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σ and π Effects on the Cu(II)/Cu(I) Redox Couple Potential in Tetraaza Macrocyclic Complexes

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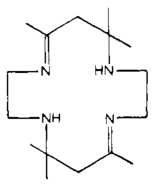
Tetraaza macrocycles are especially effective in stabilizing oxidation states of the complexed metal ion that are inaccessible to the simply solvated cation or to complexes with noncyclic chelating agents.[1] Formation of fairly stable tetraaza macrocyclic complexes of Fe(I),[2] Co(I),[3] Ni(I),[4,5] Ni(III),[4,5] Cu(III),[6] Ag(II) and Ag(III)[7] obtained through chemical or electrochemical reactions in aqueous or nonaqueous solution has been documented. The stability of the cation produced has usually been expressed through the half-wave potential $E_{1/2}$ associated with the electrochemically reversible or quasi-reversible redox change from the reference oxidation state (usually the divalent complexed metal ion). The oxidized and reduced cations of the couple profit to different extents from CFSE, depending on their electrical charge and on the electronic configuration, of the donor properties of the macrocycle. It is essentially for this reason that the $E_{1/2}$ parameter for a $M^{(n+1)+}/M^{n+}$ couple in a series of tetraaza macrocyclic complexes has been found to be strongly dependent upon structural modifications of the ligand, e.g., size of the macrocyclic cavity[4,8,9] and the presence of substituents,[4] and may cover a substantial range of potentials.

We are presently focusing our attention on the Cu(II)/Cu(I) redox couple in some selected tetraaza macrocyclic systems: unlike the redox systems cited before, the Cu(II)/Cu(I) couple involves the change from a transition-metal ion (d^9), which benefits considerably from the crystal field stabilization offered by the macrocycle, to a non-transition-metal ion configuration (d^{10}), which cannot profit from a square arrangement of the donor atoms. The Cu(II)/Cu(I) system in macrocyclic complexes was first considered by Olson and Vasilevskis, who described the formation of a thermodynamically stable Cu(I) complex by reduction of the Cu(II) complex of the diene macrocycle **1**, using a mercury or a platinum cathode in MeCN solution.[10] On the other hand, the Cu(I) complex with the fully saturated analogue **2** is poorly stable and immediately disproportionates on the mercury electrode surface, giving rise to a composite cathodic-anodic wave ($2CuL^+ = CuL^{2+} + Cu^0 + L$).[10] Subsequently, Busch and associates[11] reported that the Cu(II) complex with the diene macrocycle **3** (3,3-CR) is cathodically reduced in MeOH to a stable monovalent species, whereas the corresponding Cu(II) complex of the saturated ligand **4** (*ms*-CRH) gives rise to a two-electron cathodic reduction process. Recent cyclic voltammetry investigations[12] have shown that Cu(**4**)$^{2+}$ in MeCN gives a quasi-reversible one-electron cathodic peak, which is immediately followed by a totally irreversible reduction to metal; however, exhaustive electrolysis at the first reduction peak results in electrodeposition of copper on the platinum gauze, with the uptake of 2 mol of electrons/mol of complex. It is noteworthy that reduction of the Cu(II) complex with the prototype of the saturated tetraaza macrocycles, *cyclam* (**5**), which definitively exhibits the most pronounced donor tendencies toward transition-metal ions, proceeds in a two-electron single step, even at the highest potential scan rate.[12]



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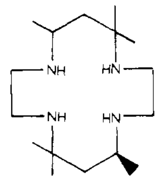

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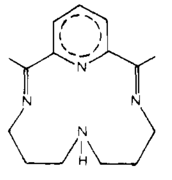

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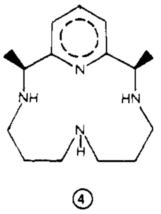

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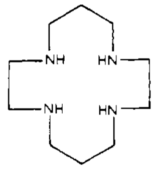

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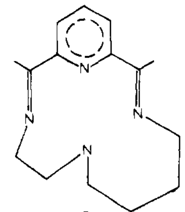

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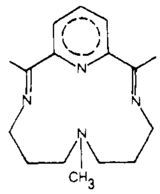

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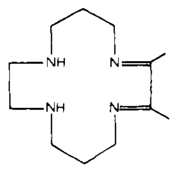

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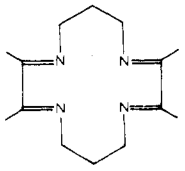

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It is therefore evident that fully saturated ligands are not effective for formation of complexes of Cu(I) that are stable enough to resist disproportionation or demetalation. Some degree of unsaturation must be introduced into the ligand system in order to get Cu(I) macrocyclic complexes in solution. It transpires that this behavior may be related to the σ- and π-bonding features of the Cu(II) and Cu(I) macrocyclic complexes. In order to make a more quantitative assessment of the above effects on the redox potential of the Cu(II)/Cu(I) couple, we have performed an electrochemical investigation of the reduction behavior of the Cu(II) complexes with the

