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The Copper(I) Complex of a Metallocyclam-Functionalized Phenanthroline: A Poorly Stable Species That Is Very Resistant to Oxidation

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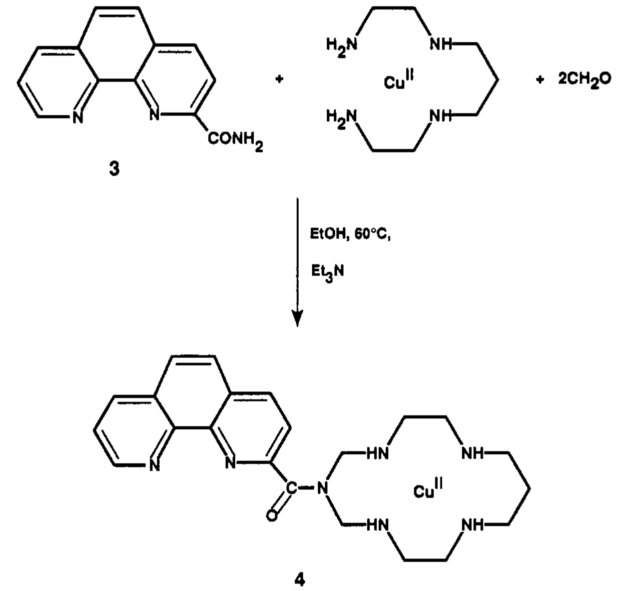
1,10-phenanthroline (phen, **1**) is a unique ligand for copper(I).[1] The unusually high stability of the tetrahedral $[Cu^I(phen)_2]^+$ complex essentially derives (i) from the rigid nature of the ligand, which enhances the chelate effect, and (ii) from the ligand's availability to accept electrons from the d^{10} metal center by a π mechanism. However, $[Cu^I(phen)_2]^+$ still behaves as a moderately strong reducing agent, being oxidized to the five-coordinate Cu^{II} complex at a somewhat more negative potential than ferrocene, taken as a reference (–0.32 V, vs Fc^+/Fc, in an acetone solution 0.1 M Bu_4NClO_4, at 25 °C).

The Cu^I/Cu^{II} oxidation process involves a drastic stereochemical change: the system of two phenanthrolines, which were almost orthogonal in the slightly distorted tetrahedral $[Cu^I(phen)_2]^+$ species,[2,3] flattens on oxidation and a solvent molecule (or a uninegative anion, in the solid complex) binds to the Cu^{II} center, to generate a distorted trigonal bipyramidal arrangement.[4] The relative stability of the Cu^I form dramatically increases when substituents (e.g. $-CH_3$ fragments) are appended to the 2- and 9-positions of 1,10-phenanthroline, **2**: $E_{1/2}(Cu^{II}/Cu^I) = 0.18$ V, vs Fc^+/Fc, in acetone, 0.1 M in Bu_4NClO_4. The steric effects of the alkyl substituents on 2,9-dimethyl-1,10-phenanthroline hinder the flattening of the two ligands, disfavoring the formation of the five-coordinated Cu^{II} species.

We wished to consider further effects besides steric hindrance. In particular, we were interested in exploring the effect generated by appending a metal center to the phenanthroline backbone. In this connection, we recently demonstrated that a metallocyclam subunit can be appended to any given aromatic substrate, provided it contains the aminocarbonyl function. In fact, aromatic amides work well as *locking fragments* in the metal template closure of an open-chain tetraamine, in the presence of excess formaldehyde and base.[5] Thus, we carried out a Cu^{II} template reaction using 2-(aminocarbonyl)-1,10-phenanthroline (**3**) as a *locking fragment*, as outlined in Scheme I.

