Oxidation and Reduction Behaviour of Copper(II) Complexes with Open-chain Analogues of Tetra-aza Macrocycles

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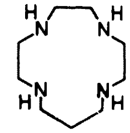
The oxidation and reduction behaviour in acetonitrile solution of the copper(II) complexes with a series of linear tetra-amines of varying chain length has been investigated by electrochemical techniques. Copper(III) tetra-amine complexes were found to persist in solution only on the time-scale of the cyclic voltammetry experiment, whereas fairly stable Cu^{I} complexes were obtained in the case of both the shortest- and the longest-chain tetra-amine ligands investigated. $E_{\frac{1}{2}}$ values for both the $Cu^{III} \longrightarrow Cu^{II}$ and the $Cu^{II} \longrightarrow Cu^{I}$ redox changes have been compared with those reported for corresponding complexes with closed-chain tetra-amines (macrocycles) in order to explore the existence of a 'macrocyclic effect'.

The introduction in co-ordination chemistry of tetra-aza macrocycles has disclosed in the past decade new perspectives in the area of the redox chemistry of transition metal complexes.[1] The incorporation of a cation in a closed co-ordinative framework allows the attainment of unusually high and low oxidation states, as solution-stable complexes. An important example is tetra-aza macrocyclic nickel(II) complexes, which in MeCN solution undergo both chemical and electrochemical one-electron oxidation and reduction to give stable authentic Ni^{III} and Ni^{I} complexes.[2,3] This type of stabilization is believed to be kinetic in nature, resulting by the trapping effect exerted by the cyclic ligand, which makes the redox activity of the encircled cation (towards solvent molecules or impurities) much slower. On the other hand, the extreme inertness of 3*d* cation macrocyclic complexes, for instance towards acid attack, is well known and documented.[4]

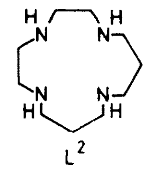
We have recently investigated [5,6] the oxidation and reduction behaviour in MeCN solution of copper(II) complexes with a complete series of saturated tetra-aza macrocycles of varying ring size (from 13- to 16-membered: L^1—L^4). In contrast to the nickel analogues, Cu^{III} and Cu^{I} complexes with the above ligands are unstable even in anhydrous acetonitrile, undergoing redox processes and demetallation through complicated mechanisms. However, cyclic voltammetric investigations showed reversible or quasi-reversible one-electron redox processes both in the oxidation and in the reduction scan. Therefore univalent or trivalent copper tetra-aza macrocyclic complexes persist in solution on the time-scale of the cyclic voltammetry experiment and their solution stability, relative to the reference divalent state, is expressed by the $E_{\frac{1}{2}}$ value associated with the quasi-reversible redox change. It was found that $E_{\frac{1}{2}}$ values for both $Cu^{III} \longrightarrow Cu^{II}$ and $Cu^{II} \longrightarrow Cu^{I}$ processes are strongly dependent upon the macrocyclic ring size. This was interpreted in terms of matching of the structural features of the ligand (cavity size, relative positions of donor atoms, flexibility) and the stereochemical requirements of the incorporated cation in the appropriate oxidation state.

We are now extending this type of study to copper(II) complexes with linear tetramines of varying length and consequently different co-ordinating tendencies, L^5—L^8. These ligands can be considered as the open-chain precursors of the previously considered macrocycles L^1—L^4.[5,6]

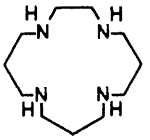
The aim of this work is to evaluate whether and to what extent the oxidation and reduction behaviour of metal complexes of a multidentate amine is affected by the cyclic or non-cyclic nature of the chelating agent. Much work has been done in the past decade to compare divalent 3*d* metal complexes (*e.g.* Ni^{II}, Cu^{II}) with cyclic and open-chain tetra-amines, from the point of view of both the kinetic and the thermodynamic aspects. A substantially different behaviour of cyclic and non-cyclic ligand complexes was ascertained and the much greater stability (both kinetic and thermodynamic) of closed-chain complexes was ascribed to a *macrocyclic effect*.[7,8] This work possibly explores the existence of a macrocyclic effect in the redox behaviour of Cu^{II} tetra-amine complexes.



