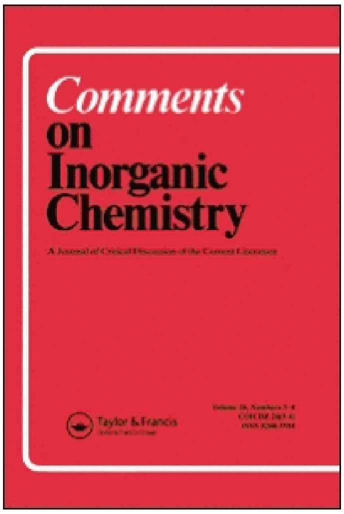

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The Stabilization of High Oxidation States of Metals Through Coordination by Poly-aza Macrocycles

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To cite this Article Fabbrizzi, Luigi(1985) 'The Stabilization of High Oxidation States of Metals Through Coordination by Poly-aza Macrocycles', Comments on Inorganic Chemistry, 4: 1, 33 — 54
To link to this Article: DOI: 10.1080/02603598508072251
URL: http://dx.doi.org/10.1080/02603598508072251

The Stabilization of High Oxidation States of Metals Through Coordination by Poly-aza Macrocycles

The incorporation of a transition metal ion into a poly-aza macrocyle favors the access to unusually high oxidation states (e.g., Ni^{III}, Cu^{III}). The tendency to stabilize trivalent cations, which is expressed by the value of the potential of the M^{III}/M^{II} redox couple, is regulated by the structural features of the macrocycle (ring size, number and type of the donor nitrogen atoms). In general, formation of trivalent complexes is favored by strong equatorial interactions and the Cu^{II}/Cu^{III} oxidation process profits from the ligand–field contribution to a larger extent than does the corresponding Ni^{II}/Ni^{III} process. The solvent may profoundly influence the M^{III}/M^{II} redox change through axial coordination of one of the redox-active macrocyclic complexes.

The classical approach to the investigation of a given chemical function is to study a class of compounds which display such a function, and to try to modulate that function through synthetic modifications of the compounds, looking for structure/function relationships. For instance, people interested in the redox chemistry of transition metal ions would profit very much from the study of the oxidation and reduction behavior of metal complexes of synthetic poly-aza macrocycles: in fact, for a given metal, the number of oxidation states that are stable in solution is extended from one (or rarely two) for the solvated ion to three and even four for the macrocyclic complexes. Moreover, the electrode potential associated with each $M^{(n+1)+}/M^{n+}$ redox couple can be varied over a substantial range through modifications of the ligand framework, which may involve changing the nature of the donor nitrogen atoms, the ligand's denticity, the size of the macrocyclic hole, the degree of unsaturation, and the presence of substituents. Furthermore, the investigated function (i.e., the ox-

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Comments Inorg. Chem.
1985, Vol. 4, No. 1, pp. 33–54
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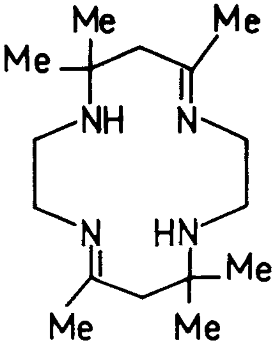
idizing or reducing tendencies of the metal ion) can be related to the stereochemical features of the complex and to its bonding parameters.

In this Comment we will try to illustrate this type of approach, taking some examples mainly from our more recent work on the thermodynamic aspects of the redox chemistry of poly-aza-macrocyclic complexes of 3*d* metal ions.

The chemistry of synthetic tetra-aza macrocycles and of their metal complexes began to develop in the early 1960's essentially due to the contribution of Busch and Curtis.[1] In 1967 Curtis reported that, by treatment with nitric acid of the Ni^{II} complexes of both the *meso* and *d,l* forms of the saturated tetra-aza macrocycle **2**, stable olive-green Ni^{III} complexes could be isolated.[2] This was the very first report on one of the special properties displayed by tetra-aza macrocycles, i.e., the ability to stabilize unusually high oxidation states of the incorporated metal ion. Whereas Curtis was not interested in further developing this topic, a few years later Olson and Vasilevskis, in a couple of classical papers, reported the redox chemistry of divalent nickel[3] and copper[4] complexes of the tetra-aza macrocycles **1** and **2**, describing in particular the electrochemical generation of the Ni^{III} and Cu^{III} complexes in acetonitrile solution. The redox chemistry of 3*d* metal complexes and tetra-aza macrocycles was also considered in the same years by Endicott.[5] In the same period, Margerum, performing solution chemistry studies on the Cu^{II} complexes of **2**, recognized two more very important solution properties of macrocyclic complexes: the extreme inertness towards demetallation (*the*



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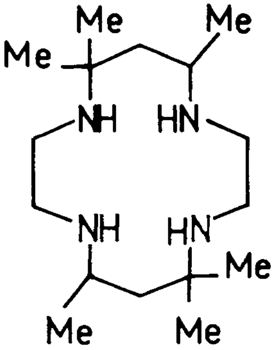

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kinetic macrocyclic effect),[6] and the unusually large thermodynamic stability when compared to that of noncyclic analogs (*the thermodynamic macrocyclic effect*).[7]

It is now clear that the stabilization of high oxidation states of the central metal ion results from the combined contribution of both thermodynamic and kinetic effects: (i) the strong coordinative interactions exerted by the cyclic ligand raise the energy of the antibonding level (essentially metallic in character) from which the electron is abstracted (*thermodynamic contribution*); (ii) the oxidized cation is trapped inside the ligand's closed framework and its reactivity towards reducing substrates (including the solvent) is drastically reduced, so that it can persist in solution for a relatively long time (up to years; *kinetic contribution*). One could reasonably remark that this latter effect should also operate in the sense of the stabilization of unusually low oxidation states: as a matter of fact, Co^I,[5,8,9] Ni^I,[3,10–12] and Cu^I tetra-aza macrocyclic complexes,[4,13,14] electochemically generated in solution, are stable enough to permit characterization and reactivity studies.

