Electrochemical Behaviour of Complexes of Copper(II) with 14-Membered Saturated Tetra-aza Macrocycles

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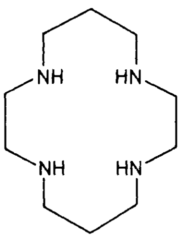
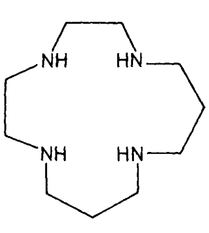
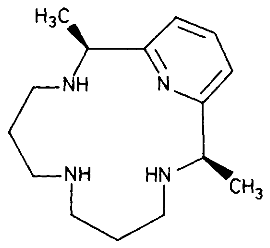
The electrochemistry of copper(II) with three 14-membered saturated tetra-aza macrocyclic ligands (L) is reported. Both anodic and cathodic electrode processes involve complicated mechanisms; nevertheless cyclic voltammetry at high potential scan rates allowed evaluation of the $E_{\frac{1}{2}}$ values for the couples $[CuL]^{3+}$–$[CuL]^{2+}$ and $[CuL]^{2+}$–$[CuL]^{+}$. Reduction and oxidation mechanisms have been studied and the half-life of the species $[CuL]^{3+}$ anodically electrogenerated has been evaluated. The thermodynamic data are discussed.

BIVALENT transition-metal cations form stable complexes with tetra-aza macrocycles, which in most cases exhibit a tetragonal stereochemistry where the metal ion and the four nitrogen atoms are coplanar. These macrocyclic complexes often undergo one-electron oxidation and reduction to produce oxidation states (I and III) which show unusual kinetic and thermodynamic stability.[1] The most well known case is that of nickel(II), for which stable and persistent $[Ni^{III}(macrocycle)]^{3+}$ and $[Ni^{I}(macrocycle)]^{+}$ complexes have been chemically or electrochemically generated in acetonitrile solution.[2,3] Due to the electrochemically reversible nature of the Ni^{III}–Ni^{II} and Ni^{II}–Ni^{I} redox systems, voltammetric techniques allow evaluation of the relative $E_{\frac{1}{2}}$ values. With the reasonable assumption that the diffusion coefficients of the oxidized and reduced forms are very similar, thermodynamic arguments can be advanced on the basis of the $E_{\frac{1}{2}}$ values, which can be related to ligand structural parameters such as ring size and degree of unsaturation. Detailed redox studies have also been reported for macrocyclic tetramine complexes of iron[4] and cobalt.[5] For copper,[6] in contrast to the numerous reports on the macrocyclic complexes of the bivalent ion, there have been few reports on the I and III oxidation states. Work on the formation of copper(I) and/or copper(III) complexes with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene,[7,8] and a pulse-radiolysis study on copper-(II) and -(III) 1,4,8,11-tetra-azacyclotetradecane (L^1),[9] have recently been reported.

We report here an electrochemical investigation on copper complexes with three 14-membered tetra-aza macrocycles: L^1 (cyclam), the prototype of the cyclic tetramines in the sense that it forms more stable complexes with bivalent 3*d* cations (both from a thermodynamic[10] and a kinetic[11] standpoint), can be more easily prepared,[12] and allows the easiest attainment of the highest oxidation states;[13] L^2 = 1,4,7,11-tetra-azacyclotetradecane (isocyclam), which exhibits a different sequence of the five- and six-membered fused chelate rings (5,5,6,6) with respect to cyclam (5,6,5,6) resulting in formation of co-ordinative bonds of reduced strength[14] and which is expected to influence redox behaviour; and L^3 = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene.


