Oxidation and Reduction of Copper(II) Complexes with Saturated Poly-aza Macrocycles of varying Size and Denticity †

Luigi Fabbrizzi * and Antonio Poggi
Dipartimento di Chimica Generale, Università di Pavia, viale Taramelli 12, 27100 Pavia, Italy
Piero Zanello
Istituto di Chimica Generale, Università di Siena, Pian dei Mantellini 44, 53100 Siena, Italy

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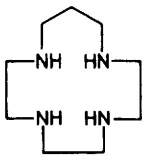
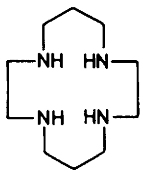
The oxidation and reduction behaviour in acetonitrile solution of copper(II) complexes with a complete series of quadri- and quinque-dentate amine macrocycles has been studied by electrochemical techniques. Both anodic and cathodic electrode processes are found to involve complicated mechanisms. However, the redox changes $Cu^{III} \longrightarrow Cu^{II}$ and $Cu^{II} \longrightarrow Cu^{I}$ have been demonstrated through cyclic voltammetry at high potential scan rate. The $E_{\frac{1}{2}}$ values for the above processes are discussed in terms of the properties and structural features of the macrocyclic ligands.

In a previous paper [1] we reported an electrochemical investigation of the redox behaviour in acetonitrile solution of the copper(II) complexes with the 14-membered saturated tetra-aza macrocycles L^2 and L^3. It was found that controlled-potential electrolysis performed both in oxidation and reduction did not produce the corresponding copper-(III) and -(I) complexes, in contrast to the nickel analogues, but in any case demetallation occurred *via* complicated mechanisms. However, cyclic voltammetry performed at high potential scan rate showed both in oxidation and in reduction a reversible one-electron redox process, ascribed to the formation of copper-(III) and -(I) complex cations, respectively.

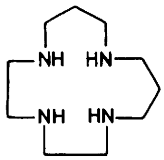
We have now extended this type of study to complexes with polyaza saturated macrocycles including (*i*) tetra-aza ligands containing less (L^1) and more (L^4, L^5) than fourteen members and (*ii*) three penta-aza macrocycles of increasing ring size (L^6—L^8). The aim of this work is to consider how the electrochemical behaviour of copper(II) macrocyclic complexes is affected by variation of the ligand's structural features and in particular to evaluate to what extent, in terms of electrode potential, the formation of uni- and tri-valent copper is influenced by modification of the macrocyclic cavity size and by increase in the number of donor atoms (from 4 to 5). This type of information may be useful in the design of appropriate ligands able to stabilize the so far scarcely known copper-(III) and -(I) cations and thus allow the investigation of their solution chemistry.



L^1



L^2



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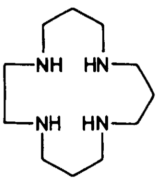

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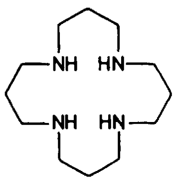
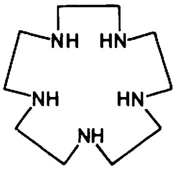
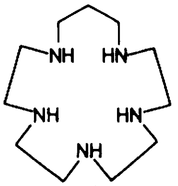


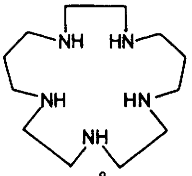
L^5



L^6



L^7



L^8

Experimental

Apparatus and Materials.—The electrochemical apparatus as well as the purification of the solvent and supporting electrolyte have been described previously.[1]

Bis(η-cyclopentadienyl)iron(II) (ferrocene) was used as an internal standard both to evaluate the number of electrons involved in the electrode processes on the cyclic voltammetry scale and to assign $E_{\frac{1}{2}}$ values not affected by the variable diffusion potential arising at the aqueous–non-aqueous interface of the aqueous saturated calomel reference electrode (s.c.e.).

Synthesis of the Macrocyclic Ligands and of their Copper(II) *Complexes.*—The ligands investigated were prepared through the Richman procedure,[2] which involves the (1 + 1) condensation of the tosylated segments (linear polyamine + dihydroxyalkylamine) in strongly basic dimethylformamide solution. The synthetic details have been reported elsewhere.[3] The copper(II) complexes were obtained as perchlorates by mixing hot equimolecular solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and of the macrocycle.