In this Comment we will restrict the discussion to the high oxidation state redox chemistry, in particular focusing our attention on the Ni^{III} and Cu^{III} complexes. Nevertheless, the macrocycle promoted attainment of unprecedented high oxidation states has also been reported for other metals and will probably be extended in the future with the introduction of more sophisticated and especially designed ligands. For instance, Allred[15] and Barefield[16] independently discovered the spectacular disproportionation reaction of Ag^I in the presence of a tetra-aza macrocycle, such as **2**, to produce a silver mirror and the very stable yellow Ag^{II} complex (the driving force of the process being the strong preference of transitional cations, such as the Ag^{II}, d^9, ion, towards the tetragonal stereochemistry offered by tetra-aza macrocycles). Furthermore, a labile red Hg^{III} tetra-aza macrocyclic complex (still a d^9 ion) has been characterized by cyclic voltammetry and ESR spectroscopy in propionitrile solution at low temperature.[17]

STEREOCHEMICAL CHANGES IN REDOX PROCESSES INVOLVING MACROCYCLIC COMPLEXES

To say that a transition cation is "trapped" by a poly-aza macrocycle (for instance a quadridentate ligand such as **1** or **2**) does not mean that the metal is completely shielded and isolated from the solution surrounding environment. On the contrary, solvent molecules and anions (coming for instance from the background electrolyte) may play a very important role, filling the remaining available coordination sites. Usually, redox processes of metal complexes involve substantial stereochemical changes, with release or uptake of solvent molecules or anions. For instance, in the case of nickel complexes with neutral tetra-aza macrocycles (e.g., **2**), the 2+/3+ redox change in a solvent S (e.g., CH_3CN) involves the change from a square (low-spin Ni^{II}) to an octahedral stereochemistry (low-spin Ni^{III}), with two solvent molecules participating in the half-reaction and ultimately occupying the axial positions of the Ni^{III} octahedron (Eq. 1).

$$[\mathrm{Ni(N_4\text{-}macrocycle)}]^{2+}_{(\mathrm{sq.})} + 2S = [\mathrm{Ni(N_4\text{-}macrocycle)}S_2]^{3+}_{(\mathrm{oct.})} + e^-. \qquad (1)$$

The stereochemistry of the low-spin Ni^{III} complexes was inferred for the first time by Busch[11] from the ESR spectra of the electrogenerated solutions. More recently, the x-ray structure of the Ni^{III} complex of the macrocycle **2** (*meso* form) has been reported,[18] the axial positions of the distorted octahedron being occupied by $H_2PO_4^-$ ions. Notably, the Ni^{III} (low-spin)–N(amine) distances (1.99–2.01 Å) are substantially greater than those usually observed for the Ni^{II}(low-spin)–N(amine) bond in tetramine complexes (about 1.90 Å). In other words, the removal of one electron from Ni^{II}, which occurs during the process (1), seems to involve an "expansion," rather than a "contraction" of the metal. However, the paradox is only apparent, since Ni^{II} is four-coordinated and Ni^{III} is six-coordinated, and it is known that the metal–donor atom distance depends not only upon the intrinsic ionic radius of the metal, but also on the coordination number.

Also the Cu^{II}/Cu^{III} oxidation process in macrocyclic systems involves a stereochemical change. In the case of tetra-aza ligands, the process can be represented as follows:

$$\underset{d^9,\ \text{distorted octahedral}}{[\mathrm{Cu(N_4\text{-}macrocycle)}S_2]^{2+}} = \underset{d^8,\ \text{low-spin, square}}{[\mathrm{Cu(N_4\text{-}macrocycle)}]^{3+}} + 2S + e^-. \qquad (2)$$

Unfortunately, structural data on Cu^{III} tetra-aza-macrocyclic complexes are not available. However, the x-ray structure of a Cu^{III} (low-spin) complex with a tripeptide, having a square geometry, has been recently reported.[19] Assuming that the Cu^{III} (low-spin)–N(amine) distance in the tetra-aza-macrocyclic complex is similar to that found in the tripeptide complex (1.90 Å) and considering also that the Cu^{II}–N(amine) distance in tetragonal tetramine complexes range between 2.05 and 2.10 Å, it should be concluded that the Cu^{II}/Cu^{III} oxidation process involves a drastic reduction of the size of the metal. Notice that in this case the Cu^{II}/Cu^{III} redox change involves a decrease of the coordination number of the metal (from "4 + 2" to 4).

EFFECT OF LIGAND STRUCTURE ON THE FORMATION OF Ni^{III} AND Cu^{III} POLYAMINE COMPLEXES

A primary structural parameter that controls the access to the trivalent state of the encircled metal is the size of the macrocyclic hole.[20] In Fig. 1 a complete series of saturated tetra-aza macrocycles of atomicity ranging from 12 to 16 (ligands **3–8**) is considered. The $E_{1/2}$ values measured in acetonitrile for the Ni^{III}/Ni^{II} redox change in the complexes with the above tetra-aza ligands are reported in the diagram in Fig. 2. The diagram shows how selective the Ni^{II}/Ni^{III} oxidation process is with respect to the ring size of tetra-aza macrocycles. The easiest attainment of the Ni^{III} state, expressed by the less positive value of $E_{1/2}$, occurs with the 14-member macrocycle **5** (known as *cyclam*), whereas both contraction and progressive expansion of the ring make the access to trivalent nickel more and more difficult.[21] It is disappointing that, due to the electrochemically irreversible nature of the redox change,[22] the $E_{1/2}$ value for the 13-member ligand complex is not available, and the Ni^{III} stabilizing ability by the 13-member cavity cannot therefore be evaluated (the comparison of the 13- and 14-member ring effects on the Ni^{III}/Ni^{II} redox couple potential has been made possible by the macrocycles described in the next paragraph). Moreover, there is evidence that the selectivity of the oxidation behavior of Ni^{II} tetra-aza-macrocyclic complexes is not a simple matter of ring size. Actually, in spite of the fact that the two 14-member macrocycles **5** (*cyclam*, forming a 5,6,5,6-sequence of chelate rings) and **6** (*isocyclam*, 5,5,6,6-sequence)

