Comparative Study of the Electrochemical and Pulse-radiolytic Oxidation of the Complexes of Nickel(II) and Copper(II) containing 1,4,8,11-Tetra-azacyclotetradecane

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Electrochemical and pulse-radiolytic oxidation of $[Ni(cyclam)]^{2+}$ and $[Cu(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) have been studied in aqueous acidic perchlorate and sulphate media. As with other nickel macrocyclic systems, $[Ni(cyclam)]^{2+}$ is oxidized to Ni^{III}, the stability of which is enhanced by sulphate complexation. In contrast, $[Cu(cyclam)]^{3+}$ is much less stable than the nickel analogue and does not form a stable sulphate complex. Electrochemical oxidation of $[Cu(cyclam)]^{2+}$ at pH 1.6 is a multistep process which is catalysed by sulphate ion. The mechanism appears to involve the transfer of four electrons resulting in a copper(II) macrocyclic diene complex.

COMPLEXES of tervalent copper and nickel with tetra-aza macrocyclic ligands are readily prepared by electrochemical oxidation in aprotic media.[1-3] However, they decompose when dissolved in water.[4,5] Copper(III) and nickel(III) complexes with amines,[6,7] amino-acids,[8] and peptides [9,10] have similar properties in aqueous solution, with nickel(III) generally being somewhat more stable. Recently it has been found that simple anions are able to stabilize the III oxidation state of nickel in complexes of 14-membered N_4 macrocyclic ligands.[5,11-14] This effect has been studied in detail for the Ni^{III}-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane system in the presence of sulphate [12] and phosphate.[13a] It therefore seemed of interest to check whether this stabilization occurs for tervalent copper macrocycles as well.

For the present study we have selected the cyclam (1,4,8,11-tetra-azacyclotetradecane) complexes of copper and nickel for comparison of the effect of sulphate *versus* perchlorate on the stability of the III oxidation state of the metal. Cyclam was chosen because it is the 14-membered N_4 macrocycle whose copper(II) and nickel(II) oxidation potentials are the lowest in aprotic media.[2] The results indicate that sulphate has a much less dramatic influence on the lifetime of $[Ni(cyclam)]^{3+}$ when compared to $[Ni(\textit{meso}\text{-}Me_6cyclam)]^{3+}$ and no stabilizing effect on $[Cu(cyclam)]^{3+}$. Furthermore, the electrochemical oxidation of $[Cu(cyclam)]^{2+}$, although catalyzed by sulphate, is a multielectron process and does not yield a copper(III) complex.

EXPERIMENTAL

Materials.—Cyclam was obtained from Strem Chemicals Co. The complexes $[Ni(cyclam)][ClO_4]_2$ and $[Cu(cyclam)][ClO_4]_2$ were synthesized according to published procedures.[15] The former has absorption maxima at 215 ($\varepsilon = 8.5 \times 10^3$) and 450 nm ($\varepsilon = 45$ dm^3 mol^{-1} cm^{-1}) in aqueous solutions, while the latter has maxima at 253 ($\varepsilon = 7.1 \times 10^3$) and 505 nm ($\varepsilon = 74$ dm^3 mol^{-1} cm^{-1}). Triply distilled water and AnalaR grade chemicals were used for the syntheses and solution preparations. Solutions were saturated with N_2O or N_2, when required, by bubbling with high-purity gases from which O_2 traces were removed by passing through acidic $V[SO_4]$ over traps containing zinc amalgam.

Equipment and Procedures.—The electrochemical equipment consisted of a P.A.R. model 373 potentiostat and IEC, F 553 function generator for linear potential-sweep voltammetry (c.v.) with output to a Bryans 26000 A-4 X–Y recorder and a Fluke 8000 A digital multimeter. Coulometric data in set-potential electrolysis experiments was recorded digitally with an Acromag 205-LX-1 electronic integrator. A Metrohm cell was used with two kinds of working electrodes: a 1.2 cm^2 gold (for c.v.) and a 34 cm^2 platinum screen (for preparative work). The coiled platinum-wire counter electrode was separated by an agar (2 mol dm^{-3} KCl) bridge and the Ag–AgCl (3 mol dm^{-3} KCl) reference electrode was connected by a Luggin capillary also containing agar (2 mol dm^{-3} KCl). Unless otherwise stated, all potential measurements in this paper will be given *versus* the Ag–AgCl reference. The working electrode area was determined by cyclic voltammetry in a ferrocyanide solution and calculated using the Randles–Ševčik equation.[16] Blank experiments with the supporting electrolyte and with the free ligand were performed under the same experimental conditions. The u.v. and visible spectra were measured using a Cary 17 (Varian) spectrophotometer. Pulse radiolytic experiments were made at the linear electron accelerator of the Hebrew University of Jerusalem, using procedures previously described;[8] N_2O-saturated solutions containing complex concentrations of 2×10^{-5}—5×10^{-4} mol dm^{-3} were employed. Under these conditions the major reacting radical is ·OH (over 90%).[12]