Results and Discussion

Electrochemical Reduction.—In analogy with the copper(II) complexes of 14-membered tetra-aza macrocycles, the complexes reported here undergo a cathodic reduction at the platinum electrode in MeCN solution, which takes place *via* two one-electron steps. The resulting cyclic voltammograms are qualitatively similar to that reported in ref. 1, Figure 1, the only difference being the absence of the small stripping peak obtained by reversing the potential scan just after traversing the less cathodic peak. This implies that the decomplexation of $[CuL]^+$ to give solvated Cu^+, postulated for 14-membered tetra-aza systems,[1] does not occur with the present complexes on the voltammetric time-scale. In other words, the $[CuL]^+$ species are in general more stable in the

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† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J; cal = 4.184 J.

Table 1. Reduction potentials (V) *vs.* s.c.e. for the cathodic processes of copper(II) complexes with tetra-aza and penta-aza macrocycles, determined at platinum and/or mercury electrodes. Values in parentheses are referred to the ferrocenium–ferrocene couple; all values are of E_p at 0.2 V s^{-1} except where indicated otherwise

	$[CuL]^{2+} + e^- \longrightarrow [CuL]^+$		$[CuL]^+ + e^- \longrightarrow Cu + L$		$[CuL]^{2+} + 2e^- \longrightarrow Cu + L$
Ligand (L)	Pt	Hg	Pt	Hg	Hg
L^1	0.62 [a] (−1.06)	—	−0.99	—	−0.66
L^2 [b]	−1.10	—	−1.34	—	−0.94
L^3 [b]	−0.81 [a] (−1.17)	−0.86	−1.34	−1.05	—
L^4	−0.55 [a] (−0.99)	−0.55 [a]	−1.33	−1.02	—
L^5	−0.31 [a] (−0.75)	−0.31 [a]	−1.54	−0.99	—
L^6	−0.73 [a] (−1.12)	−0.72 [a]	−1.35	−0.89	—
L^7	−0.78 [a] (−1.10)	—	−1.45	—	−0.82
L^8	−1.01	—	−1.31	—	−0.80

[a] $E_{\frac{1}{2}}$ value. [b] Values taken from ref. 1.

short term than the corresponding complexes with 14-membered tetra-aza ligands. As observed previously,[1] the more cathodic charge transfer is always totally irreversible in character, whereas the less cathodic one appears as a quasi-reversible electrode process [4] for some complexes (see Table 1). A different cathodic pathway may sometimes occur at the mercury electrode; some complexes are reduced in two one-electron steps, while others are reduced in a single two-electron step. This difference, which has been observed also for 14-membered systems,[1] can be ascribed to the different degrees of reversibility of the two one-electron charge transfers.

In Table 1 are reported the reduction potentials corresponding to the cathodic processes for the investigated complexes, both at the platinum and mercury electrodes. Where possible, the $E_{\frac{1}{2}}$ values, which can be reasonably assumed as the formal electrode potential $E^{\ominus}$, have been calculated as the mean value between the reduction peak potential ($E_p{}^c$) and the directly associated re-oxidation peak potential ($E_p{}^a$), in the likely hypothesis that the charge-transfer coefficient, α, ranges between 0.3 and 0.7.[4] Controlled-potential coulometric tests at a platinum electrode at the potential corresponding to the less cathodic reduction step allow one to verify whether, at times longer than those of the voltammetric experiment, the $[CuL]^+$ complexes decompose and the generated solvated copper(I) cations are reduced to copper metal (Table 2). The results indicate that the first reduction step (the less cathodic one) involves 2 mol of electrons per mol of starting copper(II) complex with quantitative deposition of copper metal for all the investigated complexes, *with the exception* of those with the larger tetra-aza macrocycles, L^4 and L^5. For the last two complexes the one-electron reduction process takes place also on the time-scale of the electrolysis experiment (see Table 2). This is not surprising if one considers that the $E_{\frac{1}{2}}$ value for the Cu^I–Cu couple in MeCN is −0.5 V *vs.* s.c.e.[5] Therefore, for the 15- and 16-membered tetra-aza macrocyclic complexes, the $[CuL]^{2+}$–$[CuL]^+$ couple is not thermodynamically unstable with respect to the electroreduction of the solvated copper(I) cation. Moreover, the cyclic voltammetric responses indicate that the reduction of the copper(II) complexes with L^4 and L^5 does not involve a simple charge transfer but is followed by unidentified chemical reactions.