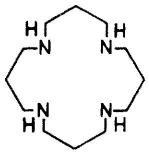
L^1



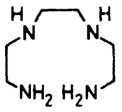
L^2



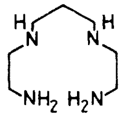
L^3



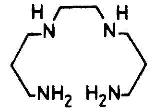
L^4



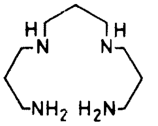
L^5



L^6



L^7



L^8

Table 1. Electrochemical results for cathodic and anodic processes of copper(II) complexes with open-chain tetra-amines: potential values (V) *vs.* ferrocenium–ferrocene in MeCN solution [a]

System	$E_{\frac{1}{2}}([CuL]^{2+}-[CuL]^+)$	$E_p([CuL]^+-[CuL])$ Hg	$E_p([CuL]^+-[CuL])$ Pt	$E_{\frac{1}{2}}([CuL]^{3+}-[CuL]^{2+})$	$t_{\frac{1}{2}}[CuL]^{3+}$/s
$[CuL^5]^{2+}$	−0.88	−1.14	−1.37	+1.07	0.6
$[CuL^6]^{2+}$	−1.0 [b]	−1.06	−1.31	+1.09	1.9
$[CuL^7]^{2+}$	−1.0 [b]	—	—	+1.05	1.8
$[CuL^8]^{2+}$	−0.79	−1.03	−1.42	+1.1	—

[a] Where not specified, redox potentials are taken from the c.v. scan at a platinum microelectrode. [b] The coupled $[CuL]^+ \rightarrow [CuL]$ process prevents an accurate determination of the potential.

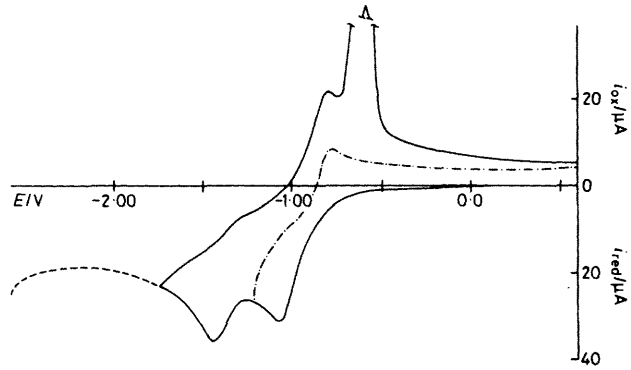


Figure 1. Cyclic voltammetry profiles of an MeCN solution of $[CuL^5][ClO_4]_2$ (1.72×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}), obtained with a platinum working microelectrode. Cathodic scan; potential scan rate 0.2 V s^{-1}

Experimental

Apparatus and Materials.—The electrochemical apparatus, as well as purification of the solvent and supporting electrolyte, has been described previously.[5] A saturated calomel electrode was used as a reference; in order to eliminate variable diffusion potentials at the aqueous–non-aqueous interface of the aqueous calomel reference electrode, ferrocene was used as an internal standard. Potential values in this paper are referred to the ferrocenium–ferrocene redox couple.

Ligands and Copper(II) *Complexes.*—Commercially available L^5 (triethylenetetramine, Fluka Purum) was distilled twice at reduced pressure. L^6, L^7, and L^8 were obtained from the reaction of the appropriate dibromoalkane with a 1 : 8 excess of the appropriate diamine, according to the procedure described by Barefield *et al.*[9] The copper(II) complexes were obtained by mixing hot equimolar solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and of the tetramine in ethanol. They were recrystallized from MeOH and gave satisfactory elemental analyses. **CAUTION**: Perchlorate salts of metal–polyamine complexes can be explosive and must be handled with care: such compounds should not be heated as solids.

