreversible peak at −0.58 V corresponds to the two terminal coordinations with N_3O_2. One quasi-reversible anodic wave at +1.42 V, that may be assigned to the oxidation of two Cu(II) atoms in an N_3O_2 environment, was also observed.

The X-band EPR spectrum for **1** as a powdered sample shows a ground state of $S = 1/2$ at either 298 or 77 K, although without clear hyperfine splitting.[2] An axial pattern with $g_{||} = 2.218 > 2.1 > g_{\perp} = 2.04 > 2.00$ may be explained by a tricopper(II) species with the spin localized on the $d_{x^2-y^2}$ orbital of an unpaired copper(II) ion in square planar or square pyramidal geometry.[10,11] The strong antiferromagnetic coupling in **1** is confirmed by SQUID.

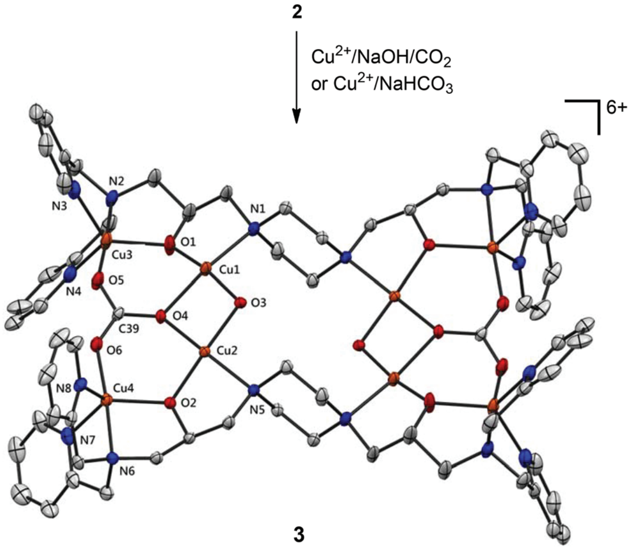
DFT calculations for the structure of **1**, performed with the Gaussian 09 package using B3LYP and the 6-31G* basis set,[12] provide the expected structure, in which three Cu(II) ions in a triangular arrangement are bridged by three oxygen atoms to constitute a $(CuO)_3$ ring subunit which is surrounded by **L** as a decadentate. There is one copper center in a distorted square planar configuration with N_2O_2 coordination, and the other two copper(II) centers, which hold N_3O_2 coordination and share a hydroxide bridge, are in trigonal bipyramidal/distorted trigonal bipyramidal configurations with τ = 0.94 and 0.57, respectively.[13] Two possible diastereomers are considered (Fig. 1). The *R*,*S*-form is only 0.6 kcal per mole more stable than the *R*,*R*-form.[14] The TD-DFT calculated electronic spectrum of **1** with the optimized structure shows similar UV peaks to the experimental data.

An N_8 ligand which comprises the combination of piperazine and bisimidazolyl amine was reported to also show coordination with di- and tri-copper.[4] On comparing this tricopper complex with **1**, the latter may form a distorted hexagonal $(CuO)_3$ ring skeleton with two alkoxides in **L** and one bridging hydroxide, as shown in Fig. 1.

Spectrophotometric titrations for the reaction of $\mathbf{H_2L}$ and $[Cu(H_2O)_6](ClO_4)_2$ in the ratio of 1 : 3 in acetonitrile without the addition of Et_3N show that the solution color becomes dark blue at pH 5.30. A maximum absorption grows at 623 nm (ε, 152 M^{-1} cm^{-1}), which is consistent with a square planar or square pyramidal configuration.[7] The ESI-MS spectrum for the same reaction gives a peak at *m*/*z* 1021 amu, corresponding to a hypodentate dinuclear cation that may fit the formula $[(H_2L)Cu_2(ClO_4)_3]^+$. The formation of **1** was not observed. For synthetic purposes, indeed, in a reaction of $\mathbf{H_2L}$ and $Cu(ClO_4)_2$ in acidic conditions, a dinuclear complex in the form of $[H_4LCu_2](ClO_4)_6$ (**2**) has been successfully isolated. Treating **2** with sufficient NaOH or triethylamine can result in the formation of **1** (Scheme 2).