In such a reaction, the two primary amine groups of a tetraamine coordinated to a Cu^{II} ion undergo Schiff base condensation with two formaldehyde molecules. Consecutive nucleophilic attack of the stepwise deprotonated amide closes the 14-membered ring, to give the Cu^{II} pentaaza macrocyclic complex **4**. Structural studies[5,6] have shown that in pentaaza macrocyclic complexes of this kind only the four primary amine nitrogen atoms are bound to the metal center, according to a coordination mode similar to that of cyclam, which accounts for the trivial name of *azacyclam* complexes. Moreover, azacyclam complexes display the typical macrocyclic inertness toward demetalation. In particular, the aqueous pink-violet Cu^{II} complex **4** is not demetalated even in strongly acidic solutions, as shown by the indefinite persistence of the absorption band at 525 nm ($\epsilon = 89$ M^{-1} cm^{-1}), characteristic of the CuN_4 chromophore.

Scheme I



The heavily functionalized phenanthroline **4** still maintains its tendency to coordinate the Cu^I ion. Addition of solid $[Cu^I(MeCN)_4]ClO_4$ to an aqueous solution of $\mathbf{4}(NO_3)_2$, according to a 1:2 molar ratio, gave a reddish-brown solution. On addition of NH_4PF_6, a microcrystalline brick-red precipitate formed, which was satisfactorily analyzed as $[Cu^I(\mathbf{4})_2](PF_6)_5$.

$[Cu^I(\mathbf{4})_2](PF_6)_5$ dissolves in water and in acetone to give a reddish-brown solution. The intense band centered at 440 nm ($\epsilon(H_2O) = 5700$ M^{-1} cm^{-1}, $\epsilon((CH_3)_2CO) = 6200$ M^{-1} cm^{-1}) is typical of tetrahedral Cu^I polypyridine complexes: it originates from a metal-to-ligand charge transfer and obscures the d–d band owing to the two appended Cu^{II}–azacyclam subunits. $[Cu^I(\mathbf{4})_2]^{5+}$ is a metal complex in which ligands themselves are metal complexes and, in this sense, can be defined as a *supercomplex* (and belongs to the realm of *supramolecular coordination chemistry*).

Whereas it is stable in solvents that do not exhibit affinity for Cu^I, such as water and acetone, $[Cu^I(\mathbf{4})_2]^{5+}$ is unstable in media with distinctive coordinating tendencies: when the brick-red $[Cu^I(\mathbf{4})_2](PF_6)_5$ supercomplex is dissolved in MeCN, the solution does not take on the expected brown color but becomes pink-violet, indicating decomposition. Decomposition derives from the intrinsically low solution stability of the $[Cu^I(\mathbf{4})_2]^{5+}$ cation and from the competition for the Cu^I center by MeCN molecules, present in an overwhelming amount, as described by eq 1.

$$[Cu^I(4)_2]^{5+} + 4MeCN = [Cu^I(MeCN)_4]^+ + 2[4]^{2+} \qquad (1)$$

The formation of a partially decomposed species $[Cu^I(\mathbf{4})(MeCN)_2]^{5+}$, in which only one phenanthroline ligand has been replaced by solvent molecules, must be ruled out. Cu^I monophenanthroline complexes present an intense absorption band at 360 nm.[7] Such a band is not observed in the spectrum of the acetonitrile solution of $[Cu^I(\mathbf{4})_2](PF_6)_5$.

The low solution stability of the $[Cu^I(\mathbf{4})_2]^{5+}$ trimetallic system seems to be ascribed to the electrostatic repulsion between the Cu^I center and the two peripheral Cu^{II} cations. It should be noted that the competing ligand MeCN does not have to be present

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(1) McMillin, D. R.; Kirchoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985,** *64,* 83.

(2) Dobson, J.; Green, B. E.; Healy, P. C.; Kennard, C. H. L.; Pakawatchai, C.; White, A. *Aust. J. Chem.* **1984,** *37,* 649.

(3) Klemens, F. K.; Fanwick, P. E.; Bibler, J. K.; McMillin, D. R. *Inorg. Chem.* **1989,** *28,* 3076.

(4) Burke, P. J.; Henrik, K.; McMillin, D. R. *Inorg. Chem.* **1982,** *21,* 1881.

(5) De Blas, A.; De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Manotti Lanfredi, A. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. Chem.* **1993,** *32,* 106.