Results and Discussion

Electrochemical Reduction.—As in the case of copper(II) complexes with saturated polyaza macrocycles,[5,6] the copper(II) complexes under study are electroreducible both at platinum and mercury electrodes in MeCN solution. The cyclic voltammetric cathodic response at a platinum electrode of a solution of $[CuL^5]^{2+}$ is reported in Figure 1 as a typical example. By comparison with the one-electron oxidation of a ferrocene solution, the cathodic process occurring on the cyclic voltammetric time-scale has to be assigned, to a first approximation, to the two successive one-electron reduction steps in equation (1).

$$[CuL^5]^{2+} + e^- \rightleftharpoons [CuL^5]^+ + e^- \rightleftharpoons [CuL^5] \quad (1)$$

It can be easily observed that the $[CuL^5]^+$ complex is stable on the time-scale of the cyclic voltammetric experiment, while the $[CuL^5]$ species tends to decompose to copper metal, as confirmed by the presence of the stripping peak in the reverse scan. The analysis of the cyclic voltammetric responses at scan rates, v, varying from 0.02 to 2 V s^{-1} (at higher scan rates the responses became ill defined) indicates that the first cathodic step involves a charge transfer with a rather low degree of reversibility ($\Delta E_p = 350$ mV at $v = 0.2$ V s^{-1}), while the more cathodic step is totally irreversible in character.

The cyclic voltammetric behaviour at a mercury electrode parallels that at platinum electrodes, but the first cathodic process is noticeably more reversible ($\Delta E_p = 90$ mV at $v = 0.2$ V s^{-1}); it can be followed at scan rates up to 100 V s^{-1} and the second step is observed closer to the first (see Table 1). In addition, it can be more easily deduced that the first step does not involve a simple one-electron charge transfer, but it is probably complicated by a slow following chemical reaction of the catalytic type; in fact, at $v = 0.05$ V s^{-1} the i_p^a/i_p^c ratio is unity and the $i_p^a/v^{\frac{1}{2}}$ ratio is constant, while at $v = 0.02$ V s^{-1} the i_p^a/i_p^c ratio is 0.85 and the $i_p^a/v^{\frac{1}{2}}$ ratio is higher than the value at $v = 0.05$ V s^{-1}. The formal electrode potential for the redox couple $[CuL^5]^{2+}$–$[CuL^5]^+$, calculated as the average of the cathodic and anodic peak potentials, was found to be −0.88 V.

Controlled-potential coulometric experiments have been performed both at a platinum macroelectrode and at a mercury pool. The closeness of the two cathodic steps at mercury electrodes allowed us to determine only the overall number of electrons per molecule of starting complex involved in the cathodic process; this number was equal to two, confirming the results of the cyclic voltammetry (c.v.) studies. At the end of the electrolysis, the presence of a black precipitate was observed at the mercury pool, while in the solution the presence of free amine was verified both by the basicity and by cyclic voltammetry tests at a mercury electrode; in fact, it is known that L^5 gives rise to an anodic process at a formal potential of −0.6 V, due to the formation of mercury(II)–amino complexes derived from the anodic dissolution of the electrode itself.[10] On the other hand, the use of a platinum macroelectrode allowed us to follow step-by-step the cathodic process on the electrolysis time-scale. At a working potential of −1.14 V only one mole of electrons per mole of $[CuL^5]^{2+}$ was consumed. The solution, initially deep blue, became colourless, being highly sensitive to air; c.v. tests revealed the presence of the one-electron reduced species; no copper metal was electrodeposited. Adjusting the potential to −1.44 V, one further mole of electrons per mole of starting complex flows and a black deposit appears on the platinum electrode.