Single crystals suitable for X-ray crystallographic analysis were obtained from cosolvents of dichloromethane–acetonitrile. The structure of **2** in *C*2/*c* symmetry has an inversion center (Fig. 2). The distance between the copper ions is extended to 12.9 Å.[11] The Addison–Reedijk parameter, τ, is 0.08, which agrees with the UV-Vis data.[15] The Cu–N bonds (2.0–2.1 Å) are of normal lengths.[16] However, the long Cu–O bonds (2.4 Å) are likely from alcohol coordination.[16] The paramagnetic complex **2** has six perchlorate counteranions, suggesting that the two nitrogen atoms of piperazine should be protonated.

The hypodentate dinuclear complex **2** is expected to be active due to its available coordination capacity. It is found that exposing **1** to air under neutral or acidic conditions results in the formation of a new species. In the reaction of **2** and $Cu(ClO_4)_2$ either under atmospheric conditions or in the presence of $NaHCO_3$, a product labeled as **3** is identified



Scheme 3 The formation pathway for **3**.

by HR-ESI-MS with a peak at *m*/*z* 714.3063, which may be assigned as a complex with the formula $[(C_{34}H_{42}N_8O_2)_2Cu_8(OH)_2(CO_3)_2(ClO_4)_4]^{3+}$. In an alternative feasible process, $\mathbf{H_2L}$ and $Cu(ClO_4)_2$ are mixed in acetonitrile in the presence of dry ice. After 10 minutes, the resulting solution may be introduced into H_2O to form the desired light blue product (Scheme 3).

The IR peaks at 1655 and 1399 cm^{-1} confirm the bridged carbonates in **3**.[17,18] Unequivocal evidence for the unprecedented octacopper structure of **3** was acquired by single crystal crystallography. In the structure of $[L_2Cu_8(CO_3)_2(OH)_2]^{6+}$, four Cu(II) centers are in a square planar geometry and the other four are in a trigonal bipyramidal arrangement. Each carbonate ion is in a new $\mu_4(\eta^1, \eta^1, \eta^2$, *syn*, *anti*, *syn*)-mode to link to four copper ions, with the C–O bond lengths being 1.250(6), 1.258(6), and 1.313(6) Å, which explain the infrared double bands at low frequencies.[18]

The SQUID data show that complex **3** is anti-ferromagnetic. Theoretical fitting suggests that four spin–spin coupling constants, J_{12}, J_{24}, J_{34}, and J_{14}, may be evaluated as −88.1, −76.3, 1.1, and 33.0 cm^{-1}, respectively.[19]

A reaction of **1** and $NaHCO_3$ under the same conditions used for the CO_2-fixation of **2** does not produce complex **3**. One may thus conclude that the formation of **3** may result *via* the carbonate-coordination, which facilitates intermolecular coupling of **2** with the assistance of additional coordination of Cu^{2+} ions.

The reactivity for the carbon dioxide capture of **2** indicates that the dinuclear complex in the framework of hypodentate N_8O_2 may also provide the mixed metal species. Indeed, the reaction of **2** with $Zn(H_2O)_6(ClO_4)_2$ in the presence of Et_3N in acetone opens a route to the formation of mixed-metal products.[20] Specifically, $LZnCu_2(OH)(ClO_4)_3$ may be identified by HR-ESI-MS and UV-Vis.[21] Research related to this is currently on going.

Conclusions

In conclusion, a new polydentate ligand with N_8O_2 donors has been successfully synthesized from the condensation of two bispyridyl amines and a piperazine bisalcohol derivative. Such a ligand can bind Cu(II) ions first through the bispyridyl moieties to yield a new hypodentate dinuclear complex in the form of $[H_4LCu_2](ClO_4)_6$. With the assistance of hydroxide, $[H_4LCu_2]^{6+}$ can react with another Cu(II) ion to generate a tricopper complex in which the metal and oxygen atoms form a $(MO)_3$ ring skeleton, which is interesting to metalloenzymes. Exposing $[H_4LCu_2](ClO_4)_6$ to CO_2 results in a new complex in the form of $[L_2Cu_8(CO_3)_2(OH)_2]^{6+}$, which is interesting for CO_2 capture and storage.

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