L^1


L^2



L^3

The techniques employed were cyclic voltammetry and controlled-potential coulometry, with the aim of obtaining thermodynamic data and, whenever possible, to throw light on the mechanisms of the electrode processes involved. Cyclic voltammetry at different potential scan rates has again been shown to be a particularly useful technique in studies of this type, allowing one to check the existence of short-lived species, as well as to study the kinetics of the chemical reactions involving them. Moreover, regarding thermodynamic studies, quite a few electrode processes which appear complicated when studied with conventional dropping mercury electrode (d.m.e.) polarography or voltammetry with periodical renewal of the diffusion layer, appear as uncomplicated electrode charge transfers in the time-scale appropriate to cyclic voltammetry at high potential scan rates.

EXPERIMENTAL

Materials.—The acetonitrile solvent was purified by repeatedly distilling reagent grade acetonitrile (Carlo Erba) from phosphorus pentaoxide; it was stored on 0.3-nm molecular sieves (Union Carbide). The supporting electrolyte tetraethylammonium perchlorate (Carlo Erba) was dried in a vacuum oven and used without further purification. Bis(η-cyclopentadienyl)iron(II) (ferrocene) (Alfa Products) was used as a standard to evaluate the number of electrons involved in the electrode processes occurring on the voltammetric time-scale. The macrocyclic ligands L^1—L^3 were prepared according to reported procedures (L^1, ref. 15; L^2, ref. 14; L^3, refs. 14 and 16). Copper complexes were obtained as perchlorates, by mixing hot equimolar solutions of $Cu[ClO_4]_2{\cdot}6H_2O$ and of the macrocycle. The complexes were recrystallized from methanol and gave satisfactory analyses.

Nitrogen (99.99%), previously equilibrated to the vapour pressure of MeCN, was employed to remove the oxygen from the tested solutions.

Apparatus.—In all the voltammetric experiments a P.A.R. model 170 Electrochemistry System was used as a polarizing unit; the recording devices were either a Houston Instruments model 2000 XY recorder or, for potential scan rates higher than 0.5 V s^{-1}, a Hewlett-Packard model 1123A storage oscilloscope. Cyclic voltammetric tests were performed either with a platinum or with a gold sphere freshly covered with mercury, as the working microelectrode, surrounded by a platinum-spiral counter electrode. The potential of the working microelectrode was probed by a Luggin capillary reference electrode compartment.

Controlled-potential electrolyses were performed in a H-shaped cell with anodic and cathodic compartments, separated by a sintered glass disc. The working electrode was either a platinum gauze or a mercury pool; in both cases the counter electrode was a mercury pool. In these tests an Amel model 551 potentiostat, with an associated Amel model 558 integrator, was used.

The potentiometric acid–base titration employed a Metrohm E 360 digital pH-meter, equipped with a Metrohm EA 147 combined electrode assembly; a standard solution of sodium methoxide in methanol was added to the electrolysed solutions by means of a Metrohm E 402 microburette.

In all voltammetric tests an aqueous saturated calomel electrode (s.c.e.) was used as reference electrode; unless otherwise specified, the reported potential values refer to it. However, in order to eliminate the effect of variable diffusion potentials at the aqueous–non-aqueous interface the $E_{\frac{1}{2}}$ values of the redox couples, when possible, are referred to the $E_{\frac{1}{2}}$ of the ferrocenium–ferrocene couple, obtained from voltammetric tests under the same experimental conditions.

All experiments were carried out at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

Electrochemical Reduction.—The cathodic reduction of $[CuL^3]^{2+}$ on a platinum electrode in MeCN solution takes place *via* two steps, as shown in the cyclic voltammogram (Figure 1). By reversing the potential scan, after traversing peak A alone, a very small stripping peak, C, is noted, attributable to the oxidation of deposited copper metal.[17] This peak is greatly enhanced if the cathodic scan is reversed beyond peak B. Controlled-potential coulometric tests at the platinum working macroelectrode polarized in correspondence to peak A led to a consumption of 2 mol of electrons per mol of starting compound. Quantitative deposition of copper metal on the electrode surface took place. The same result is obtained by electroreducing the starting solution at a potential corresponding to peak B.