Electrochemical Oxidation.—The anodic oxidation of copper(II) complexes with 14-membered tetra-aza macrocycles involves complicated electrode processes, in which more than one chemical reaction is coupled to more than two subsequent electrode charge transfers.[1] Also the present complexes exhibit an anodic process involving complicated mechanisms, which in cyclic voltammetry appears as a well defined anodic peak, followed by other ill shaped peaks. When the appropriate potential scan rate has been selected, a cathodic peak appears which is directly associated with the well defined anodic one.

Table 2. Controlled-potential coulometric results of the cathodic reduction of copper(II) complexes with tetra-aza and penta-aza macrocycles at a platinum working electrode

Ligand	Working potential (V *vs.* s.c.e.)	Number of electrons per molecule of starting complex	Quantitative electrodeposition of copper metal
L^1	−0.80	2	Yes
L^2	−1.20	2	Yes
L^3	−1.10	2	Yes
L^4	−0.93	1	—
L^5	−0.70	1	—
L^6	−0.95	2	Yes
L^7	−1.10	2	Yes
L^8	−1.10	2	Yes

As a typical example, the anodic portion of the cyclic voltammogram of a MeCN solution of $[CuL^7]^{2+}$ obtained at a platinum electrode is shown in Figure 1. At a scan rate, v, of 0.2 V s^{-1} no cathodic peak is directly associated with the anodic peak A. In fact, on the basis of controlled-potential coulometry experiments (see below), peak C is attributable to the reduction of the solvated copper(II) ion released from the product of oxidation of the $[CuL]^{2+}$ complex. However, at v = 20 V s^{-1} a cathodic peak B, directly associated with peak A, appears, with a cathodic to anodic peak-current ratio, $(i_p)_B/(i_p)_A$, equal to 0.6. At v = 100 V s^{-1} (the highest potential scan rate used) this ratio becomes very close to unity (see Figure 1) and, by comparison with the one-electron oxidation of ferrocene, the process appears as an uncomplicated one-electron step; under these conditions an $E_{\frac{1}{2}}$ value of 1.56 V *vs.* s.c.e. (1.12 V *vs.* ferrocenium–ferrocene) has been computed. At the potential scan rates investigated (0.2—100 V s^{-1}), the $(i_p)_A/v^{\frac{1}{2}}$ ratio progressively decreases with increasing v to a constant value, which is about half of that found at the slowest scan rate. Controlled-potential coulometry at 1.77 V *vs.* s.c.e. involved the consumption of 4 mol of electrons per mol of starting complex $[CuL^7]^{2+}$. Furthermore, 4 mol of hydrogen ions (per mol of starting complex) were titrated in the electrolyzed solution. Moreover, the quantitative release of solvated Cu^{II}, following the bulk oxidation process, was ascertained, through cyclic voltammetry experiments on the electrolyzed solution.[1] This evidence is consistent with oxidation of the ligand framework, prob-

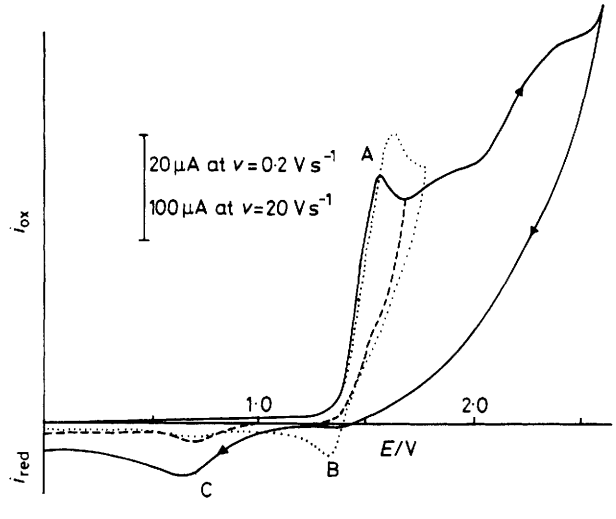


Figure 1. Cyclic voltammetric responses recorded on a MeCN solution containing $[CuL^7]^{2+}$ (1.53×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}) with a platinum working microelectrode. Scan rates: (——) and (– – –), 0.2 V s^{-1}; (· · ·), 20 V s^{-1}