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Table I. Half-Wave Potentials for the Redox Changes $Cu(macrocycle)^{2+} = Cu(macrocycle)^{+}$ in Methanol with 0.1 M Et_4NBF_4, at 25 °C[a]

macrocycle	$E_{1/2}$, V[b]	macrocycle	$E_{1/2}$, V[b]
3	−0.492	8	−0.624
6	−0.401	9	−0.410
7	−0.398		

[a] Measured at a mercury electrode. [b] All values are ±0.005 V and were measured vs. SCE.

series of *14-membered macrocycles* **3**, **6**, **7**, **8**, and **9**, which contain different structural features or varying degrees of unsaturation. All these complexes were obtained as perchlorates through template reactions (see the Experimental Section) and behave in MeOH as 2:1 electrolytes. Electrochemical investigation showed that each complex undergoes a reversible one-electron reduction process at the mercury electrode in MeOH solution (0.1 M in Et_4NBF_4), at a moderately negative potential (vs. SCE): the dc curve at DME was typically S-shaped and the slope of the log $(i/i_d - i)$ vs. E plot was very close to the theoretical value (59 mV). Furthermore, in the CV profile, obtained with use of an HMD electrode, the cathodic and anodic peaks were separated by 60 mV and exhibited a peak current intensity ratio of 1. The $E_{1/2}$ values obtained from the above techniques, as well as from differential pulse polarography, were all coincident within experimental error (±5 mV) and are reported in Table I.

A first comparison can be done for the complexes with the two isomeric ligands **3** (3,3-CR) and **6** (2,4-CR), which present the same set of donor atoms and have the same atomicity (14) but differ in the length of the aliphatic chains of the saturated moiety; this generates a different sequence of the chelate rings on complexation: 5, 5, 6, 6 for **3** and 5, 5, 5, 7 for **6**. The more symmetrical (5, 5, 6, 6) arrangement is expected to favor the formation of stronger in-plane Cu(II)–N interactions relative to the 5, 5, 5, 7 system, which contains an unfavorable seven-membered chelate ring and which is structurally forced to deviate its donor atoms from the positions preferred by the Cu(II) ion, i.e., the corners of a square. This is documented by the considerably larger value of the energy of the absorption d–d band, ν(d–d), an empirical parameter that has been found to be proportional to the strength of the Cu–N equatorial interactions in copper(II) polyamine complexes[13] ($Cu(\mathbf{3})^{2+}$ 18.08 × 10^3 cm^{-1}, $Cu(\mathbf{6})^{2+}$ 17.15 × 10^3 cm^{-1}, from spectra measured in MeOH solution). The $E_{1/2}$ value for the $Cu(\mathbf{6})^{2+/1+}$ redox couple is appreciably less negative than that for the $Cu(\mathbf{3})^{2+/1+}$ homologous system, suggesting that the reduction to give the Cu(I) cation is easier when the Cu(II)–macrocycle interactions (σ in nature) are weaker. Furthermore, one cannot exclude that the change in the structure of the ligand may favor to a different extent the Cu(I) state, even if the stereochemistry of the complexes with the latter cation has not been established. In any case, rearrangement of the 5, 5, 6, 6 chelate ring system of **3** to the 5, 5, 5, 7 system of **6** makes the reduction to Cu(I) easier. The same effect is obtained by introducing a methyl group on the amine nitrogen atom of the **3** framework (ligand **7**, see Table I). The origin of this effect is not immediately clear, and several hypotheses can be put forward: the methyl group on the sp^3 nitrogen atom may exert some steric repulsion on one of the apically coordinated solvent molecules, inducing some distortion of the complex and of the macrocyclic system and destabilizing the divalent state; one of the reviewers remarked that methylation of an amine nitrogen in a macrocyclic framework can make the M–N distance greater (as has been demonstrated by X-ray studies on the six-coordinate high-spin Ni(II) complexes with cyclam and its fully N-methylated counterpart Me_4-cyclam).[14,15] According to this view, the divalent state should be destabilized, and the Cu(II)/Cu(I) potential made less negative, by weaker Cu^{II}–N interactions.