The electrode mechanism involved in the reduction process of $[CuL^5]^{2+}$ can therefore be summarized as in equation (2).

$$\begin{array}{ccccc} [CuL^5]^{2+} + e^- & \rightleftharpoons & [CuL^5]^+ & + e^- \rightleftharpoons & [CuL^5] \\ & & \Big\downarrow \text{slow} & & \Big\downarrow \text{slow} \\ & & \text{unknown} & & Cu^0 + L^5 \end{array} \quad (2)$$

From a qualitative point of view, the same electrochemical trend has also been found for the cathodic reduction of

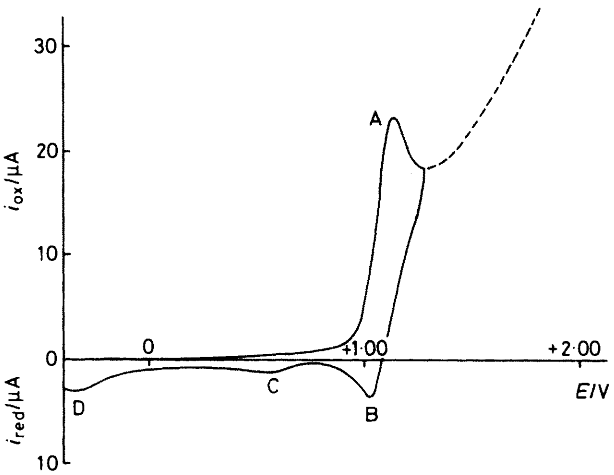


Figure 2. Cyclic voltammetry profiles of an MeCN solution of $[CuL^5][ClO_4]_2$ (1.72×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}), obtained with a platinum working microelectrode. Anodic scan; potential scan rate 0.2 V s^{-1}

$[CuL^8]^{2+}$. A somewhat different pathway has been obtained for the electroreduction of $[CuL^6]^{2+}$ and $[CuL^7]^{2+}$. In the case of the $[CuL^6]^{2+}$ complex, c.v. profiles obtained at the platinum electrode show two one-electron steps, still separated, even if very close to each other. However, with a mercury electrode the two cathodic peaks coalesce into a two-electron single one. In the case of $[CuL^7]^{2+}$, the cathodic process appears in c.v. as a single two-electron peak both at platinum and mercury electrodes. The above mentioned different degree of reversibility of the two steps as a function of electrode material may account for this trend, and it can be discussed either in terms of an inner-sphere electrode mechanism[11] or through the formation of stable mercury intermediates at the mercury electrode surface.[12]

In the cases of $[CuL^6]^{2+}$ and $[CuL^7]^{2+}$ it was impossible to obtain the corresponding copper(I) complexes by controlled-potential coulometry, either at platinum or mercury electrodes. In both cases, two moles of electrons per mole of starting complex were consumed. The formation of a black precipitate occurred, coupled to the liberation of free amine from the decomposition of the complex.

The electrode potentials for the above reported reduction processes are summarized in Table 1.

Electrochemical Oxidation.—The copper(II) complexes investigated undergo anodic oxidation processes at platinum electrodes. The anodic c.v. response of a $[CuL^5]^{2+}$ solution is illustrated in Figure 2. The analysis of the process occurring in correspondence to peak A as a function of the scan rate could be performed only at scan rates up to 5 V s^{-1}; at higher scan rates the response becomes ill defined. As in the case of tetra-aza macrocyclic complexes with copper(II),[5,6] the trends of i_p^c/i_p^a and $i_p^a/v^{\frac{1}{2}}$ ratios indicates that an electron transfer–chemical reaction–electron transfer type mechanism is operative.[13] At the highest reliable scan rate of 5 V s^{-1}, the i_p^c/i_p^a ratio reaches the value of 0.9, indicating that the complications following the first one-electron charge transfer are almost overcome. This enabled us to determine the formal potential for the $[CuL^5]^{3+}$–$[CuL^5]^{2+}$ redox couple, which was calculated to be +1.07 V.