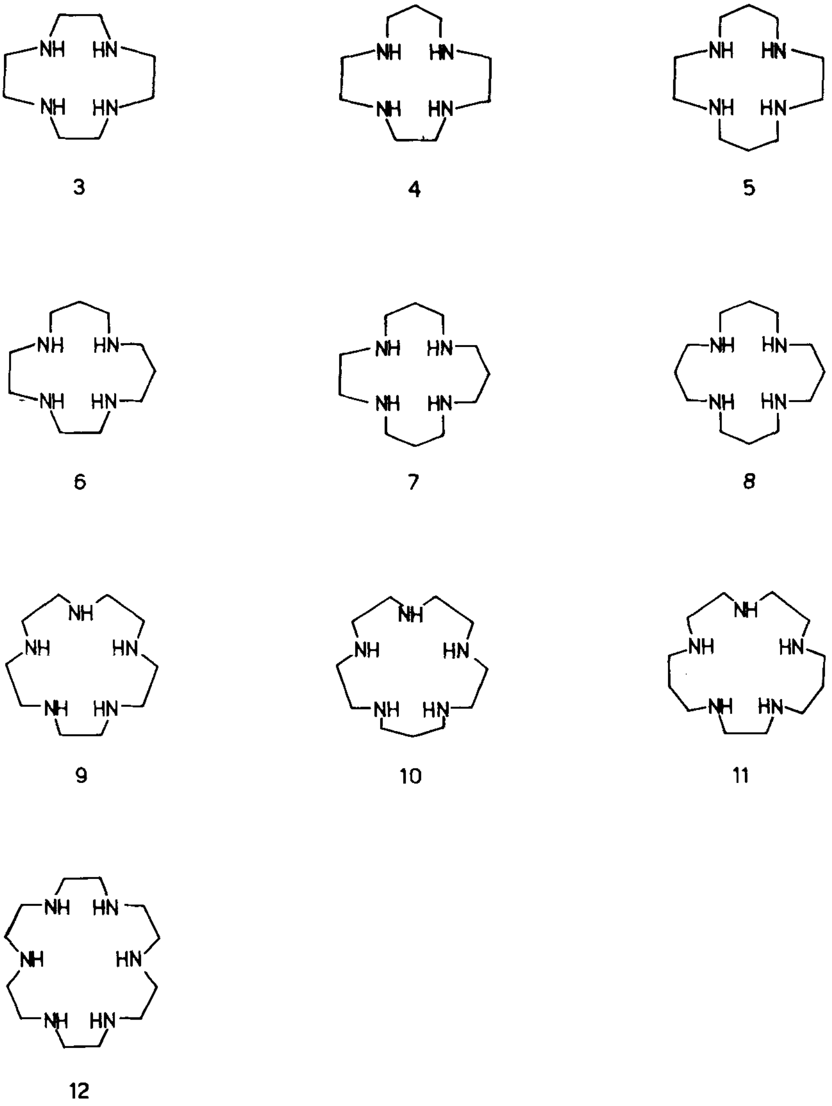


FIGURE 1 Saturated poly-aza macrocycles of varying ring size and denticity, used in the investigation of the Ni^{III}/Ni^{II} and Cu^{III}/Cu^{II} redox changes in acetonitrile solution.

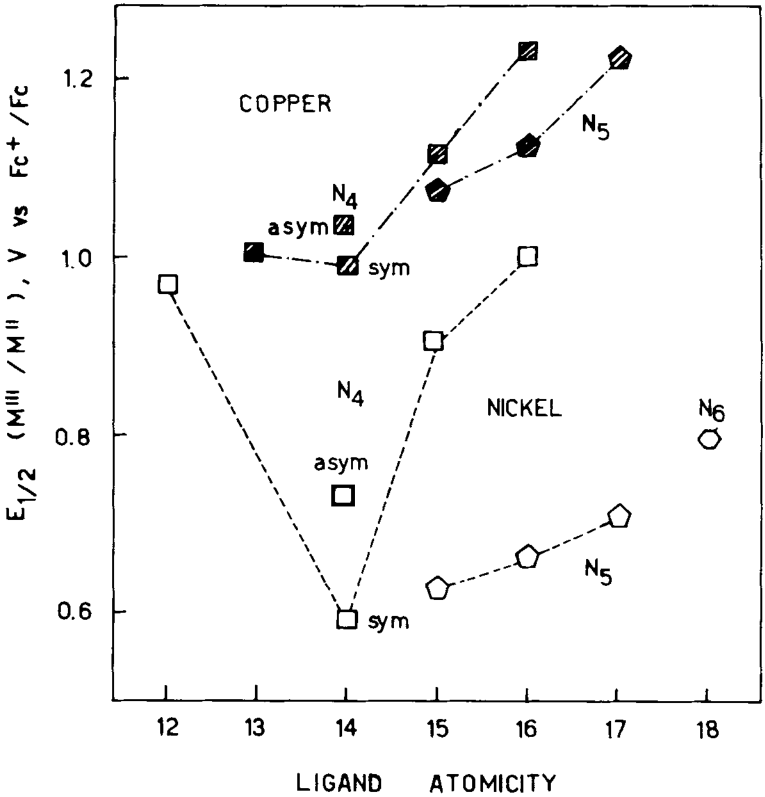


FIGURE 2 Ring size effect on the potential of the M^{III}/M^{II} redox change for the nickel and copper complexes of *n*-dentate macrocycles ($n = 4, 5, 6$). $E_{1/2}$ values measured in acetonitrile solution (0.1 M Et_4NBF_4), at 25 °C.

are likely to have the same ring amplitude, their Ni^{II} complexes present a distinct oxidation behavior.[23] In particular, the formation of the $Ni(cyclam)^{3+}$ complex is markedly favored (by 140 mV, see Fig. 2) with respect to $Ni(isocyclam)^{3+}$. This indicates that not only ring size, but also the geometrical arrangement of the donor set is a determining parameter for the stabilization of Ni^{III}.

Some help in understanding the origin of the above effects is given by the diagram in Fig. 3, which presents an inverse linear relationship between $E_{1/2}(Ni^{III}/Ni^{II})$ and the bonding parameter Dq^{xy}, obtained for the Ni^{II}, high-spin, *trans*-octahedral complexes: the stronger the in-plane Ni^{II}–N interactions, the easier the oxidation to the trivalent

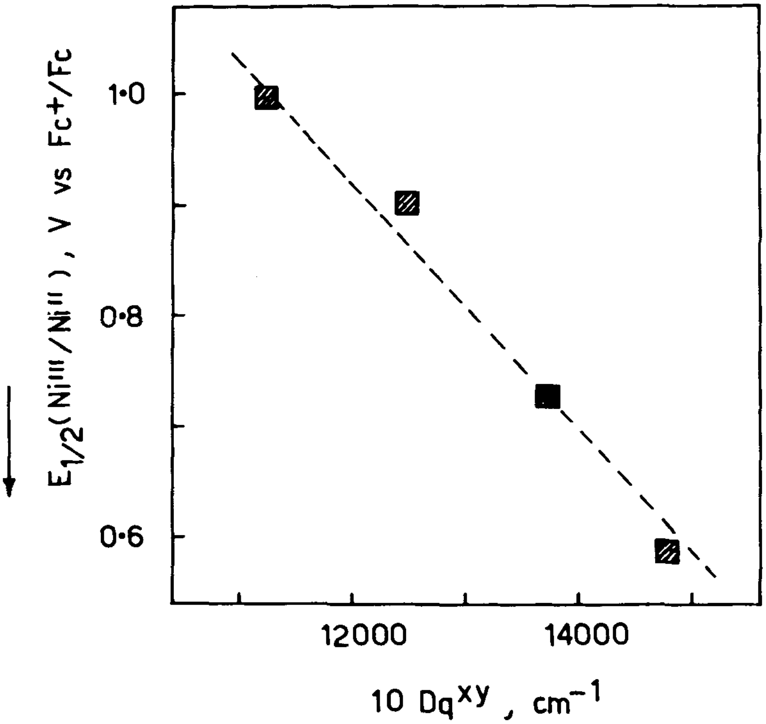


FIGURE 3 Correlation of the potentials of the Ni^{III}/Ni^{II} redox couple in acetonitrile solution with the $Dq^{xy}(Ni^{II})$ values, for complexes of tetra-aza macrocycles of atomicity ranging from 14 to 16. $Dq^{xy}(Ni^{II})$ values, obtained from *trans*-octahedral high-spin chloride complexes at 77 K, are taken from Refs. 23 and 24. Data refer to the ligands: **8**, **7**, **6** and **5** in Fig. 1, in order of decreasing $E_{1/2}$ values.