(6) Fabbrizzi, L.; Manotti Lanfredi, A. M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991,** 3263.

(7) Atkins, C. E.; Park, S. E.; Blaszak, J. A.; McMillin, D. R. *Inorg. Chem.* **1984,** *23,* 569.

0020-1669/93/1332-3385$04.00/0

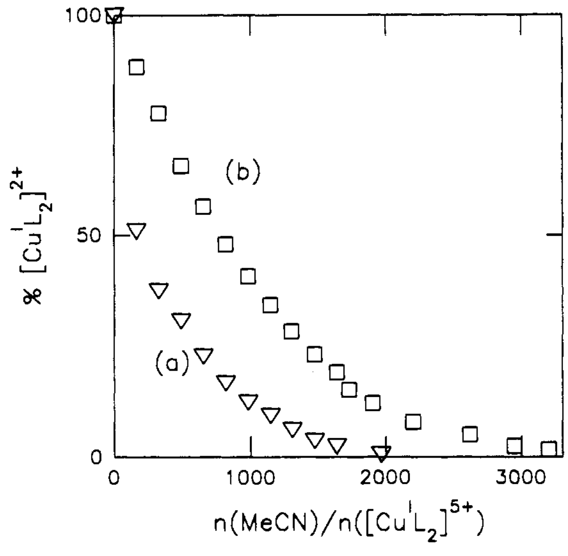


Figure 1. Decomposition of the $[Cu^I(4)_2]^{5+}$ supercomplex on progressive addition of MeCN to (a) an acetone solution and (b) an aqueous solution. The horizontal axis shows the ratio of the added MeCN molecules to the molecules of the supercomplex.

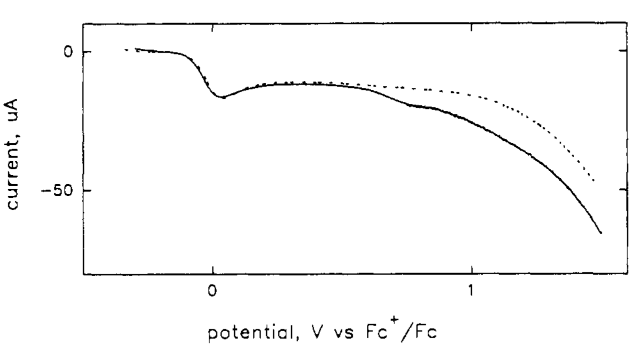


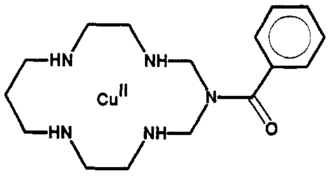
Figure 2. Single-sweep voltammetric profile of acetone solutions, 0.1 M in Bu_4NClO_4, of $[Cu^I(4)_2]^{5+}$ (solid line) and of $[5]^{2+}$ (dotted line). The less anodic peak in both profiles corresponds to the one-electron oxidation of ferrocene (Fc), used as an internal standard.

in so large an excess as in the pure solvent: when moderate amounts of MeCN are added to an *acetone* solution of $[Cu^I(4)_2]^{5+}$, the brown color progressively disappears, indicating that decomposition takes place, according to eq 1.

Figure 1 reports the variation of the percent concentration of $[Cu^I(4)_2]^{5+}$, spectrophotometrically determined through the 440-nm band, as the MeCN/$[Cu^I(4)_2]^{5+}$ molar ratio increases. The figure shows that the supercomplex is completely decomposed in presence of 2×10^3 molecules of MeCN per molecule of $[Cu^I(4)_2]^{5+}$ (which was 10^{-4} M). Again, the existence of the $[Cu^I(4)(MeCN)_2]^{3+}$ species after the excess acetonitrile addition should be excluded, as no band is observed around 360 nm. It should also be noted that if an excess of the strongly donating ligand 2,9-dimethyl-1,10-phenanthroline (2)[7] is added, the pink-violet solution takes on an intense brown color. Measuring the absorbance of the band centered at 454 nm indicates that 100% of the $[Cu^I(2)_2]^+$ complex is formed. Such an experiment demonstrates that, after the $[Cu^I(4)_2]^{5+}$ decomposition, Cu^I remains intact in solution.