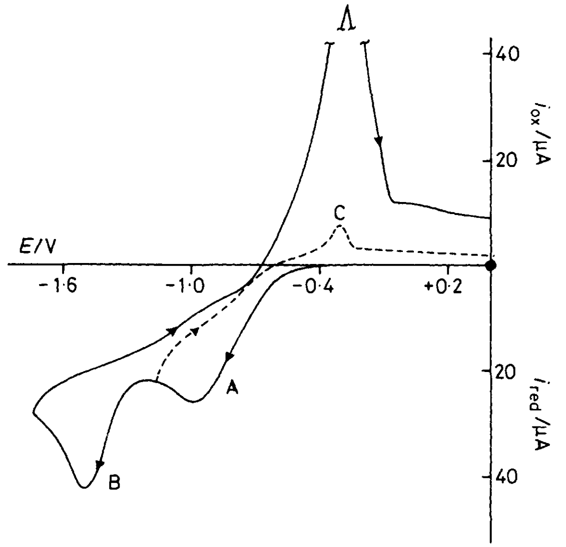
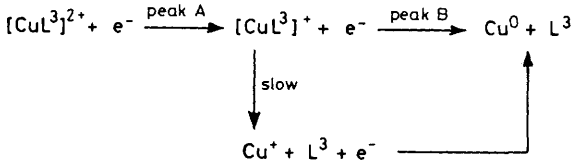


FIGURE 1 Cyclic voltammetric curves recorded on a MeCN solution containing $[CuL^3]^{2+}$ (2.56×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}) with a platinum working microelectrode; scan rate 0.2 V s^{-1}. Cathodic scan

Taking into account that the reduction potential of free copper(I) ions is anodic with respect to peak A,[17] these results suggest the reduction pathway shown in the Scheme. Cyclic voltammetric tests performed at



SCHEME

different scan rates, *v*, in the range 0.02—50 V s^{-1} indicated the irreversible nature of the two subsequent charge transfers. Moreover, the current peak ratio $(i_p)_A/(i_p)_B$ is only very slightly higher than unity at the lowest scan rates. This implies that the decomposition reaction of $[CuL^3]^+$ occurs only to a minor extent on the voltammetric time-scale, in agreement with the low height of peak C after traversing peak A alone. Although thermodynamic arguments are prevented by the irreversible nature of the charge transfers, it does not seem correct to hypothesize a disproportionation reaction of $[CuL^3]^+$ to $[CuL^3]^{2+}$ and $[CuL^3]$,[7,18] which in turn decomposes to give copper metal, in view of the quantitative deposition of copper on the electrode surface and of the independence of the voltammetric data on the depolarizer concentration.

The reduction of $[CuL^3]^{2+}$ on the mercury electrode also involved two subsequent steps; cyclic voltammetry indicates two cathodic peaks very close to each other ($E_p = -0.65$ V and -0.81 V respectively, at $v = 0.2$ V s^{-1}) but unlike the behaviour on the platinum electrode, the charge transfer which occurs at the less negative potential is characterized by a higher degree of reversibility, as shown by the appearance of an anodic peak directly associated with the cathodic one. Although an accurate analysis of the cyclic voltammetric data is prevented by the closeness of the two reduction peaks, in the likely hypothesis that the charge-transfer coefficient, α, of the process $[CuL^3]^{2+} + e^- \rightleftharpoons [CuL^3]^+$ ranges between 0.3 and 0.7,[19] it is possible to evaluate approximately the $E_{\frac{1}{2}}$ value for the couple $[CuL^3]^{2+}$–$[CuL^3]^+$ to be -0.62 V.

The cathodic reduction of $[CuL^2]^{2+}$ in MeCN solutions at a platinum electrode, like that of $[CuL^3]^{2+}$, proceeded through two subsequent one-electron steps, which in cyclic voltammetry gave rise to two distinct reduction peaks ($E_p = -0.96$ and -1.34 V respectively at $v = 0.2$ V s^{-1}). The only difference with respect to $[CuL^3]^{2+}$ is the partially reversible character of the first charge transfer on the platinum electrode; an anodic peak is directly associated with the cathodic one. Cyclic voltammetric tests at different scan rates are in accord with a first charge transfer, quasi-reversible in character, which leads to a species irreversibly reducible at the more cathodic peak. In addition, the decomposition of $[CuL^2]^+$ occurs only to a minor extent on the voltammetric time-scale. To a good approximation, the $E_{\frac{1}{2}}$ value for the couple $[CuL^2]^{2+}$–$[CuL^2]^+$ can be evaluated as -0.81 V (-1.17 V *vs.* ferrocenium–ferrocene).