RESULTS AND DISCUSSION

Electrochemical Oxidation of $[Ni(cyclam)]^{2+}$.—Cyclic voltammograms of $[Ni(cyclam)]^{2+}$ in 0.1 mol dm^{-3} $Na_2[SO_4]$ and in 0.3 mol dm^{-3} $Na[ClO_4]$ at pH 1.6 are shown in Figure 1. The peak currents and a peak separation of 60 mV at 5.6 mV s^{-1} are consistent with a reversible one-electron oxidation process in both media (see below). However, the peak separation increases somewhat with increasing scan rate, *e.g.* ΔE(peak) = 100 mV at 112 mV s^{-1} in sulphate.

From the cyclic voltammograms the redox potential of the $[Ni(cyclam)]^{3+}$–$[Ni(cyclam)]^{2+}$ couple was determined to be 0.53 V in 0.1 mol dm^{-3} SO_4^{2-} and 0.75 V in 0.3 mol dm^{-3} ClO_4^-. The difference between these values indicates that $[Ni(cyclam)]^{3+}$ is complexed by SO_4^{2-} [E(complex) = 0.46 V] with a stability constant of *ca.* 5×10^4 dm^3 mol^{-1}. This value is higher than that found by pulse radiolysis for complexation between [Ni(*meso*-Me_6cyclam)]$^{3+}$ and SO_4^{2-}, $K = 3 \times 10^3$ dm^3 mol^{-1}, at the same ionic strength [12] but probably within a factor of five when activity corrections are made.[17]

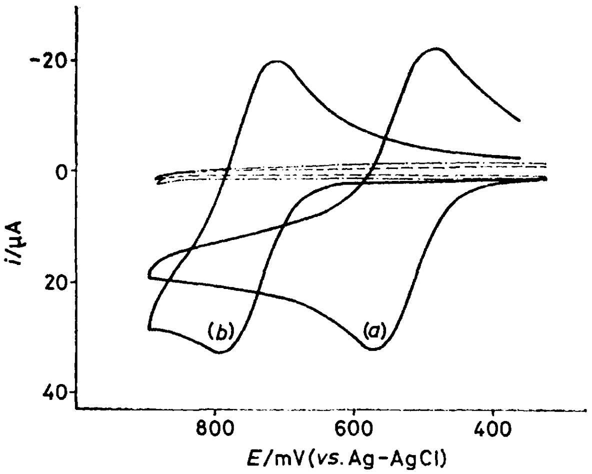

FIGURE 1 Linear potential-sweep voltammetry on a 1.2 cm^2 gold electrode of 5×10^{-4} mol dm^{-3} $[Ni(cyclam)]^{2+}$ solutions at pH 1.6, at a scan rate of 11.2 mV s^{-1}. Supporting electrolyte: (*a*) 0.1 mol dm^{-3} $Na_2[SO_4]$; (*b*) 0.3 mol dm^{-3} $Na[ClO_4]$. Blanks: (-----), 0.1 mol dm^{-3} SO_4^{2-}; (—·—·—), 0.3 mol dm^{-3} ClO_4^-

A linear dependence of the peak current (i_p) as a function of the square root of the scan rate ($v^{\frac{1}{2}}$) was obtained, as expected for a pure electron-transfer process.[16,18] C.v. measurements at potential scan rates of 2—90 mV s^{-1} were performed and compared to a standard $K_4[Fe(CN)_6]$ solution under the same conditions. From the known diffusion coefficient of $[Fe(CN)_6]^{4-}$ (6.5×10^{-6} cm^2 s^{-1}) [19] and the ratios of the slopes of the i_p *versus* $v^{\frac{1}{2}}$ plots, the diffusion coefficient of $[Ni(cyclam)]^{2+}$ was calculated to be 4.6×10^{-6} cm^2 s^{-1}. This diffusion coefficient was also determined from a chronoamperometric experiment using Cottrell's equation.[20] A value of 3.8×10^{-6} cm^2 s^{-1} was found. Thus $D = (4.2 \pm 0.4) \times 10^{-6}$ cm^2 s^{-1} for $[Ni(cyclam)]^{2+}$, identical to that reported [21] for (*trans*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecadiene)copper(II).