species. This behavior can be explained considering that strong equatorial interactions raise the energy of the "redox orbital" $(x^2 - y^2)$ and make easier the abstraction of the electron from Ni^{II}. Among the investigated tetra-aza macrocycles, cyclam (**5**) is the champion, since it is able to better satisfy the stereochemical preferences of the central cation (to have the four donor atoms at the corners of a square, at the right distances) and to establish strong coordinative bonds. The other 14-member macrocycle, isocyclam (**6**), could have the appropriate ring size, but, probably due to the steric repulsions between the adjacent interfering trimethylenic chains, the N_4 arrangement deviates from the metal-preferred square geometry. Moreover, the 15- and 16-member macrocycles (**7** and **8**) have a cavity size too large to properly fit the divalent cation and to establish strong in-plane interactions.

At this stage, the problem of finding a ligand able to favor the Ni^{II}/Ni^{III} oxidation process has simply become the problem of finding a ligand able to strongly coordinate the Ni^{II} ion. Furthermore, the consideration that the low-spin Ni^{II} ion prefers an octahedral stereochemistry indicated that a ligand able to span by its amine donor atoms all the sites of the octahedron could favor the Ni^{II}/Ni^{III} oxidation process, and suggested the use of macrocycles having one or two more nitrogen atoms in the ring.

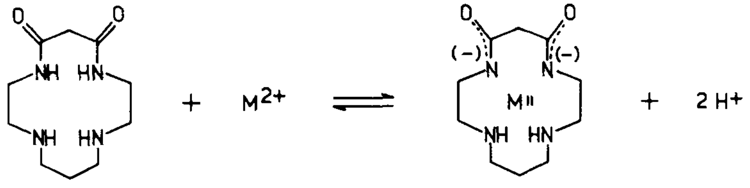
In this connection, three penta-aza macrocycles of varying atomicity (from 15 to 17; ligands **9**, **10** and **11** in Fig. 1) were designed as candidates to further stabilize Ni^{III}.[22] In fact, fairly stable low-spin Ni^{III} complexes of octahedral stereochemistry can be generated through oxidation of the corresponding high-spin Ni^{II} complexes in CH_3CN (the sixth coordination site being occupied by a solvent molecule). However, electrochemical investigation showed that quinquedentate macrocycles are less successful than cyclam in stabilizing Ni^{III}, even if they do a better job than the remaining tetra-aza ligands (see $E_{1/2}$ values in Fig. 2). Probably, apical coordination by the fifth nitrogen atom generates steric constraints in the ligand framework, which disturb in-plane interactions. Moreover, it is possible that the contrasting effects of apical and equatorial coordination balance themselves, so that the ring-size-dependent oxidation selectivity almost disappears.

In the case of the sexidentate macrocycle **12**,[22] steric constraints produce a spectacular stereochemical consequence: the ligand is fully coordinated in both Ni^{II}(high-spin) and Ni^{III}(low-spin) octahedral complexes, but the trivalent species presents the rare *compressed octahedral* stereochemistry . In this case, too, the advantage expected from the axial binding is cancelled out by the presumably severe deviations from the correct coordination sites, induced by strain: in fact, the $E_{1/2}(Ni^{III}/Ni^{II})$ value for the hexa-aza-macrocyclic complex (see Fig. 2) is remarkably more positive than for the penta-aza macrocycles and also for the two 14-member tetra-aza ligands.

In the case of copper complexes the 2+/3+ oxidation process is expected to occur at a substantially more positive potential than observed for nickel, simply considering the M^{II}/M^{III} process for the gaseous ions (I_3(Cu): 36.83 V; I_3(Ni): 35.16 V). As a matter of fact, the much lower solution stability of Cu^{III} macrocyclic complexes with respect to the corresponding Ni^{III} complexes is demonstrated by a simple experiment: controlled potential electrolysis, using a platinum gauze as an anode, of an acetonitrile solution of the Ni^{II} complex of one of the poly-aza macrocycles of Fig. 1 generates, according to a one-electron process, the Ni^{III} complex (in most cases of green color), which lasts in solution for hours or more. The same experiment, carried out on a Cu^{II} analogous complex, causes liberation of Cu^{II}, fragmentation of the macrocycle, and release of protons, according to a multi-electron process.[25] This behavior can be explained by postulating a first one-electron step in which Cu^{II} is oxidized to Cu^{III}, and a second one, in which the trivalent metal ion oxidizes the ligand through a complicated process. However, cyclic voltammetry experiments performed at very high potential scan rate (> 5 V s^{-1}) have made it possible to isolate the first step, which involves the reversible one-electron oxidation of the metal center.[26] This has permitted the determination of the $E_{1/2}(Cu^{III}/Cu^{II})$ values for poly-aza-macrocyclic complexes which are shown in Fig. 2. To a first approximation, the Cu^{II}/Cu^{III} oxidation process displays the same pattern of ring-size-dependent selectivity observed with nickel. The analogy is not surprising, if one considers that all the ions involved in the Cu^{III}/Cu^{II} and Ni^{III}/Ni^{II} redox couples have a strong preference for tetragonal stereochemistry and impose on the ligands very similar coordination modes. Moreover, comparison of $E_{1/2}$ values shows that formation of Cu^{III} complexes is disfavored with respect to the formation of corresponding Ni^{III} complexes from a thermodynamic point of view, as already anticipated on the basis of the I_3 values. However, the difference of the $E_{1/2}(M^{III}/M^{II})$ values for the complexes of a given macrocycle (0.2–0.5 V) is substantially reduced with respect to the gas-phase process ($\Delta I_3 = 1.67$ V). Therefore, coordination by the macrocycle of the gaseous metal ion (plus solvation terms) operate in favor of the stabilization of trivalent copper.