Comparison of the behavior of the complexes with **8** and **9** emphasizes a second effect on the stabilization of Cu(I) in tetraaza macrocyclic systems: the two ligands **8** and **9** are both 14-membered and have therefore a comparable ring amplitude but possess different degrees of unsaturation, having one or two α-diimine groups, respectively. They differ also in the number of methyl substituents on the carbon backbone, but these are not expected to influence the redox process, as they lie in the equatorial plane and cannot interfere with extraplanar, axially coordinated solvent molecules.[16] The Cu(II)/Cu(I) redox change in the tetraene macrocycle **9** occurs at a markedly less negative potential (more than 200 mV) than for the diene system **8**. In order to explain this difference, one should consider that the Cu(I), d^{10}, ion can transfer electronic charge, through a back-donation mechanism, onto the donor atom system, provided it possesses orbitals of the appropriate type and energy. This situation is probably achieved with the nitrogen atoms of the imine bonds. Therefore, the easier reduction of the Cu(II) complex having four C=N groups should reflect the more pronounced stabilization of the Cu(I) complex, due to the establishing of a more extended system of Cu(I)—N π interactions.[17]

These results demonstrate that the Cu(II)/Cu(I) process in macrocyclic systems can be promoted through modifications of the ligands that (i) reduce its σ-donor ability (destabilizing Cu(II)) and (ii) increase its π-acceptor properties (stabilizing Cu(I)).

It is apparent that tetraaza macrocycles are not the best ligands for the Cu(I) ion, as they greatly favor the transition-metal cation Cu(II). It should be recalled that, whereas many metal redox couples of biological interest operate in a coplanar tetraaza macrocyclic system (of the porphyrin type), the Cu(II)/Cu(I) couple, which is also physiologically important, is active in a noncyclic, noncoplanar four-coordinating system. In some synthetic model systems, which have been recently proposed for the active site of the copper proteins, the oxidizing power of the copper(II) has been increased by introducing donor atoms that exhibit an affinity for Cu(I) (e.g., sulfur)[18] or inducing some distortions in the coordination geometry, e.g., producing, through steric effects, in a set of four nitrogen atoms a progressive deviation from a square to tetrahedral array.[19] The present work has shown that geometrical effects favorable to the formation of copper(I) can be induced in a fixed coplanar array of four nitrogen atoms, by rearranging the system of fused chelate rings, for instance from the 5, 5, 6, 6 to the 5, 5, 5, 7 sequence.

Experimental Section

Complexes. Copper(II) complexes with the macrocycles **3**, **6**, and **7** were obtained as perchlorates through template Schiff base condensation of 2,6-diacetylpyridine and the appropriate triamine in the presence of $Cu(ClO_4)_2 \cdot 6H_2O$, in a 1:1 water/methanol mixture, as previously reported.[11,20,21] As also found for Ni(II) analogues, yields were improved by conducting the reactions in dilute solution and at low temperature (stirring of a 10^{-2} M solution for 20–24 h at 25–30 °C). Perchlorate complexes of **8** and **9** were prepared by following

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a method similar to that reported by Tait and Busch for the synthesis of the nickel(II) analogues.[22] The synthesis of Cu(**9**)$(ClO_4)_2$ was done as follows: To a 100-mL methanolic solution containing 0.04 mol of both 1,3-propanediamine and HCl (added as the concentrated aqueous solution), cooled in an ice bath, was added dropwise 0.04 mol of 2,3-butanedione (biacetyl) with vigorous stirring. After addition of the biacetyl, the solution was removed from the ice bath and allowed to stand at room temperature. After about 30 min copper(II) acetate (0.02 mol) dissolved in 80 mL of MeOH was added and the solution was stirred for 12 h after which 0.04 mol of 70% $HClO_4$ was added dropwise and the solution was evaporated to about 50 mL on a rotary evaporator. When the solution stood, large, square, violet crystals formed, which were removed by filtration, washed with small portions of cold ethanol, and dried in vacuo over P_4O_{10}. The yield was 25%. An analogous procedure was employed for the synthesis of Cu(**8**)$(ClO_4)_2$. All the complexes analyzed satisfactorily for carbon, hydrogen, and nitrogen.

Electrochemistry. Conventional and differential pulse polarography studies were performed with use of a Metrohm Polarecord E 506 apparatus. CV measurements were carried out with the Electrochemolab system (Amel, Milan, Italy) by using a hanging mercury drop electrode (Metrohm). In any case the counterelectrode was a platinum electrode and the reference electrode (SCE) was separated from the solution by a bridge containing aqueous 0.1 M NaCl. Erba RPE methanol was employed without further treatment. Polarographic grade tetraethylammonium fluoborate (Erba, Milan) was kept over P_4O_{10} in vacuo for 1 day or more prior to use.

Registry No. Cu(**3**)$^{2+}$, 60836-37-5; Cu(**3**)$^+$, 80502-45-0; Cu(**6**)$^{2+}$, 60836-37-5; Cu(**6**)$^+$, 80502-46-1; Cu(**7**)$^{2+}$, 80502-47-2; Cu(**7**)$^+$, 80502-48-3; Cu(**8**)$^{2+}$, 80502-49-4; Cu(**8**)$^+$, 80502-50-7; Cu(**9**)$^{2+}$, 71170-97-3; Cu(**9**)$^+$, 80502-51-8.