Table 3. Voltammetric data of the oxidation of copper(II) complexes with tetra-aza and penta-aza macrocycles at a platinum anode

Ligand (L)	$E_{\frac{1}{2}}(CuL^{3+}–CuL^{2+})$/V		$t_{\frac{1}{2}}(CuL^{3+})$/s
	^{a}	^{b}	
L^1	1.41	1.00	3
$L^{2\ c}$	1.35	0.99	7
$L^{3\ c}$	1.40	1.03	60
L^4	1.56	1.12	38
L^5	1.66	1.23	3
L^6	1.50	1.07	0.20
L^7	1.56	1.12	0.02
L^8	1.62	1.22	0.004

^{a} vs. s.c.e. ^{b} vs. ferrocenium–ferrocene. ^{c} Values taken from ref. 1.

ably to an unsaturated system;[1] the quick release of the copper(II) cation suggests that oxidation finally leads to open-chain products. The whole data indicate that the electrode process is rather complicated, but on the cyclic voltammetry time-scale a simple electron transfer–chemical reaction–electron transfer (e.c.e.) mechanism, involving two one-electron charge transfers, occurs. Furthermore, for cyclic voltammetry performed at a potential scan rate high enough that the electrode process consists of an uncomplicated one-electron charge transfer, it is possible to evaluate roughly the half-life of the species $[CuL]^{3+}$ primarily formed at the electrode,[1] *ca.* 0.02 s for $[CuL^7]^{3+}$.

All the other copper(II) complexes investigated behave substantially as reported for $[CuL^7]^{2+}$, hence the same type of analysis has been performed and similar conclusions have been drawn. The most significant cyclic voltammetry results are summarized in Table 3. It should be noted that controlled-potential electrolysis of L^4 and L^5 complexes leads to the consumption of 6 mol of electrons and to the formation of 6 mol of hydrogen ions per mol of starting complex, as observed also in the case of complexes with the 14-membered tetra-aza ligands L^2 and L^3. In some cases, particularly with $[CuL^1]^{2+}$ and $[CuL^8]^{2+}$, electrode poisoning occurred, necessitating periodic cleaning of the working electrode.

Thermodynamic Aspects of the Cu^{III}–Cu^{II} *and* Cu^{II}–Cu^{I} *Redox Couples in Macrocyclic Complexes.—The* Cu^{II}–Cu^{I} *redox couple.* The amine nitrogen atom shows a large affinity towards 3*d* bivalent metal cations, in particular Cu^{II}. The co-ordination chemistry of Cu^{II} with macrocyclic polyamines is well documented.[6] The solution stability of $[Cu(polyamine)]^{2+}$ complexes is related to the ability of the ligand to exert strong in-plane Cu^{II}–N interactions in tetragonally distorted octahedral chromophores.[7]

On the other hand, the Cu^I, d^{10}, cation forms stable complexes with polyaza macrocycles only if the ligand possesses some degree of unsaturation.[8] In this situation, the Cu^I can transfer electron density to low-energy antibonding orbitals of the ligand through a π mechanism. Stable copper(I) polyamine complexes have been isolated, but in mixed-ligand complexes containing also the π-acceptor molecule CO.[9] From these considerations it is concluded that the reduction $Cu^{II} \longrightarrow Cu^{I}$ in amine macrocyclic systems must be a particularly unfavourable process.