REPLACING AMINE NITROGEN ATOMS BY DEPROTONATED AMIDO GROUPS

The observation that the increase of the in-plane coordinating tendencies of the macrocycle favors the oxidation of the metal center may suggest the use of ligands of enhanced donor properties. The macrocycle reported below, **13**, the so-called *dioxocyclam*, incorporates Cu^{II} and Ni^{II} ions in aqueous solution with simultaneous deprotonation of the amido groups, to give neutral complexes which are stable over a substantial range of *p*H.[27,28] The *dioxocyclamato(2−)* framework (**14**) presents structural features very similar to *cyclam* (**5**) (being 14-membered, with the same alternating sequence of five- and six-member chelate rings), but it should exhibit enhanced coordinating tendencies, due to the presence of two deprotonated amido groups. Moreover, the doubly negative charge of the ligand should favor the achievement of the tripositive charge of the encircled cation. As a matter of fact, it has been observed[29,30] that not only [Ni^{II}(dioxocyclamato(2−))], but also [Cu^{II}(dioxocyclamato(2−))] undergoes a reversible one-electron oxidation process, to give au-



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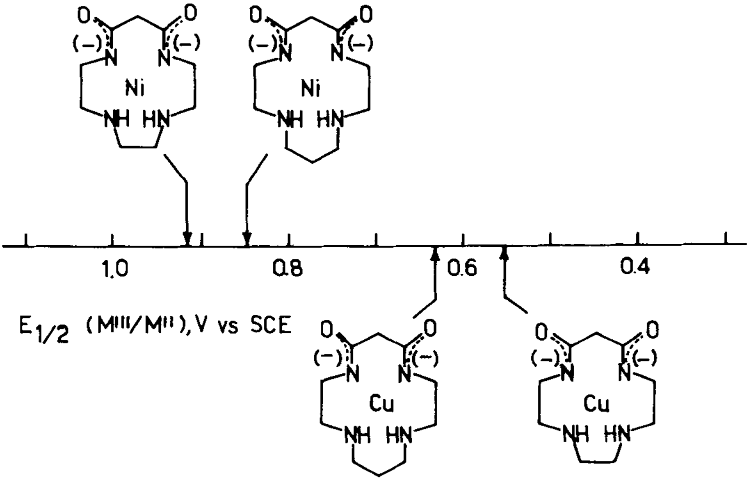

FIGURE 4 Selective stabilization of trivalent copper and nickel ions in 13- and 14-dioxocyclamato(2−) complexes. $E_{1/2}(M^{III}/M^{II})$ values measured in aqueous 3 M $NaClO_4$, at 25 °C.

thentic trivalent species, which are stable in aqueous solution. Furthermore, as shown in Fig. 4, the Cu^{II}/Cu^{III} redox change occurs at a potential substantially less positive than the corresponding Ni^{II}/Ni^{III} process,[31] inverting the "natural order," observed for polyamine complexes in CH_3CN solution. Inversion can be rationalized on the basis of the CFSE contributions to the considered redox changes.

First, the increase of the charge of the metal ion from 2+ to 3+ causes an increase of the *Dq* value, independent of the nature of the metal (this is an alternative way to explain the stabilization of high oxidation states induced by strongly coordinating ligands). Furthermore, the CFSE contribution to the redox change may be very selective, depending upon the electronic structure and the stereochemistry of the involved complexes. The appropriate CFSE diagram is reported in Fig. 5. In the case of copper, for sake of simplicity, the stereochemical arrangement of the divalent species, an axially distorted octahedron, has been extrapolated to the square. Figure 5 shows that the oxidation of the Cu^{II} complex to the Cu^{III}(low-spin) square species involves a very favorable CFSE contribution (12.28 *Dq* units), whereas the oxidation of the square low-spin Ni^{II} to the Ni^{III}(low-spin) octahedral species is disfavored (by 6.56 *Dq*). Therefore, on increasing the donating tendencies of the ligands (as occurs by replacing two amino groups by two deprotonated amido groups

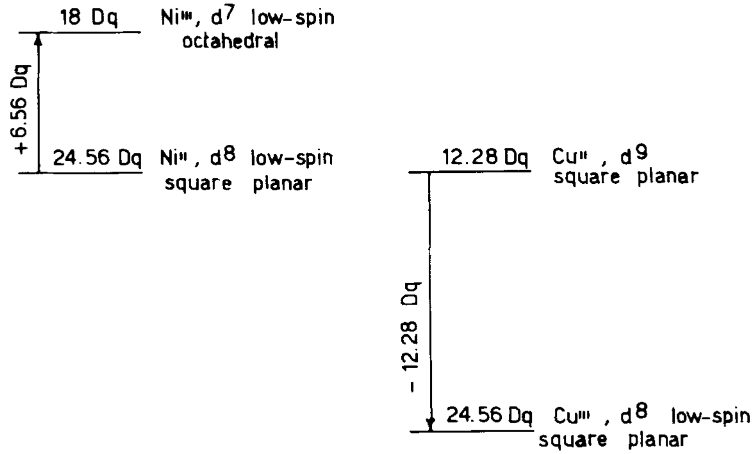

FIGURE 5 CFSE diagram for the Ni^{II}/Ni^{III} and Cu^{II}/Cu^{III} oxidation processes in tetra-aza-macrocyclic complexes.

in the framework of cyclam), the Cu^{II}/Cu^{III} oxidation process can profit from coordination to so large an extent as to regain and exceed the natural handicap suffered with respect to the Ni^{II}/Ni^{III} process.

The inverted trend of the nickel and copper M^{III}/M^{II} potentials is also displayed by the 13-member analog of dioxocyclam, as shown in Fig. 4. Moreover, data reported in this figure disclose some novel ring-size effects with 13- and 14-member macrocycles: in the case of nickel, it is the 14-member ring that favors the access to the trivalent state, compared to the 13-member ring. For copper, the opposite occurs. This behavior is probably related to the dimensions of the ions involved in the redox couples: the Cu^{II}/Cu^{III} oxidation process, which involves a drastic contraction of the metal-ion radius, is favored by the smaller 13-member ring; the Ni^{II}/Ni^{III} process, which involves an increase of the size of the metal, profits from the coordination of the larger 14-member macrocycle.

