

Stabilization of Copper(I) in Aqueous Solutions by Ligation with the Saturated Tetra-aza Macrocyclic Ligand 1,4,5,7,7,8,11,12,14,14-Decamethyl-1,4,8,11-tetraazacyclotetradecane

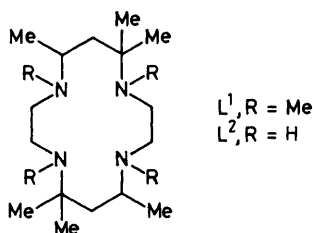
Nusrallah Jubran, Haim Cohen, Yaacov Koresh, and Dan Meyerstein*

Chemistry Departments, Ben-Gurion University of the Negev and Nuclear Research Centre Negev, Beer-Sheva, Israel

The title perchlorate complex is stable in air-saturated aqueous solutions and is reversibly oxidized to the divalent complex at +0.47 V vs. Ag/AgCl.

Amino ligands, including 1,4,8,11-tetra-azacyclotetradecane,¹ are known to catalyse the rate of disproportionation of copper(I) ions. However, stable monovalent copper complexes with tetra-aza macrocyclic ligands are obtainable in oxygen-free aprotic solvents.² In aqueous solutions the results indicated that several tetra-aza macrocyclic complexes of copper(I) decompose *via* loss of the ligand.^{1,3} It seemed of interest to check the redox properties of the copper complex with 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetra-azacyclotetradecane, CuL¹, as it is known that *N*-methylation considerably slows the rate of ligand exchange.⁴ Furthermore this ligand stabilizes nickel(I) in oxygen-free aqueous solutions.⁵

To a stirred solution of CuL²(ClO₄)₂ (10 g) (L² = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) in dimethyl sulphoxide (120 ml) under nitrogen,



ground KOH (20 g) was added. After 15 min MeI (40 ml) was added slowly. The reaction was exothermic, and the slurry was cooled slowly to room temperature. Ethanol (50 ml) was added and the rose precipitate formed was filtered off and washed with ethanol. The precipitate was dissolved in a minimum amount of hot water, the solution filtered, and then NaClO₄ added. The red precipitate formed was recrystallized from hot water. Elemental analyses suggested that the product was surprisingly the copper(I) complex CuL¹ClO₄.

The i.r. spectrum of CuL¹ClO₄ has no absorption band at 3210 cm⁻¹ where the band due to the N-H stretching of CuL²(ClO₄)₂ is observed. Its n.m.r. spectrum [δ 1.66 (s), 1.72 (s), 1.80 (d), 3.12 (s), 3.43 (s), and 3.53 (s)] is in good agreement with the formulation as CuL¹ClO₄ and with the spectrum of NiL¹(ClO₄)₂^{4a} although resonances are shifted slightly to lower field. The observation of the n.m.r. spectrum clearly proves that the complex has a diamagnetic copper(I) and not a paramagnetic copper(II) central cation; no e.s.r. spectrum was observable. The u.v.-visible spectrum of CuL¹ClO₄ consists of two bands: λ_{max} 470 (ϵ_{max} 6 dm³ mol⁻¹ cm⁻¹) and 321 nm (ϵ_{max} 235).

The complex CuL¹ClO₄ can be oxidized electrochemically. The cyclic voltammogram (Figure 1) shows a reversible single-electron oxidation process at +0.47 V vs. Ag/AgCl. A second irreversible wave is observed at +1.33 V vs. Ag/AgCl and is attributed to an oxidative degradation of the ligand

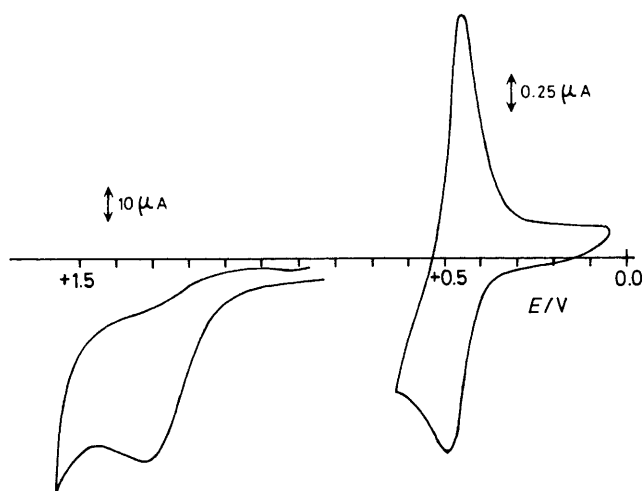


Figure 1. Cyclic voltammogram of CuL^1ClO_4 ($1 \times 10^{-2} \text{ M}$) in neutral $1 \text{ M Na}_2\text{SO}_4$ solution; Pt working and counter electrodes; Ag/AgCl reference electrode. Sweep rate 72 mV/s for the wave at $+0.47 \text{ V}$ and 76 mV/s for the second wave. Note the difference in the current scales.

probably coupled to water oxidation. (Note that the current is larger by a factor of 40 than that of the first wave.) $\text{CuL}^2(\text{ClO}_4)_2$ is oxidized to the tervalent complex in a quasi-reversible process at $+1.09 \text{ V vs. Ag/AgCl}$, reduced to the monovalent complex at $-1.08 \text{ V vs. Ag/AgNO}_3$ in MeCN,^{2a} and reduced in a two-electron process to Cu^0Hg at $-0.62 \text{ V vs. Ag/AgCl}$ in this study.

Attempted preparative electrolytic oxidation of CuL^1ClO_4 in $0.5 \text{ M Na}_2\text{SO}_4$ at $0.65 \text{ V vs. Ag/AgCl}$ resulted in a product with absorption maxima at 450 and 250 nm, using an identical solution of CuL^1ClO_4 in $0.5 \text{ M Na}_2\text{SO}_4$ as a reference solution. The product is unstable and decomposes within several hours. Oxidation of CuL^1ClO_4 with $\text{Na}_2\text{S}_2\text{O}_8$ in $1 \text{ M H}_2\text{SO}_4$ yields a solution which, when frozen at 77 K , has an extremely

unsymmetrical e.s.r. absorption with $g = 2.101$ and a width of 60 G ($1 \text{ G} = 10^{-4} \text{ T}$).

The results thus indicate that CuL^1ClO_4 is surprisingly formed during the methylation of $\text{CuL}^2(\text{ClO}_4)_2$. Furthermore the redox potential of CuL^1ClO_4 is considerably higher than expected and it is not oxidized by air in aqueous solutions. These results emphasise the special stabilization of low-valent transition metal cations by the ligand L^1 .⁵ The complex CuL^1ClO_4 seems to be the first complex of copper(I) with a fully saturated amino ligand which is air-stable and has such a high redox potential in aqueous solutions. This finding is of interest in the framework of the search for model copper complexes for some copper enzymes.⁶

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- 6 See for example: T. G. Spiro, 'Copper Proteins,' Wiley-Interscience, New York, 1981.