The present results indicate that this is in general true, since in most cases (with two significant exceptions) the copper(I) species has a limited lifetime in solution and controlled-potential electrolysis leads to its reduction to copper metal. However, the quasi-reversible nature of the $Cu^{II} \longrightarrow Cu^{I}$ reduction on the cyclic voltammetry time-scale allows the evaluation, in terms of thermodynamically meaningful $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ values, to what extent the access to the copper(I) state is affected by the structural features of the ligand (number of nitrogen atoms, size of the macrocyclic hole). In Table 1 the values of $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ for tetra-aza and penta-aza systems are reported. It is significant that the more negative $E_{\frac{1}{2}}$ value, *i.e.* the more difficult access to the univalent state, occurs with L^2 (cyclam), the macrocycle which has the strongest co-ordinative interactions with Cu^{II}. The latter property has been ascribed to the fact that L^2 has the right cavity size to encircle Cu^{II}.[10] Deviations from the ideal size are expected to destabilize the bivalent cation and to favour the attainment of the copper(I) state. Complexes of smaller size, $[CuL^1]^{2+}$, and of larger size, $[CuL^4]^{2+}$, present considerably less negative $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ values. Further enlargement of the macrocyclic hole (to L^5) produces a further stabilization of the copper(I) state. Moreover, the two larger tetra-aza ligands form copper(I) complexes which are stable with respect to reduction to copper metal also on the time-scale of the electrolysis experiments.

The non-transitional copper(I) cation can be considered to possess a definite preference towards tetrahedral co-ordination: larger tetra-aza macrocycles can better achieve this geometrical arrangement. Therefore, the increase of the $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ value along the series of 14- to 16-membered tetra-aza macrocycles is to be ascribed also to the progressive increase in flexibility of the macrocycle.

Increase in the number of nitrogen atoms of the donor set does not seem to favour further the formation of copper(I) complexes. The $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ values for the complexes with L^6 and L^7 are remarkably more negative than those for the complexes with tetra-aza ligands of the same atomicity. The complex with the largest quinquedentate macrocycle, L^8, gave rise to an irreversible reduction process.

The Cu^{III}–Cu^{II} *redox couple.* In Table 3 the values of $E_{\frac{1}{2}}$ associated with the reversible one-electron oxidation of the copper(II) complexes are reported. The reduced lifetime of the oxidized species does not allow its characterization. However, it seems probable that this species is an authentic copper(III) polyamine complex. It can be seen (see Table 2 and also Figure 3) that the easiest attainment of the trivalent state,

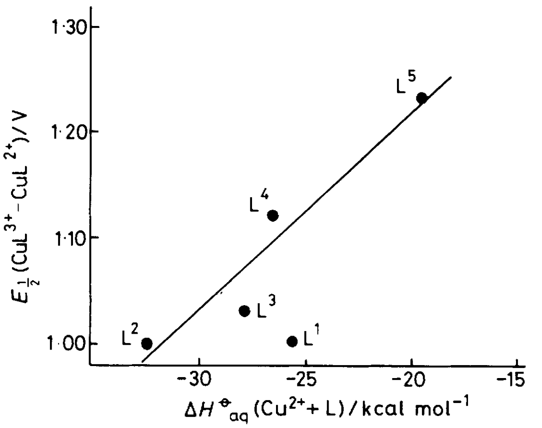


Figure 2. Plot of the $E_{\frac{1}{2}}(\mathrm{CuL^{3+}-CuL^{2+}})$ values (in MeCN solution, *vs.* ferrocenium–ferrocene) *vs.* the enthalpy change for complexation of $\mathrm{Cu^{2+}}$ in aqueous solution, $\Delta H^{\ominus}_{\mathrm{aq}}(\mathrm{Cu^{2+}} + \mathrm{L})$, for tetra-aza macrocyclic complexes

expressed by the least positive value of the half-wave potential, occurs with the symmetric 14-membered ring. Modification of this preferred framework results in a destabilization of the copper(III) state and makes the $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$ values more positive. In particular, as far as tetra-aza macrocycles are concerned, both contraction (to a 13-membered ring) and expansion (to a 15-membered ring) produce an increase of the $\mathrm{Cu^{III}-Cu^{II}}$ redox potential. Further enlargement of the tetra-aza macrocyclic hole (to 16 atoms) makes the oxidation process even more difficult. In order to explain this behaviour it is useful to consider the energy terms involved in the redox change: (*i*) the unfavourable contribution associated with the further ionization of $\mathrm{Cu^{II}}$ (I_3); (*ii*) the solvation term, *i.e.* the difference between the solvation energies of the macrocyclic complexes of $\mathrm{Cu^{III}}$ and $\mathrm{Cu^{II}}$, which, although very important, is considered, to a first approximation, to remain constant for a series of analogous complexes thought to have the same stereochemical arrangement; (*iii*) the crystal field stabilization energy (c.f.s.e.) contribution, *i.e.* the difference of the c.f.s.e. terms for the complexes of $\mathrm{Cu^{III}}$ and $\mathrm{Cu^{II}}$ in solution. Contribution (*iii*) is especially favourable to the formation of the copper(III) complex.