Comparison of $E_{1/2}(M^{III}/M^{II})$ values of cyclam and dioxocyclamato(2−) complexes affords the opportunity to make a direct eval-

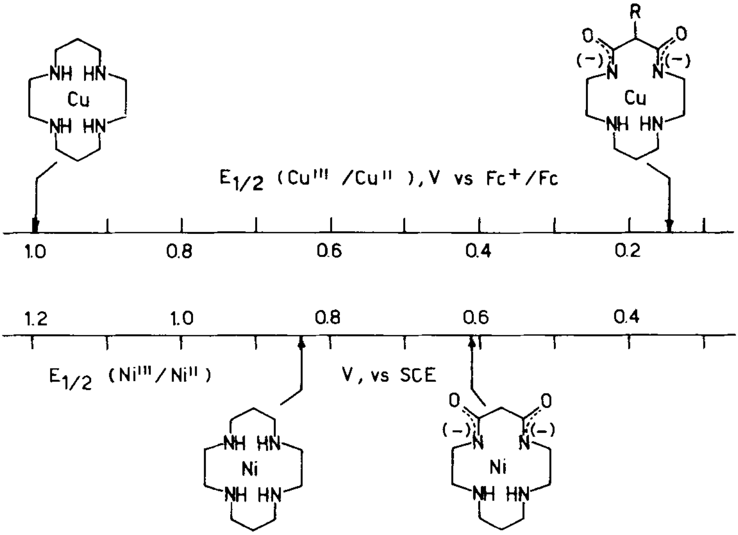

FIGURE 6 The amino group vs. the amido group in the stabilization of trivalent copper and nickel ions in tetra-aza-macrocyclic complexes. For copper, $E_{1/2}$ values refer to an acetonitrile solution, made 0.1 M in Et_4NBF_4 (the substituent R in the dioxocyclamato(2−) skeleton is $CH_2C_6H_5$); for nickel, $E_{1/2}$ values refer to a 7 M $NaClO_4$ aqueous solution.

uation of the stabilizing effect exerted by the deprotonated amido group compared to the amino group.[32] The copper data reported in the diagram in Fig. 6 refer to a CH_3CN solution, where the $Cu(cyclam)^{3+}$ complex is stable (on the time scale of the cyclic voltammetry experiment); due to the insolubility of the Cu^{II}(dioxocyclamato(2−)) species in that solvent, the soluble complex of a C-substituted dioxocyclam molecule has been considered (see Fig. 6). Indeed, a spectacular stabilizing effect is observed, the $E_{1/2}(Cu^{III}/Cu^{II})$ value measured for the dioxocyclamato(2−) complex being 840 mV less positive than for the cyclam complex. On the other hand, the stabilizing effect is much more moderate in the case of nickel (230 mV, see Fig. 6; data refer to an aqueous solution, in view of the stability in this solvent of the Ni^{III} complexes of both cyclam and dioxocyclamato(2−)). This behavior fits well with the above considerations on the selective CFSE contributions to the 2+/3+ redox change in copper and nickel complexes. Furthermore, it demonstrates that the stabilization of trivalent copper by dioxocyclamato(2−) results essentially from ligand field rather than from simple electrostatic effects (i.e., the quenching of the tripositive charge of the metal due to the complexation by the twice negatively charged ligand, which should favor the oxidation process in a nonselective way).

MEDIUM EFFECTS (SOLVENT, SUPPORTING ELECTROLYTE, ACIDITY)

The choice of the solvent is very crucial to the formation of stable highly charged species, such as Ni^{III} and Cu^{III} poly-aza-macrocyclic complexes. First, the solvent should present very low reducing tendencies, or, in the language of electrochemistry, the potential value associated with its anodic discharge should be as high as possible. The advantage of acetonitrile as solvent for the investigation of macrocyclic complexes of highly charged cations is based essentially on its relatively high oxidation limit.

Moreover, the solvent molecules may participate directly in the coordination of the macrocyclic metal complex in its oxidized and/or reduced form, occupying the vacant sites, and can influence profoundly the value of $E_{1/2}$.

This is demonstrated by an electrochemical investigation on the

$Ni(cyclam)^{3+}/Ni(cyclam)^{2+}$ redox couple performed in some solvents in current use (DMSO, DMF, CH_3CN, CH_3NO_2).[33] Figure 7 reports the above potential values referred to the Fc^+/Fc redox couple. Making the usual assumption that the value of $E_{1/2}(Fc^+/Fc)$ is not too seriously affected by the nature of the solvent, the $E_{1/2}(Ni(cyclam)^{3+/2+})$ values reported in Fig. 7 give a direct measure of solvent effect on the stabilization of the Ni^{III} state. In particular, DMSO and DMF show a pronounced stabilizing effect, much greater than that exerted by CH_3CN, in spite of the much wider use of the latter solvent in the investigation of trivalent nickel macrocyclic complexes.

The potential values in Fig. 7 refer to the following half-reaction:

$$\underset{\text{low-spin, octahedral}}{[Ni^{III}(cyclam)S_2]^{3+}} + e^- = \underset{\text{low-spin, square}}{[Ni^{II}(cyclam)]^{2+}} + 2S, \tag{3}$$

where S represents a solvent molecule.[34] The observed effect can be interpreted in terms of more or less intense axial interactions in the octahedral Ni^{III} complex, exerted by the solvent molecules and, in this sense, the sequence of the $E_{1/2}$ values in Fig. 7 can be considered a sort of *basicity scale* for the investigated media. Comparison with the popular Gutmann's donor number scale (D.N.: DMSO, 29.8; DMF, 26.6; CH_3CN, 14.1; CH_3NO_2, 2.7)[35] shows a qualitative agreement, as far as the first three solvents are concerned: the strongly donating solvents DMSO and DMF markedly stabilize Ni^{III} through

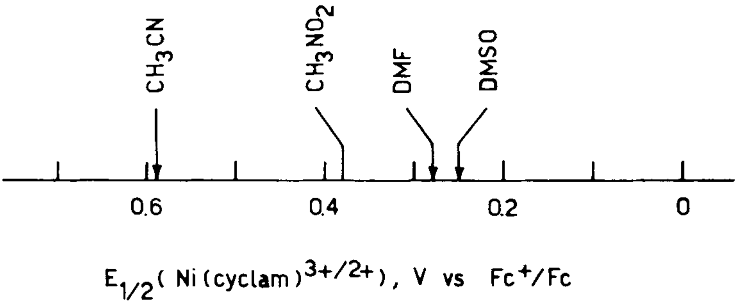

FIGURE 7 Solvent effect on the Ni^{III}/Ni^{II} redox couple potential in the cyclam (5) complex. Each electrochemically investigated solution was 0.1 M in Et_4NBF_4 and 10^{-3} M both in $Ni(cyclam)(ClO_4)_2$ and ferrocene (Fc).

axial coordination, compared to the less donating (in the Gutmann's sense) CH_3CN. On the contrary, CH_3NO_2 exerts stronger axial interactions (and a more profound Ni^{III} stabilization) than expected on the basis of the very small value of the donor number. Disagreement should not be too surprising if one keeps in mind the selective character of the acid/base interaction and the very different nature of the reference acids considered ($SbCl_5$, in the D.N. scale).[36]

It should be noticed that the role of the solvent is not univocal and it may happen that strongly coordinating solvents disfavor the formation of a metal complex in a high oxidation state. This should be the case, for instance, in which the reduced form of the redox couple binds solvent molecules, and the oxidized one does not. The Cu^{III}/Cu^{II} redox change could be a candidate to display this behavior.