Set-potential coulometric experiments in both supporting electrolytes yielded nickel(III) complexes as products [11] (see spectra inserted in Figure 4 below).

At pH 1.6 both nickel(III) species are relatively stable with half-lives at room temperature of *ca.* 10 h for $[Ni(cyclam)]^{3+}$ in 0.3 mol dm^{-3} $Na[ClO_4]$ and 5 d for $[Ni(cyclam)(SO_4)]^+$ in 0.1 mol dm^{-3} $Na_2[SO_4]$ for solutions containing 5×10^{-4} mol dm^{-3} total nickel–cyclam.

Electrochemical Oxidation of $[Cu(cyclam)]^{2+}$.—Cyclic voltammograms of $[Cu(cyclam)]^{2+}$ in 0.3 mol dm^{-3} ClO_4^- and 0.1 mol dm^{-3} SO_4^{2-} at pH 1.6 are shown in Figure 2. No reduction wave was observed during the scan backward at scan rates up to 100 mV s^{-1}. The high anodic peak currents in both media and the shoulder observed in the presence of SO_4^{2-} are indicative of a multielectron oxidation process which involves at least two steps in SO_4^{2-} media. The free ligand does not undergo oxidation under these conditions. Although the results suggest a multistep mechanism for electrochemical oxidation, plots of the peak current *versus* the square root of the scan rate are, nevertheless, linear and identical for both media. The ratio of the slopes for copper– and nickel–cyclam is 6.7 : 1. This value seems to indicate a four-electron process [22] for the oxidation of $[Cu(cyclam)]^{2+}$ in agreement with the coulometric results (see below).

Set-potential coulometric oxidation of $[Cu(cyclam)]^{2+}$ at 1 250 mV required four equivalents of charge per equivalent of complex in both perchlorate and sulphate media at pH 1.6 for the current to decrease to the background level. During stepwise coulometric experiments there was a progressive decrease in the $[Cu(cyclam)]^{2+}$ absorbance maxima at 505 and 253 nm which was accompanied by a corresponding increase in intensity of a band with $\lambda_{max.} = 293$ nm and $\varepsilon_{max.} = 2\ 500$ dm^3 mol^{-1} cm^{-1} (±20%). These results are in agreement with the above conclusions that electrochemical oxidation of $[Cu(cyclam)]^{2+}$ yields one major product in a four-electron process. The product of the oxidation of $[Cu(cyclam)]^{2+}$, which is not a strong oxidizing agent, could plausibly be the corresponding diene complex of copper(II) or its hydrolysis product. No examples of complexes of this ligand have previously been reported.

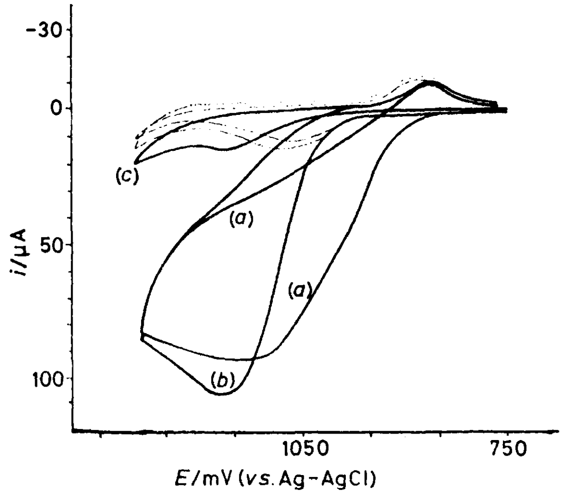

FIGURE 2 Sweep voltammetry of 5×10^{-4} mol dm^{-3} [Cu-(cyclam)]$^{2+}$ solutions at a scan rate of 2.24 mV s^{-1}. Other details as in Figure 1, except that (*c*) is for 10^{-3} mol dm^{-3} cyclam in 0.5 mol dm^{-3} $Na_2[SO_4]$ at pH 1.6 mol dm^{-3}

The preservation of a macrocyclic system after oxidation seems supported by a variety of chemical tests (*e.g.* addition of strong acid or basic glycine) which should otherwise cause dissociation of the complex. However, the spectral peak at 293 nm decays over a period of several days and we were unable to further characterize this product.