It can be hypothesized that, in analogy with other copper(III) complexes with multidentate nitrogen-containing ligands (*e.g.* polypeptides),[11] the present macrocyclic complexes are square-planar species of the low-spin type. In this situation, the change from d^9 square-planar $\mathrm{Cu^{II}}$ to d^8 low-spin square-planar $\mathrm{Cu^{III}}$ is strongly favoured by a large c.f.s.e. contribution (12.28 *Dq*). A further favourable c.f.s.e. contribution arises from the increase in the cationic charge. Therefore, ligands which exhibit enhanced donor properties are expected to favour the attainment of the copper(III) state. A parameter which is directly related to the donor properties of ligands towards a metal ion is the enthalpy change upon complex formation, $\Delta H^{\ominus}$. Values for the complexation of $\mathrm{Cu^{II}}$ by tetra-aza macrocycles in aqueous solution, $\Delta H^{\ominus}_{\mathrm{aq}}(\mathrm{Cu^{2+}} + \mathrm{L})$, have been reported.[6] In Figure 2 the values of $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$ *vs.* the ferrocenium–ferrocene reference couple have been plotted against $\Delta H^{\ominus}_{\mathrm{aq}}(\mathrm{Cu^{2+}} + \mathrm{L})$ values, for the complexes with the tetra-aza macrocycles studied in this work. A very rough linear correlation exists between the two quantities: the greater the exothermicity of complexation of $\mathrm{Cu^{II}}$, the less positive is the value of $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$. The system which deviates most strongly from linearity is the 13-membered ring complex, which exhibits a low $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$ value, compared to the moderate $\Delta H^{\ominus}$ value. If this complex is disregarded, a reasonable linear correlation is found (correlation coefficient = 0.995). The anomalous behaviour of the $[\mathrm{CuL^1}]^{2+}$ complex could be explained by considering that the 13-membered ligand $\mathrm{L^1}$ has a too small cavity to encompass the $\mathrm{Cu^{II}}$,[10] which probably lies over the $\mathrm{N^4}$ plane (reducing the intensity of co-ordinative interactions and lowering the $\Delta H^{\ominus}$ value). Oxidation to the low-spin d^8 copper(III) involves a drastic reduction of the ionic radius and may allow a co-planar co-ordination of the macrocycle, favouring the formation of stronger Cu–N bonds and removing the strain from the co-ordinated ligand. This extra contribution makes the attainment of the trivalent state more favourable than expected on the basis of the bonding properties of the bivalent metal complex.

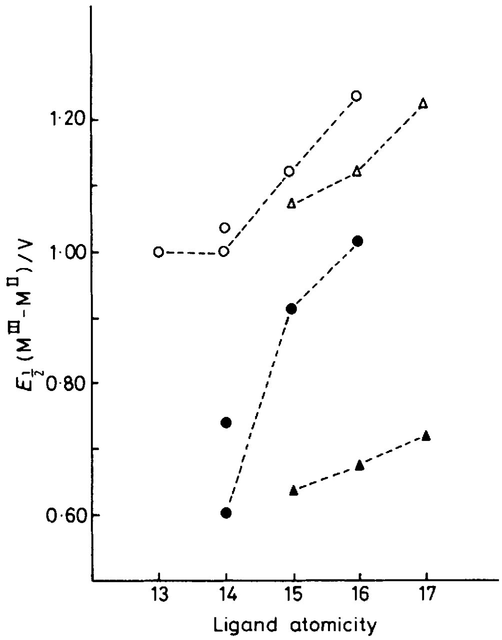


Figure 3. Plot of the $E_{\frac{1}{2}}(\mathrm{M^{III}-M^{II}})$ values for copper (open symbols) and nickel complexes (closed symbols) with quadri- (○,●) and quinque-dentate (△,▲) amine macrocycles in MeCN solution *vs.* the ligand's atomicity (number of carbon and nitrogen atoms in the ring). The $E_{\frac{1}{2}}(\mathrm{Ni^{III}-Ni^{II}})$ for the complex of $\mathrm{L^1}$ was not obtained, due to the ill defined, poorly reversible electrochemical response [3]