At the mercury electrode the reduction process also involves two subsequent steps ($E_p = -0.86$ and -1.05 V respectively, at $v = 0.2$ V s^{-1}), but an accurate analysis of the cyclic voltammetric data cannot be performed owing to the irreproducibility of the voltammograms due to electrode poisoning by adsorption phenomena.

The complex $[CuL^1]^{2+}$ in MeCN solutions undergoes a reduction process at the platinum electrode which, like the previous cases, takes place *via* two subsequent one-electron steps, both irreversible in character. The corresponding cyclic voltammetric picture is qualitatively similar to that in Figure 1 ($E_p = -1.10$ and -1.34 V at $v = 0.2$ V s^{-1}). On the mercury electrode the cathodic reduction of $[CuL^1]^{2+}$ differs from those of $[CuL^3]^{2+}$ and $[CuL^2]^{2+}$, involving a single two-electron charge transfer ($E_p = -0.94$ V at $v = 0.2$ V s^{-1}). The difference in behaviour on different electrode materials can be explained by assuming a different degree of reversibility of the one-electron charge transfers. The $E_{p/2} - E_p$ and $\partial E_p/\partial \log v$ values both agree with a two-electron process, the first electron transfer being the rate-determining step with the usual α value of 0.5.[20] The dependence of the degree of reversibility of the first reduction step on the electrode material for all the studied complexes suggests that the charge transfer occurs *via* an inner-sphere mechanism.[21]

Electrochemical Oxidation.—The cyclic voltammetric curve recorded for $[CuL^1]^{2+}$ in MeCN solution with a platinum electrode by scanning the potential initially in the anodic direction is shown in Figure 2 (full line). It shows an anodic peak D, with a directly associated cathodic one E.

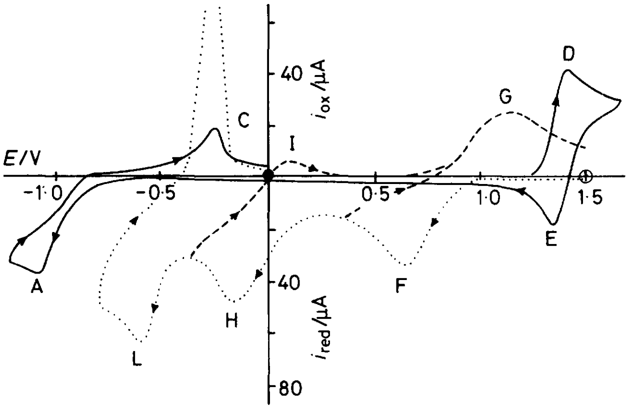


FIGURE 2 Cyclic voltammetric responses obtained from a MeCN solution containing $[CuL^1]^{2+}$ (2.78×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}) (——); after exhaustive anodic oxidation at +1.5 V (· · · ·). Platinum working micro-electrode. Starting potentials: ●, for the anodic scan; ○, for the cathodic scan

Controlled-potential coulometric tests at +1.5 V show that the anodic process involves the overall consumption of 6 mol of electrons per mol of starting compound. The complicated nature of the oxidation process is supported by cyclic voltammetric data at different potential scan rates. By comparison with the one-electron oxidation of ferrocene, it can be deduced that the oxidation of $[CuL^1]^{2+}$ is an uncomplicated one-electron process only at scan rates higher than 5 V s^{-1} when the cathodic to anodic peak current ratio $(i_p)_E/(i_p)_D = 1$. In addition, in the potential scan rate range 5—20 V s^{-1} the parameters $[(E_p)_D - (E_p)_E]$ and $[(E_p)_D - (E_{p/2})_D]$ assume the values typical of a one-electron reversible charge transfer, while at higher scan rates they indicate the incompletely reversible character of the charge transfer.