Decomposition occurs also on addition of MeCN to an *aqueous solution* of $[Cu^I(4)_2]^{5+}$. Progress of the dissociation process with the increasing concentration of MeCN is illustrated in Figure 1. It can be noted that the aqueous $[Cu^I(4)_2]^{5+}$ supercomplex is more resistant to demetalation, the decomposition being complete for an MeCN/supercomplex molar ratio distinctly higher than that observed in acetone. Higher stability of the Cu^{II}–Cu^I–Cu^{II} species in aqueous solution than in acetone can be accounted for considering that in water, whose dielectric constant is much greater than that of acetone (at 25 °C: 78.5 and 20.7, respectively), mutual electrostatic repulsion between metal centers should be lower and dissociation more difficult.

A cyclic voltammetry investigation of an acetone solution of $[Cu^I(4)_2]^{5+}$, 0.1 M in Bu_4NClO_4, did not disclose any reversible wave until the anodic discharge. In particular, Figure 2 displays the single-sweep profile (oxidation scan). For comparison, the figure also displays the profile obtained with a solution of the $[Cu^{II}$azacyclam$]$ complex 5, chosen as a reference. It is seen that



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the $[Cu^I(4)_2]^{5+}$ supercomplex does not show any redox activity until 0.8 V (vs Fc^+/Fc). At this potential an ill-defined oxidation peak appears, which is followed by the anodic discharge. Controlled-potential electrolysis at the potential of 0.8 V causes decomposition of the $[Cu^I(4)_2]^{5+}$ complex, with disappearance of the brown color. On the other hand, no peak is observed in the oxidation scan on the solution of $[5]^{2+}$ before the anodic discharge. Such evidence indicates that the trimetallic $[Cu^I(4)_2]^{5+}$ species resists the oxidation of the Cu^I center up to a very positive potential (0.8 V; whereas the oxidation of the $[Cu^I(2)_2]^+$ complex takes place at 0.2 V). At 0.8 V the oxidized $[Cu^{II}(4)_2]^{6+}$ species forms, which is very unstable due to the strong electrostatic repulsion between the three Cu^{II} metal centers and immediately decomposes. It should be noted that the decomposition process is too fast to be prevented by a rapid reverse scan in cyclic voltammetry experiments carried out at a high potential scan rate. Even at a rate of 5 V s^{-1} (the highest value available with the employed apparatus), the oxidation peak is still irreversible and no reduction peak is observed on the reverse scan. The anodic discharge is probably induced by the oxidation of the peripheral Cu^{II} macrocyclic subunits to Cu^{III} species, followed by ligand oxidation and fragmentation. Such a process takes place at the same potential in the case of the aza macrocyclic complex $[5]^{2+}$, taken as a reference (see Figure 2). Rapid decomposition of electrochemically generated Cu^{III} species is a well documented phenomenon for polyaza macrocyclic complexes.[8] The electrochemical behavior of $[Cu^I(4)_2]^{5+}$ is confirmed by redox chemistry experiments in aqueous solution carried out with conventional oxidizing agents: when treated with peroxydisulfate, an aqueous solution of $[Cu^I(4)_2]^{5+}$ loses its brown color and turns pink-violet.

We have described the paradoxical situation of a Cu^I complex of a functionalized 1,10-phenanthroline, i.e. $[Cu^I(4)_2]^{5+}$, which is poorly stable in solution (it is demetalated by moderately coordinating ligands such as MeCN) but which is extremely resistant to the oxidation to Cu^{II}. In particular, it is oxidized at a potential 0.6 V more positive than the corresponding Cu^I complex with 2,9-dimethyl-1,10-phenanthroline (2), the *champion* of the resistance to the oxidation among copper(I) polypyridine complexes. The paradox is only apparent, as an electrode potential is not a measure of the intrinsic solution stability of a given redox-active species but is related to (the logarithm of) the ratio of the formation constant of the reduced complex over the formation constant of the oxidized species. In the case of the functionalized phenanthroline system 4, the solution stability of the Cu^I form is rather low, due to the repulsive electrostatic effects between the peripheral Cu^{II} subunits and the Cu^I center (they can be roughly evaluated to $(2 \times 1 + 2 \times 1)e^2/r = 4e^2/r$). On oxidation, the electrostatic repulsion becomes much larger ((2 × 2 + 2 ×

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(8) Fabbrizzi, L.; Poggi, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2191.