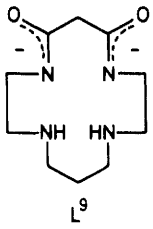
The copper(III) complexes with the three investigated quinquedentate macrocycles seem to be much less stable from a kinetic standpoint than the corresponding tetra-aza analogues, as indicated by the much smaller lifetime. From a thermodynamic point of view, the addition of a fifth nitrogen atom to a tetra-aza framework does not favour the formation of the copper(III) complex: the $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$ values are in every case more positive than for the 13- and 14-membered tetra-aza systems. Among quinquedentate ligand complexes, the easiest oxidation process occurs with the smallest 15-membered macrocyclic complex and progressive expansion of the ring, to 16 and 17 members, makes the oxidation process more and more difficult.

In Figure 3 the $E_{\frac{1}{2}}(\mathrm{Cu^{III}-Cu^{II}})$ values are plotted *vs.* the ligand's atomicity. For comparative purposes, data for the corresponding nickel complexes are also shown.[3] Values for nickel complexes are less positive, essentially as a consequence of the lower energy to be spent in the oxidation process for the gaseous cations (I_3 for Ni is 35.16 eV, 36.83 eV for Cu). However, the dependence of the potential upon the ring size and the number of donor atoms is the same. In other words, the M^{II}–M^{III} couple for both nickel and copper complexes is affected in the same way and approximately to the same extent by modifications of the macrocyclic framework and of the donor properties of the ligand. This is reasonable in the sense that bi- and tri-valent copper and nickel are transition-metal cations of similar size and stereochemical preferences, but it is surprising that the d^9–d^8 (Cu^{II}–Cu^{III}) and the d^8–d^7 (Ni^{II}–Ni^{III}) couples profit to a quite different extent from the c.f.s.e. term.

A major difference (see Figure 3) concerns the relatively higher stability of nickel(III) complexes with penta-aza macrocycles (with respect to the reference complex with L^2) compared to the copper analogues. In this connection, the d^7 low-spin nickel(III) cation has a strong preference towards an octahedral stereochemistry [3] and can profit from the axial co-ordination of a fifth nitrogen atom (the sixth position being occupied by a solvent molecule). The same is not expected to be true with the d^8 low-spin copper(III) cation, which has a much lower affinity towards this type of stereochemistry.

Conclusions

For both nickel and copper, the easiest attainment of the trivalent state occurs with the ligand L^2, known better as cyclam. If the cyclam framework is disturbed (by changing the size of the ring or inserting another donor atom) the relative stability of the tripositive cation decreases. However, whereas $[Ni(cyclam)]^{3+}$ is stable in solution, not only in acetonitrile, but also in water, $[Cu(cyclam)]^{3+}$ only persists in anhydrous acetonitrile for a few seconds. Due to the very large c.f.s.e. advantage of the Cu^{II}–Cu^{III} couple, ligands of greater electron-donor properties than polyamines are expected to stabilize Cu^{III}. It is comforting that the ligand L^9, which has the same framework as cyclam, but in which two amine nitrogen atoms have been replaced by two deprotonated amido-groups, forms, at a moderately positive potential (0.65 V *vs.* s.c.e.), a copper(III) complex which is stable in water for hours.[12]



An opposite strategy should be followed in order to obtain solution-stable copper(I) complexes. Destabilization of the bivalent state will provoke an easier attainment of the copper(I) state. Therefore, the ligand structure should deviate as much as possible from that of the 14-membered symmetric ligand. The present work shows that the most favourable situation is obtained on expanding the tetra-aza ring to 16 members. Recent work from this laboratory [8] has stressed the role of the π-acceptor properties of the macrocycle in the stabilization of Cu^I. The present work indicates that another factor, the ligand's flexibility, may operate in the same sense, also in complete absence of π effects.

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