Pulse Radiolysis of [Ni(cyclam)]$^{2+}$ *Solutions.*—When [Ni(cyclam)]$^{2+}$ reacts with hydroxyl radicals in solutions containing ClO_4^- or SO_4^{2-}, two consecutive reactions result in spectra (Figure 3) which at pH 3.1 have similar features to those obtained in the electrochemical oxidation. (Below pH 3 production of ·OH in pulse radiolyses is not quantitative.)[12] At pH 6 in perchlorate, the absorbance maximum at 300 nm is decreased in intensity in the first reaction and a second maximum at 545 nm is observed which is totally absent at pH 1.6 (electrochemical preparation) and is very weak at pH 3. This pH dependence has been noted in other Ni^{III}–macrocycle systems and may be attributed to hydrolysis of [Ni(cyclam)]$^{3+}$ (p*K* *ca.* 4), probably accompanied by some sort of stereochemical reorientation.[12, 23-25, *] The peak at 545 nm is not observed in the presence of high SO_4^{2-} concentration.

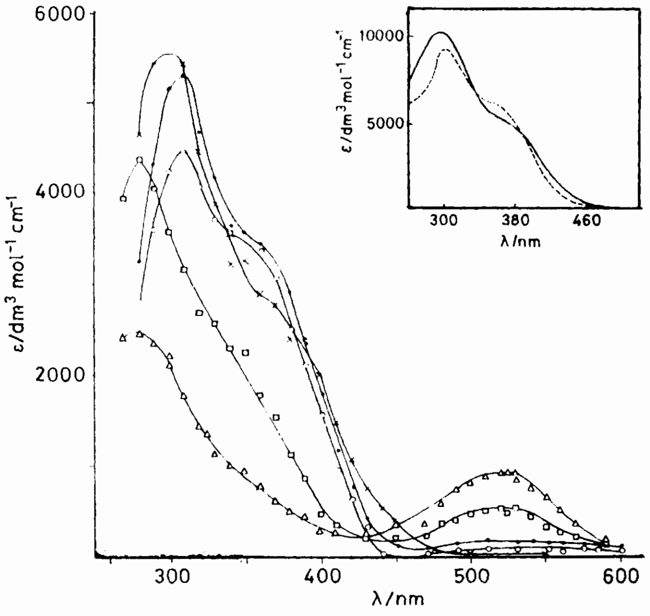

FIGURE 3 U.v.–visible spectra of pulse radiolytically generated nickel(III) intermediates from N_2O-saturated solution of 1×10^{-4} mol dm^{-3} [Ni(cyclam)]$^{2+}$. (*i*) pH 3.1: in 0.3 mol dm^{-3} ClO_4^-, (●) 40 μs and (○) 50 ms after the pulse; in 0.1 mol dm^{-3} SO_4^{2-}, (×) 50 ms after the pulse. (*ii*) pH 6: in 0.3 mol dm^{-3} ClO_4^-, (△) 8 μs and (□) 200 μs after the pulse. Insert: electrochemically generated [Ni(cyclam)(SO_4)]$^+$ (——) and [Ni(cyclam)]$^{3+}$ (– – – –) at pH 1.6 and $I = 0.3$ mol dm^{-3}

In 0.3 mol dm^{-3} perchlorate at pH 3.1 the rates of formation of the two intermediates are *ca.* 2×10^9 dm^3 mol^{-1} s^{-1} {first order in [·OH] and [Ni(cyclam)$^{2+}$]} and 75 ± 7 s^{-1} respectively. The corresponding values at pH 6 are $(5 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1} and $(1.3 \pm 0.2) \times 10^4$ s^{-1}. In contrast to the electrolytic oxidation at pH 1.6, these intermediates decompose rather quickly with first-order rate constants of 0.36 ± 0.03 and 3.5 ± 0.7 s^{-1} respectively at pH 3 and 6. The stabilizing influence of sulphate is quite definite with decomposition as observed at 300 nm occurring with a half-life greater than 10 s even at pH 5.5.†

Kinetics of the formation of [Ni(cyclam)(SO_4)]$^+$ are somewhat more complicated than for oxidation in ClO_4^- media and, since the spectra of [Ni(cyclam)]$^{3+}$ and [Ni(cyclam)(SO_4)]$^+$ are similar, we were unable to accurately measure the rate of the complexation step.