Stabilization of Ni^{III} through axial ligation can be exerted by coordinating anions present in solution (Cl^-, Br^-, SO_4^{2-}, $H_2PO_4^-$).[18,37] Therefore, the choice of the supporting electrolyte to be used in electrochemical investigations must be made with caution. To give an example, we first reported the $E_{1/2}(M^{III}/M^{II})$ values for nickel and copper 14-dioxocyclamato(2−) complexes measured in aqueous 1M KCl[29]: in that medium the "inversion of the natural trend" was not observed (1M KCl: Ni^{III}/Ni^{II}, 0.56 V vs. SCE; Cu^{III}/Cu^{II}, 0.65 V; compared to aqueous 1M $NaClO_4$: Ni^{III}/Ni^{II}, 0.83 V; Cu^{III}/Cu^{II}, 0.65 V).[31] In practice, the extra contribution from axial ligation by Cl^- ions masked the intrinsically lower stability of Ni^{III} compared to Cu^{III}.

Its very small coordinating tendencies make perchlorate the ideal (or the best available) counterion to be used in redox studies of the type outlined above. However, it has been recently discovered that ClO_4^- ions exert some unexpected effects on the M^{III}/M^{II} redox couple potential in macrocyclic complexes through a mechanism which indirectly involves the coordination sphere of the metal.[31] This effect is illustrated by the diagram in Fig. 8, where the $E_{1/2}(M^{III}/M^{II})$ values for the nickel and copper complexes of 13- and 14-member dioxocyclamato(2−) ligands, measured in aqueous $NaClO_4$ solution, of concentration ranging from 0.1 to 7 M, are presented. On increasing the electrolyte concentration, the $E_{1/2}(M^{III}/M^{II})$ values increase for nickel and decrease for copper. In other words, concentrated electrolyte solutions make the attainment of Cu^{III} easier and disfavor the formation of Ni^{III}. The observed behavior could not be ascribed to

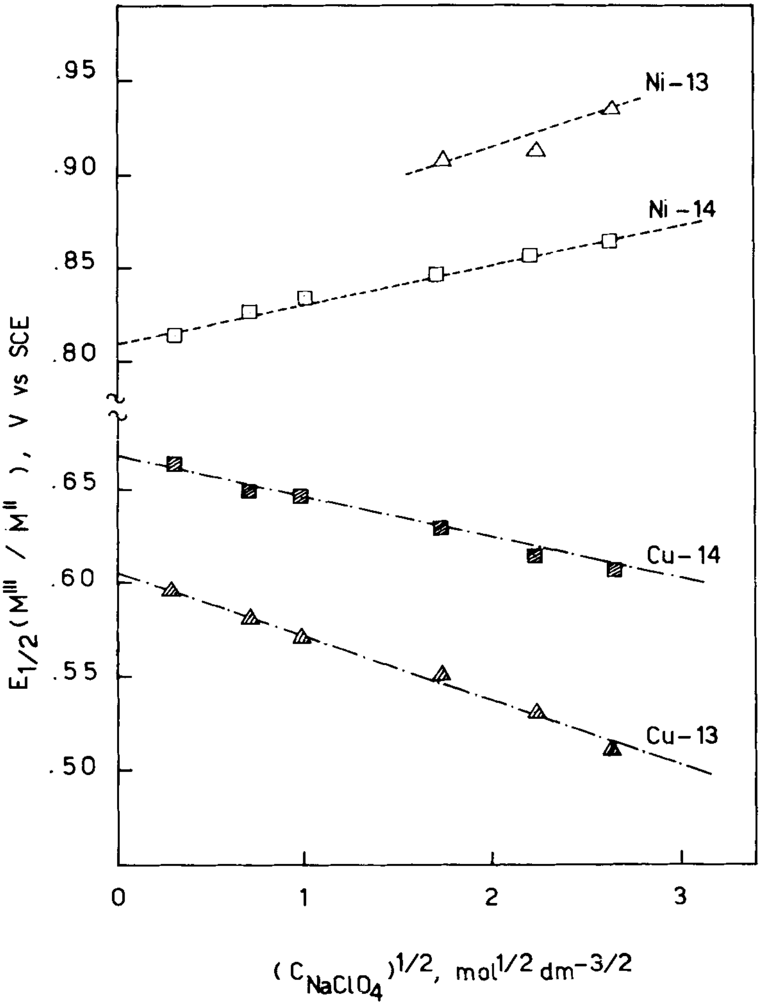

FIGURE 8 Effect of the supporting electrolyte on the Ni^{III}/Ni^{II} and Cu^{III}/Cu^{II} redox couple potentials in dioxocyclamato(2−) complexes. Data refer to the complexes of the 13- and 14-member Ligands, in aqueous solutions with a $NaClO_4$ concentration ranging from 0.1 to 7 M.

junction potential effects, since in that case the trend of $E_{1/2}$ values had to be parallel, and not divergent for nickel and copper. Also possible axial ligation effects by ClO_4^- ions must be ruled out, since in this case the increases of the anion concentration would operate to stabilize Ni^{III}, whereas the opposite effect is observed. It has been suggested[31] that the electrolyte effect should be ascribed to the hydrogen bonding interaction between ClO_4^- ions and the water molecules axially coordinated in some of the redox-active species present in the following half-reactions:

$$\underset{\text{octahedral}}{[\mathrm{Ni^{III}(dioxocyclamato(2-))(H_2O)_2}]^+} + e^- = \underset{\text{square}}{[\mathrm{Ni^{II}(dioxocyclamato(2-))}]} + 2\mathrm{H_2O}, \tag{4}$$

$$\underset{\text{square}}{[\mathrm{Cu^{III}(dioxocyclamato(2-))}]^+} + 2\mathrm{H_2O} + e^- = \underset{\text{distorted octahedral}}{[\mathrm{Cu^{II}(dioxocyclamato(2-))(H_2O)_2}]}. \tag{5}$$