At scan rates lower than 5 V s^{-1} the $(i_p)_D/v^{\frac{1}{2}}$ ratio progressively increases, and the $(i_p)_E/(i_p)_D$ ratio decreases, with decreasing v; at the lowest scan rate (0.02 V s^{-1}), $(i_p)_D/v^{\frac{1}{2}}$ almost doubles, but $(i_p)_E/(i_p)_D$ is still equal to 0.6, indicating that the species primarily electrogenerated, $[CuL^1]^{3+}$, undergoes a chemical reaction leading to the formation of species which are further oxidized according to a complicated electrode mechanism. The overall electrode process does not involve a simple electron transfer–chemical reaction–electron transfer (e.c.e.) mechanism; more than one chemical reaction must be coupled to more than two subsequent electrode charge transfers. This is not surprising in view of the coulometric results. In the hypothesis that when the

$(i_p)_E/(i_p)_D$ ratio is only a little lower than unity, a simple e.c.e. mechanism involving two one-electron charge transfers is operative, the experimental responses at suitable scan rates have been compared with the theoretical ones computed by means of a digital simulation technique.[22,23] A half-life of *ca.* 7 s could be evaluated for the species $[CuL^1]^{3+}$ initially formed at the electrode. That further charge transfers do not occur in the voltammetric time span has been confirmed by the fact that a very similar half-life value could be obtained on the basis of the theoretical trend of the ratio $(i_p)_E/(i_p)_D$ as a function of log $k\tau$, τ being the time spent in going from $E_{\frac{1}{2}}$ to the switching potential, for a mechanism in which an irreversible first-order chemical reaction follows a reversible charge transfer.[24] Values of $(i_p)_D$ and the current at the switching potential could be computed within a reasonable approximation from the current function values at scan rates high enough that the electrode process consisted of an uncomplicated one-electron charge transfer.

Cyclic voltammetric experiments on solutions from exhaustive electrolysis at +1.5 V indicate the presence of three cathodic peaks, F, H, and L, each having a directly associated anodic peak (Figure 2, dotted line). The peaks F,G and L,C are attributable to the redox couples for uncomplexed Cu^{II}–Cu^{I} and Cu^{I}–Cu^{0} respectively.[17] The peak potentials of the system H,I are the same as those of the couple H^+–H_2,[25] in agreement with the acidic character of the electrolysed solution. Potentiometric acid–base titration shows the presence in solution of 6 mol of hydrogen ions per mol of starting compound. Subsequent reduction coulometric tests on the oxidized solution in correspondence to peaks F, H, and L indicate the consumption of 1, 2, and 1 mol of electrons per mol of starting compound, respectively. During the electrolysis at peak H, gas generation at the electrode surface could be observed; electrolysis at peak L led to the quantitative electrodeposition of copper metal.

All the electrochemical and acid–base titration data indicate that the six-electron oxidation process leads to the formation of six protons (only two coming from a strong acid) and the quantitative release of copper(II) ions. In aqueous solution the oxidation of $[CuL^1]^{2+}$ occurs *via* a four-electron process with the plausible formation of the corresponding diene complex of copper(II);[9] hence it is likely that in MeCN solutions a further unsaturation centre forms, leading to a species which undergoes solvolysis with ring opening and release of the copper(II) ion.