Table 2. $E_{\frac{1}{2}}$ values (V) for the Cu^{II}–Cu^{I} and Cu^{III}–Cu^{II} redox couples for copper(II) complexes with open-chain and macrocyclic tetra-amines

System	$E_{\frac{1}{2}}(Cu^{II}$–$Cu^{I})$ [a]	$E_{\frac{1}{2}}(Cu^{III}$–$Cu^{II})$ [a]	$t_{\frac{1}{2}}([CuL]^{3+})$/s
$[CuL^5]^{2+}$ [b]	−0.88	+1.07	0.6
$[CuL^6]^{2+}$ [b,c]	−1.0	+1.09	1.9
$[CuL^7]^{2+}$ [b,c]	−1.0	+1.05	1.8
$[CuL^8]^{2+}$ [b]	−0.79	+1.1	—
$[CuL^1]^{2+}$ [d]	−1.06	+1.00	3
$[CuL^2]^{2+}$ [d]	−1.17	+1.03	60
$[CuL^3]^{2+}$ [d]	−0.99	+1.12	38
$[CuL^4]^{2+}$ [d]	−0.75	+1.23	3

[a] *vs.* ferrocenium–ferrocene. [b] This work. [c] The coupled $[CuL]^+ \longrightarrow [CuL]$ process prevents an accurate determination of the $E_{\frac{1}{2}}(Cu^{II}$–$Cu^{I})$ value. [d] Ref. 6.

Figure 2 also shows that irreversible, ill defined oxidation processes occur at potentials more positive than peak A; these processes can be ascribed to the ligand itself. Controlled-potential coulometric experiments show peaks C and D to be attributable to the reduction of Cu^{2+} ions and hydrogen ion respectively, released by the oxidation of the starting complex. In these coulometric tests, performed at +1.07 V, after the consumption of two moles of electrons per mole of $[CuL^5]^{2+}$, the electrolysis current abruptly drops to about one tenth of the initial value and holds this value up to the overall consumption of two moles of electrons; the current drops again; but still it remains higher than the background current, showing the complexity of the underlying electrode mechanism. However, as previously demonstrated,[5,6] it seems plausible to assume that on the cyclic voltammetric time-scale, a simple electron transfer–chemical reaction mechanism occurs, in which a first-order chemical reaction follows a reversible one-electron charge transfer. This enabled us to evaluate the half-life of the $[CuL^5]^{3+}$ species primarily electrogenerated:[14] it was 0.6 s. Potentiometric acid–base titrations on the electrolyzed solutions, made after the consumption of two moles of electrons per mole of starting complex, showed the presence of two moles of H^+. This behaviour was previously ascertained for closed-chain tetra-amine complexes and was associated with the oxidation of the ligand framework, probably to give an unsaturated system.[6]

Qualitatively, all the other copper(II) tetra-amine complexes studied follow the same type of electrode oxidation processes described for $[CuL^5]^{2+}$, except $[CuL^8]^{2+}$, where the oxidation process, formally attributable to the Cu^{2+} centre, is not sufficiently distinct from that of the ligand. This prevented the determination of the half-wave potential value. Table 1 summarizes the significant electrochemical parameters for the anodic behaviour of all the complexes investigated.

Ligand Effects on the Redox Behaviour: Macrocycles and Open-chain Analogues.—The $Cu^{II} \longrightarrow Cu^{I}$ *redox change.* The one-electron first reduction step, which is ascribed to a Cu^{II}–Cu^{I} change, shows a reversible behaviour (in particular at the mercury electrode). The $E_{\frac{1}{2}}$ (Cu^{II}–Cu^{I}) values, reported in Table 2, are noticeably dependent upon the structural features of the tetra-amine. This behaviour is shown in Figure 3, in which $E_{\frac{1}{2}}$ values are plotted *vs.* the 'ligand length', *i.e.* the number of atoms (C and N) forming the chain. It is seen that the more difficult reduction processes (corresponding to a more negative electrode potential) occur with tetra-amines of intermediate length (L^6 and L^7) whereas in the case of the shortest (L^5) and longest (L^8) ligands the attainment of the Cu^{I} state is much easier. The observed stability difference is confirmed by bulk electrolysis studies (at the platinum electrode): solution-stable $[CuL]^+$ species are obtained after consumption of one electron with both L^5 and L^8; on the contrary, $[CuL^6]^{2+}$ and $[CuL^7]^{2+}$ complexes undergo a two-electron process. A fairly similar