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Molybdenum Nuclear Magnetic Resonance Studies of Trifluorophosphine Complexes

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The similarity of carbon monoxide and phosphorus trifluoride as ligands toward lower valent metals has been well documented.[1] During the characterization of the complexes, the NMR spectra of various species of the type $M(PF_3)_x(CO)_y$ have been examined in some detail.[2] These studies have utilized either the phosphorus-31 or the fluorine-19 resonance and occasionally carbon-13, but the central metal atoms have been little studied. The first two nuclei have inherently high sensitivity, but there are some limitations to ^{31}P and ^{19}F NMR. For instance, diphosphines of the type $Mo(PF_3)_2(CO)_4$ have an $AA'X_3X'_3$ second-order pattern that is not always totally resolved. The second-order coupling in the triphosphines and higher phosphines generally prevents one from obtaining much information from the spectra.

NMR and other spectroscopic studies generally support the original assumption[3] that CO and PF_3 are quite similar as ligands. However, recent results in some nuclear hot-atom studies[4] and investigations into photocatalysis[5] have clearly shown them not to be identical. These results have, in turn, led to our current efforts to determine the equilibrium constants in the scrambling reactions among species in systems such as $Mo(PF_3)_x(CO)_{6-x}$.

The recent availability of a versatile multinuclei spectrometer[6] has led us to attempt an in situ analysis by metal NMR. One immediate potential benefit is that all spectra would be first order. The two nuclei are ^{95}Mo and ^{97}Mo. Both nuclei have spin $^5/_2$ with reasonable abundances and similar receptivities, about twice that of carbon.

The line width of ^{95}Mo has been reported as 0.7 Hz for the octahedral $Mo(CO)_6$. A ^{97}Mo spectrum will be 132 times broader than that of ^{95}Mo owing to a difference of 11.4 in the quadrupole moments for the two nuclei.[7] Accordingly, only limited efforts were made to obtain ^{97}Mo spectra. If the PF_3 and CO ligands are as much alike as we suppose, then the $Mo(PF_3)_x(CO)_{6-x}$ species will have pseudo-O_h symmetry and will not be too broadened by the lower symmetry.

The chemical shift is expected to be a sensitive parameter. Estimates and measurements have indicated a chemical shift range of about 4000 ppm.[8] One example of the known sensitivity is the substitution of D_2O for H_2O as a solvent for Li_2MoO_4 and Na_2MoO_4, which results in a shift of 1 ppm in the ^{95}Mo resonance.[9] Substituting sulfur for oxygen in $MoO_4{}^{2-}$ causes a shift of 500 ppm for each substitution.[10]

After this investigation was completed, Schmidt and Rehder[11] published a report of some phosphine complexes of vanadium carbonyls. The shielding differences between the various PF_3 complexes, although small, is significant (10–20 ppm). Similarly, a report[12] of some phosphine complexes of molybdenum indicates significant chemical shifts are present when CO is replaced by $P(OCH_3)_3$ and $P(OC_2H_5)_3$.

This investigation concerns the study of the chemical shifts, coupling constants, and line widths of a series of $Mo(PF_3)_x(CO)_{6-x}$ species.

Experimental Section

The molybdenum compounds were prepared by literature methods[13] from $Mo(CO)_6$ and PF_3. The $Mo(PF)_x(CO)_{6-x}$ mixtures were made in quantities such that before gas chromatographic separation, preseparation was done on a 24-in. spinning-band distillation column under reduced pressure. By this technique, residual $Mo(CO)_6$ was quantitatively removed (left in the pot). Of the remaining species, only $Mo(PF_3)(CO)_5$ was obtained essentially pure. The higher phosphines (at least up to the tetraphosphines) were the more volatile with progressively lower volatility down to the hexacarbonyl. At constant pressure, the distillation temperature range was only about 6° for the seven compounds between $x = 4$ and 1.

^{95}Mo and ^{97}Mo were both observed in 25-mm NMR tubes generally with $CDCl_3$, C_6F_6, or cyclohexane as solvents. The SEMINOLE magnet operates at a field of 3.52 T, and ^{95}Mo was observed at 9.754 MHz and ^{97}Mo at 9.961 MHz. Pulse widths were 40–50 μs for a 90° flip. Chemical shifts were checked relative to $Mo(CO)_6$ dissolved in the same solvent as the sample. At the time this work was done, an internal lock and absolute frequency standard was not available. However, the drift of the solenoid was not significant.

Results and Discussion

The first sample run showed clear evidence that there is less chemical shift among the species than we expected. A neat,

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