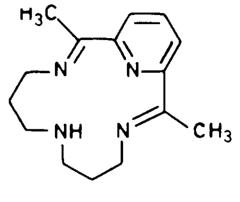
On the basis of cyclic voltammetric data at scan rates 5—20 V s^{-1} it is possible to calculate an $E_{\frac{1}{2}}$ value of +0.99 V *vs.* ferrocenium–ferrocene for the couple $[CuL^1]^{3+}$–$[CuL^1]^{2+}$. Cyclic voltammetry and controlled-potential electrolyses of $[CuL^2]^{2+}$ in MeCN solutions gave results similar to those obtained for $[CuL^1]^{2+}$ solutions. The electrode oxidation appears as an uncomplicated reversible one-electron process in the potential scan rate range 0.5—10 V s^{-1}. An $E_{\frac{1}{2}}$ value of +1.03 V *vs.* ferrocenium–ferrocene can be computed for the couple $[CuL^2]^{3+}$–$[CuL^2]^{2+}$. Under the same assumptions, computations similar to those reported previously for $[CuL^1]^{3+}$ allow evaluation of the half-life of the species $[CuL^2]^{3+}$ to be *ca.* 60 s.

The complex $[CuL^3]^{2+}$ also undergoes a single oxidation process, which in cyclic voltammetry appears as an uncomplicated one-electron quasi-reversible charge transfer at scan rates higher than 10 V s^{-1}. The voltammetric responses, mis-shapen and less reproducible than the previous ones, do not allow an accurate estimation of the half-life of the species $[CuL^3]^{3+}$, permitting one to conclude only that it is slightly less stable than $[CuL^1]^{3+}$.

Controlled-potential coulometric tests indicate an overall consumption of 4 mol of electrons per mol of starting compound.

In cyclic voltammetry the $i_p/v^{\frac{1}{2}}$ ratio increases as v decreases for $v < 10$ V s^{-1}, and at the lowest scan rates it assumes values more than twice that at the highest scan rates. These data, together with the coulometric result, indicate that the electrode mechanism involved is very complicated.

It has been possible to check the presence of 4 mol of hydrogen ions per mol of starting complex in the electrolysed solution, as well as to ascertain the occurrence of the quantitative release of free copper(II) ions as a consequence of the oxidation process. If one considers that the diene of L^3, *i.e.* L^4, forms stable complexes with copper(II) ($E_{\frac{1}{2}} = -0.47$ V for $[CuL^4]^{2+}$–$[CuL^4]^+$ in MeCN),[26] it must be concluded that the exhaustive anodic oxidation of $[CuL^3]^{2+}$ does not lead to the formation of the corresponding diene complex, but probably to open-chain products which release the copper(II) ions.



L^4

In the likely hypothesis (supported by a cathodic to anodic peak-current ratio of one at high enough scan rates) that the charge transfer $[CuL^3]^{2+} \xrightarrow{-e^-} [CuL^3]^{3+}$ proceeds with an α value of *ca.* 0.5, an $E_{\frac{1}{2}}$ value of +1.23 V *vs.* ferrocenium–ferrocene can be computed. The values of $E_{\frac{1}{2}}$ for the redox couples $[CuL]^{3+}$–$[CuL]^{2+}$ and $[CuL]^{2+}$–$[CuL]^+$ are summarized in the Table.

Half-wave potential values (V) for the redox couples $[CuL]^{3+}$–$[CuL]^{2+}$ and $[CuL]^{2+}$–$[CuL]^+$

Complex	$[CuL]^{2+}$–$[CuL]^+$		$[CuL]^{3+}$–$[CuL]^{2+}$	
$[CuL^1]^{2+}$			$+1.35$ [a]	$+0.99$ [b]
$[CuL^2]^{2+}$	-0.81 [a]	-1.17 [b]	$+1.40$ [a]	$+1.03$ [b]
$[CuL^3]^{2+}$	-0.62 [a]		$+1.60$ [a]	$+1.23$ [b]

[a] *versus* s.c.e. [b] *versus* ferrocenium–ferrocene.