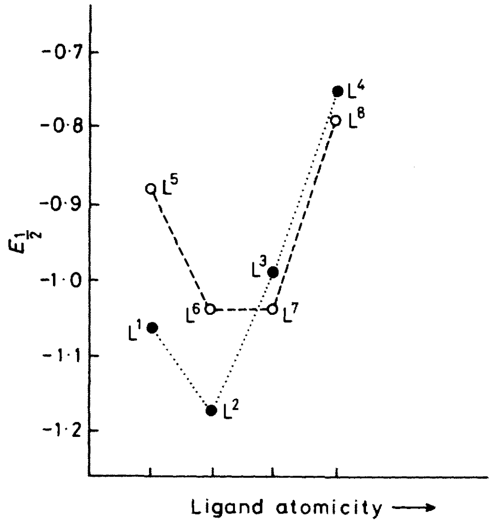


Figure 3. Plot of $E_{\frac{1}{2}}([CuL]^{2+}-[CuL]^{+})$ values (V) for open-chain (○) and macrocyclic tetra-amines (●) *vs.* ligand atomicity (number of carbon and nitrogen atoms in the chain or ring)

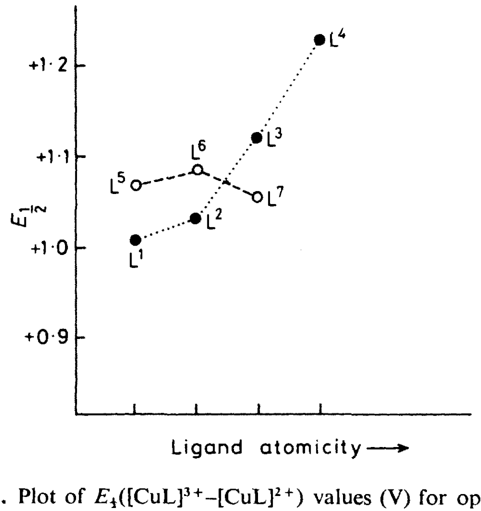


Figure 4. Plot of $E_{\frac{1}{2}}([CuL]^{3+}-[CuL]^{2+})$ values (V) for open-chain (○) and macrocyclic tetra-amines (●) *vs.* ligand atomicity (number of carbon and nitrogen atoms in the chain or ring)

behaviour has been observed [5,6] with corresponding complexes of cyclic tetra-amines of varying chain length. The $E_{\frac{1}{2}}$ (Cu^{II}–Cu^{I}) *vs.* ligand atomicity plot (see Figure 3) for macrocyclic complexes is reminiscent of that found for open-chain analogues, in the sense that the more difficult reduction process to the Cu^{I} species occurs with the intermediate size ligand L^2 and both shortening and lengthening of the aliphatic chain makes the redox change remarkably easier. In particular, fairly stable $[CuL]^{+}$ species were prepared through controlled-potential electrolysis in the case of the larger ligands L^3 and L^4.[5,6]