In particular, in the case of nickel (Eq.(4)), due to the hydrogen bonding interactions between the ClO_4^- ions and the water molecules apically coordinated in the Ni^{III} octahedral complex, the Ni^{III}–O axial bonds are weakened. As a consequence, the trivalent complex is destabilized and the $E_{1/2}(Ni^{III}/Ni^{II})$ value becomes more positive. On the other hand, in the case of copper (Eq.(5)), it is the divalent complex that is destabilized through perchlorate-induced weakening of the axial bonds, so that an increase of the electrolyte concentration makes the access to Cu^{III} easier. Moreover, for copper complexes, there exists direct spectroscopic evidence of a modification of the stereochemistry of the Cu^{II} chromophore induced by perchlorate ions: in fact, the energy of the *d-d* absorption band of the Cu^{II} complexes show a distinct and progressive increase with the $NaClO_4$ concentration (Cu^{II}(13-dioxocyclamato(2−)), $\nu_{d\text{-}d}$, cm^{-1}: 0.1 M $NaClO_4$, 19 230; 7 M, 20 750; Cu^{II}(14-dioxocyclamato(2−)): 0.1 M, 19 840; 7 M, 20 240). This is consistent with a Jahn-Teller mechanism, by which weakening of the axial bonds induces a simultaneous increase of the equatorial interactions, whose energy is empirically expressed by the $\nu_{d\text{-}d}$ value.[38] Remarkably, the energy of the *d-d* band of the Ni^{II} corresponding complexes, which do not contain water in the coordination sphere, is not affected by the increase of the salt concentration. In any case, after the above findings, whatever the mechanism of the salt effect is, it is a bit difficult for the author to continue to consider $NaClO_4$ "the inert electrolyte."

Varying *p*H may influence the formation of aqueous Ni^{III} complexes. This further medium effect can be interpreted in terms of the following hydrolytic equilibrium of the Ni^{III} complex:

$$[Ni^{III}L(H_2O)_x]^{3+} = [Ni^{III}L(OH)(H_2O)_{x-1}]^{2+} + H^+, \qquad (6)$$

the pK_A value of the above acid being about 4 for quadridentate macrocycles.[39] This means that the $E_{1/2}(Ni^{III}/Ni^{II})$ value below *p*H 4 remains constant, whereas above *p*H 4 it decreases linearly with a slope of 59 mV pH^{-1}. Notice that the present stabilization effect on Ni^{III} associated with the *p*H increase is still an "axial ligation effect," the coordinating anion now being OH^-.

The acidity of the solution may operate also in the sense of a kinetic stabilization of the oxidized metal complex. For instance, the use of concentrated $HClO_4$ as solvent permits the formation of otherwise unstable trivalent copper tetra-aza-macrocyclic complexes: in particular, the electrogenerated $Cu^{III}(\mathbf{1})^{3+}$ species persists in aqueous 10 M $HClO_4$, with a $t_{1/2}$ value of 1.5 h.[40] This kinetic acidity effect fits well with the evidence that Cu^{III} tetramine complexes, in aqueous and nonaqueous solutions, decompose through ligand fragmentation and liberation of protons[25,26,41] and with the mechanism proposed for the base promoted decomposition of Ni^{III} tetra-aza-macrocyclic complexes.[42] Addition of strong acid quenches or decreases the role of the very crucial step of the decomposition process that involves a release of protons.

Notably, the use of concentrated perchloric acid as solvent has permitted the discovery of the second case (among macrocyclic complexes) of the copper/nickel inversion in the trend of $E_{1/2}(M^{III}/M^{II})$ values. The inversion occurs with the complexes of the classical diene tetra-aza-macrocycle **1** (see the diagram in Fig. 9), but it does not occur with the complexes of the saturated analog **2** and with those

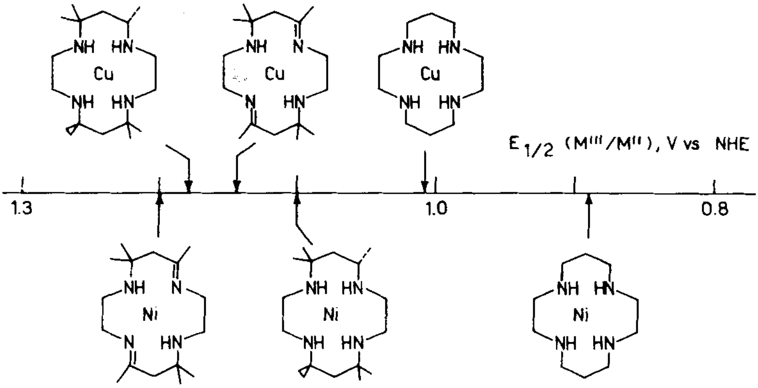

FIGURE 9 Redox chemistry in 10 M $HClO_4$ solution. For the unsaturated macrocycle complexes, trivalent copper is formed at a less positive potential than trivalent nickel, whereas for the complexes of the saturated analog the "natural trend" is respected.

of the saturated and unsubstituted analog cyclam. While the well-known ability of the diene macrocycle **1** to exert a strong in-plane ligand field may contribute substantially to the selective stabilization of trivalent copper, also the high concentration of the electrolyte (10 M $HClO_4$) can play some additional role.

It is implicit that redox chemistry in strongly acidic solutions is possible only with complexes which are inert towards demetallation by acidic attack, typically those with poly-aza macrocycles, in particular the quadridentate 14-member ligands.

MORAL OF THE STORY

The introduction of poly-aza macrocycles in inorganic chemistry has helped to make familiar some metal oxidation states which had been previously considered quite unusual, and, in particular, has substantially increased our knowledge of their electronic properties, stereochemical preferences and reactivity. The approach which we have outlined was aimed at correlating the solution stability of Ni^{III} and Cu^{III} complexes with the structural features of the macrocycle, and can serve as a very rough guide to the design of novel, tailor-made ligands. At this stage, as far as polyamine macrocycles are concerned, results are not encouraging: in fact, the most powerful ligand in stabilizing Ni^{III} and Cu^{III} is the tetra-aza macrocycle *cyclam* (**5**), which is obtained through a simple metal template synthesis, rather than all the other more elaborate ligands (in the sense of a tedious multistep synthetic procedure) of different atomicity and denticity. The coincidence is not fortuitous, since template condensation and easy metal oxidation are both related to the possibility of establishing strong in-plane M–N interactions, and demonstrates the rather primitive nature of the macrocycles we have previously considered.

The knowledge of the stereochemical requirements of the metal ion in the desired oxidation state can lead to the design of the proper ligand to stabilize it. For example, metal ions having a preference for a coordination number larger than 4 could profit from the complexation by a ligand having its N_5- or N_6-donor set organized in three dimensions (as a macrotricycle), rather than by the strongly *xy*-coordinating cyclam-like ligands. The cyclic nature of the ligand remains a prerequisite, in that it guarantees kinetic stability.

Acknowledgment

I wish to thank all my students who have participated in this project, whose names appear in the references.

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