CONCLUSIONS

The copper(III) macrocyclic complexes studied are much less stable than the corresponding nickel(III) species: they are formed at potentials *ca.* 0.4 V more positive than those of nickel and persist in solution only for short times, as shown by the cyclic voltammetric experiments. Conversely, nickel(III) macrocyclic tetramine complexes can be prepared in anhydrous MeCN solution through oxidation at a platinum anode [2] or by $[NO][BF_4]$ [13] and remain in solution for hours. The greater oxidizing power of copper(III) compared to nickel(III) complexes essentially reflects the higher value of the third ionization energy of the elements ($I_3 = 36.83$ eV for Cu, 35.16 eV for Ni);* it appears that the disadvantage experienced by copper with respect to nickel in the gas-phase (+2)–(+3) redox process ($\Delta I_3 = 1.6$ eV) is reduced to one-fourth on complexation by the macrocycle and dissolution in MeCN. This behaviour should reflect the greater gain in crystal field stabilization energy (c.f.s.e.) experienced in a d^9–d^8 change rather than in a d^8–d^7 in complexes of tetragonal stereochemistry;[27] for ligands of pronounced σ-donor properties, *e.g.* some deprotonated tetrapeptides, the c.f.s.e. gain for copper is large enough to more than compensate the I_3 disadvantage, and the copper(III) complex is formed at a less positive potential than the nickel(III) analogue (and is stable for days in solution).[28] The trend of the $E_{\frac{1}{2}}$ values ($L^1 < L^2 < L^3$) for the Cu^{III}–Cu^{II} couple is the same as found for the Ni^{III}–Ni^{II} couple.[14]

It is noteworthy that opposite trends have been found for the enthalpy of formation of $[Cu(macrocycle)]^{2+}$ and for the energy of the *d–d* absorption band of the same complex,[29] *i.e.* the exothermicity (expressed by $-\Delta H^{\ominus}$) of complex formation and the $\nu(d\text{–}d)$ parameter decrease along the series $L^1 > L^2 > L^3$; these two parameters must be considered as proportional to the in-plane Dq [which directly reflects the strength of the copper(II)–macrocycle interactions].[30] On the other hand, the trivalent metal complex, due to its increased electrical charge, has a Dq which is considerably larger than that of the bivalent species: it is this enhanced stabilization that makes easier the access to the trivalent state for complexes in which strong in-plane interactions are present. A linear inverse correlation between $E_{\frac{1}{2}}(M^{III}$–$M^{II})$ and the Dq^{xy} value has been found for high-spin octahedral nickel(II) complexes with a complete series of tetra-aza macrocycles.[31]

Nickel(II) complexes with the same 14-membered ligands exhibit an electrochemically reversible one-electron reduction leading to a stable authentic nickel(I) (d^9) complex, at a potential range of -1.1 to -1.4 V.[14] Considering the values for the gas-phase process ($I_2 = 20.29$ eV for Cu, 18.15 eV for Ni) one would expect easier formation of the univalent complex for copper than for nickel. In the case in which it has been possible to extract $E_{\frac{1}{2}}$ values, II–I redox change occurs at a potential which is considerably less negative than for the corresponding nickel complexes; however, the copper(I) species produced show an extremely low stability with respect to the release of copper(I) ions, which are further reduced to metal. This apparently anomalous behaviour with respect to nickel could be explained by considering that the Ni^{II}–Ni^{I} redox change involves two transition cations (d^8–d^9) which profit in terms of the c.f.s.e. of the co-ordination mode of the macrocycle, which offers its four donor atoms in a fixed and rigid array, *i.e.* at the corners of a square. On the other hand, the d^9 copper(II) cation is reduced to the non-transitional d^{10} copper(I), which cannot profit to any extent by the stereochemical features presented by the ligand and which therefore must offer a very weak resistance both to dissociation and to further reduction.

As to the complexes for which an $E_{\frac{1}{2}}$ value can be estimated, the reduction is easier (*i.e.* the $E_{\frac{1}{2}}$ value is less negative) with L^3 than with the structural analogue L^2. In this connection one must consider that substitution of an sp^3 amine nitrogen atom by a pyridine nitrogen atom weakens the copper(II)–ligand interactions, destabilizing the bivalent state and favouring access to copper(I).

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.