$2)e^2/r = 8e^2/r)$, which makes the complex unstable with respect to the demetalation. Thus, the astonishingly high resistance to the oxidation of the $[Cu^I(\mathbf{4})_2]^{5+}$ complex seems to be ascribed mainly to the existence of destabilizing repulsive electrostatic effects, which are much larger for the oxidized species than for the reduced species. However, it is possible that also steric effects associated with the bulky metallocyclam subunits further contribute to the relative stabilization of the Cu^I supercomplex.

The redox behavior of coordination compounds can be controlled through steric effects and through the variation of the donor tendencies of the bound ligand(s), as shown by hundreds of examples and electrochemical studies. This work has demonstrated that one can profit from repulsive electrostatic effects (generated by placing positively charged groups, e.g. metal ions, near the redox site) to extend the stability of the reduced form of a given redox couple.

Experimental Section

2-(Aminocarbonyl)-1,10-phenanthroline was prepared via the Cu^{II}-promoted hydrolysis of 2-cyano-1,10-phenanthroline,[9] which had been obtained from the reaction of 1,10-phenanthroline 1-oxide with benzoyl chloride and potassium cyanide.[10] **$[\mathbf{4}](NO_3)_2 \cdot H_2O$.** To an ethanolic solution of copper(II) nitrate (1.3 mmol in 10 mL) were added consecutively 1.3 mmol of 1,4,8,11-tetrazaundecane and 2.6 mmol of triethylamine. Then, an ethanolic solution of 2-(aminocarbonyl)-1,10-phenanthroline (1.3 mmol in 15 mL) was added dropwise, after which five 1-mL portions of 40% aqueous formaldehyde were added over 10 h. The solution was kept at 50 °C for 12 h. During this period, a violet precipitate formed, which was isolated by filtration, washed with ethanol, and dried under vacuum at 50 °C. Yield: 49%. Anal. Calcd for $C_{22}H_{31}N_9O_8Cu$: C, 43.1; H, 5.1; N, 20.3. Found: C, 43.1; H, 4.8; N, 20.2. **$[Cu^I(\mathbf{4})_2](PF_6)_5$.** A 0.34-mmol sample of $[\mathbf{4}](NO_3)_2 \cdot H_2O$ was dissolved in the minimum amount of water. A 0.17-mmol quantity of $[Cu^I(MeCN)_4]ClO_4$ was then added to the stirred solution, which immediately became brown. On addition of NH_4PF_6, a brick-red microcrystalline solid formed, which was recrystallized from water. Yield: 84%. Anal. Calcd for $C_{44}H_{58}N_{14}O_2P_5F_{30}Cu_3$: C, 30.5; H, 3.4; N, 11.3. Found: C, 30.8; H, 3.6; N, 11.5.

Cyclic voltammetry (CV) studies and controlled-potential electrolysis (CPE) experiments were carried out using a PAR 273 galvanostat/potentiostat controlled by a personal computer. The working electrode was a platinum microsphere (CV) or a platinum gauze (CPE). In CV experiments, a platinum wire was used as a pseudoreference electrode, which was internally calibrated through the Fc^+/Fc couple. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer or on a Varian Cary 2300 spectrophotometer.

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(9) Breslow, R.; Fairweather, R.; Keana, J. *J. Am. Chem. Soc.* **1967**, *89*, 2135.

(10) Corey, E. J.; Borror, A. L.; Foglia, T. *J. Org. Chem.* **1965**, *30*, 288.