To a first approximation, the relative solution stability of the Cu^{II} and Cu^{I} tetra-amine complexes is dominated by the ability of the ligand to establish strong in-plane interactions, according to a square-coplanar co-ordination arrangement (which strongly stabilizes the transition metal cation Cu^{II}, d^9). L^6 and L^7 are ideally suited to form strong Cu^{II}–N bonds, as shown for instance by the high value of the frequency of the *d–d* band ($\nu_{d\text{-}d}$), an empirical parameter which is strictly related to the Dq^{xy} value [15] ($[CuL^6]^{2+}$, 18 940; $[CuL^7]^{2+}$, 18 400 cm^{-1}). The large ligand-field stabilization effect makes particularly difficult the electron uptake to give Cu^{I}, which is a d^{10}, 'non-transition' metal cation. On the contrary, this process is favoured for complexes with L^5 and L^8 which are too small and too large, respectively, properly to dispose their donor atoms in the sites required by Cu^{II} (the corners of a square) and to establish strong Cu^{II}–N interactions ($\nu_{d\text{-}d}$: $[CuL^5]^{2+}$, 17 240; $[CuL^8]^{2+}$, 16 750 cm^{-1}). Similar considerations can be proposed to explain the behaviour of tetra-aza macrocyclic complexes of varying ring size. For both open-chain and cyclic ligand complexes, least-negative potentials are observed with the largest tetra-amines, L^8 and L^4, in which the nitrogen atoms are connected by trimethylene chains. Morever, easier reduction has been shown to occur with the closed-chain system than with the open-chain analogue.

The Cu^{III} ⟶ Cu^{II} *redox change.* In Table 2 are reported the values of $E_{\frac{1}{2}}$ associated with the Cu^{III} ⟶ Cu^{II} redox change for complexes of both open-chain and cyclic tetra-amines. C.v. studies performed at varying potential scan rates have enabled us to evaluate the life-time of the Cu^{III} species. In Table 2 $t_{\frac{1}{2}}$ values of open-chain complexes are compared with those for corresponding macrocyclic systems. It is seen that open-chain Cu^{III} complexes are considerably less resistant with respect to the following chemical reaction than macrocyclic species. In particular, the most kinetically stable (towards redox decomposition) macrocyclic species, *i.e.* the intermediate-size ligand complex $[CuL^2]^{3+}$, has a half-life of the order of minutes, rather than a few seconds or less.

Ligand structure effects on the thermodynamic aspects of the Cu^{III} ⟶ Cu^{II} redox change are considered in Figure 4, in which $E_{\frac{1}{2}}$ values are plotted *vs.* ligand atomicity. Comparison of Figures 3 (Cu^{II} ⟶ Cu^{I} redox change) and 4 (Cu^{III} ⟶ Cu^{II} redox change) first indicates that the reduction process is much more influenced by the structural features of the ligand (*i.e.* length of the chain) than the Cu^{II} oxidation process. Moreover, it would appear from Figure 4 that the attainment of the trivalent state with open-chain tetra-amines is more or less independent of the ligand size, whereas, in the case of macrocycles, it becomes increasingly difficult on progressive expansion of the cavity. This state of affairs could be interpreted considering that the Cu^{II} ⟶ Cu^{III} oxidation process (from a d^9 cation to a d^8 cation, probably of the low-spin type) involves a drastic decrease of the ionic radius. Therefore, during the process, the ligand is forced to contract the co-ordination cavity in order to bring the nitrogen donor atoms to the new, shorter bond distances. This process should be quite easy for an open-chain, flexible tetra-amine, irrespective of its length, but, for steric reasons, it must be remarkably more difficult for a macrocycle if it has a cavity too large to fit the Cu^{III} ion. It is probably this unfavourable energy contribution (essentially of steric origin) that makes the Cu^{II} ⟶ Cu^{III} redox change for macrocyclic complexes remarkably selective with respect to the ligand size.

In conclusion, this study has shown that, in the formation of a highly charged transition metal complex, such as that of Cu^{III}, a *macrocyclic effect* exists, in the sense that the reactivity of the macrocyclic complex is reduced, allowing a longer persistence in solution, with respect to the corresponding species with open-chain analogues. Moreover, the structure of the ligand may have important effects on the trend of the $E_{\frac{1}{2}}$ values for a given redox change, but this essentially reflects the ability of the ligand to adapt itself to the stereochemical requirements of the $M^{(n+1)+}$ and M^{n+} cations involved. The cyclic or non-cyclic nature of the ligand may or may not favour the process, according to the particular co-ordination situation.

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Received 1*st August* 1983; *Paper* 3/1340