Pulse Radiolysis of [Cu(cyclam)]$^{2+}$ *Solutions.*—The reaction of [Cu(cyclam)]$^{2+}$ with pulse radiolytically generated hydroxyl radicals in solutions containing either ClO_4^- or SO_4^{2-} results in transient spectra with absorbance maxima at *ca.* 400 and below 300 nm. As demonstrated in Figure 4, the spectral intensities (measured at $I = 0.3$ mol dm^{-3} and pH 3) are similar for the two media with the sulphate system exhibiting a somewhat higher absorbance after the initial formation reaction (10 μs after the pulse). Also for both media, the initial intermediate is transformed into a somewhat more stable species within *ca.* 40 ms and the second intermediate has a lifetime of *ca.* 10 s. The kinetics of these reactions do not seem to follow either pure

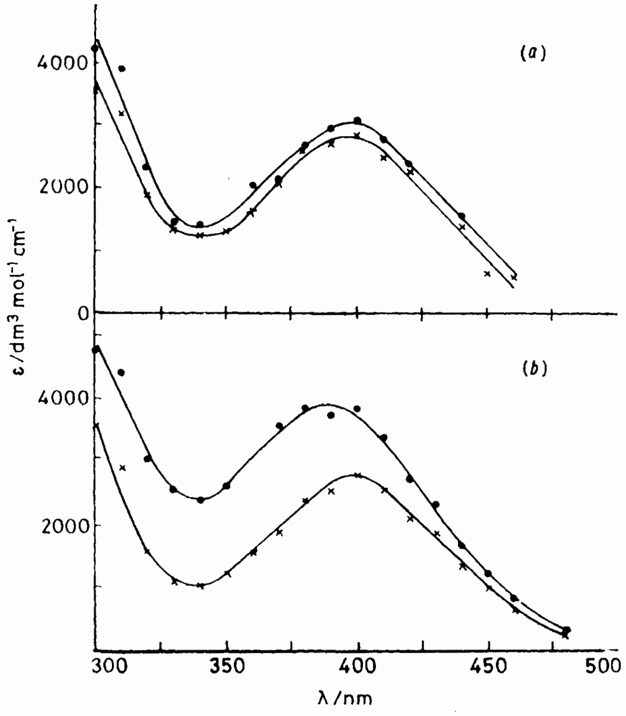

FIGURE 4 U.v.–visible spectra of copper(III) intermediates formed in the reaction of 1×10^{-4} mol dm^{-3} [Cu(cyclam)]$^{2+}$ with ·OH in N_2O-saturated solutions at pH 3.2: (*a*) in 0.3 mol dm^{-3} ClO_4^-, (*b*) in 0.1 mol dm^{-3} SO_4^{2-}; (●) 10 μs and (×) 45 μs after the pulse

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[*] The authors of ref. 25 favour an explanation involving a cation-stabilized ligand radical. References 23 and 24 present arguments in support of the presence of hydrolyzed Ni^{III}.

[†] As the upper time resolution of our instrumentation is shorter than the lifetimes of this intermediate, we were unable to accurately determine the rate of this reaction, nor were we able to determine the origin of a residual absorbance that remains after 40 s both at pH 3 and 5.6.

first- or second-order rate laws and, thus, the rate data will not be presented in detail. However, it is clear that the presence of sulphate ion has no measurable effect on the stabilization of an oxidized form of copper. Since, in contrast to the possibility of multielectron reactions in the electrochemical experiments, •OH is a strong one-electron oxidizing agent which clearly oxidizes [Ni(cyclam)]$^{2+}$ to tervalent nickel, it seems that the spectra in Figure 4 are those of tervalent copper cyclam complexes. These spectra are indeed similar to those reported for other copper(III) macrocyclic complexes in acetonitrile;[16] most notable is the existence of absorption maxima near 400 and 300 nm (albeit with lower intensities). The absence of this type of confirmation has led to the suggestion that the product of the reaction of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)copper(II) with •OH is a copper(II)–ligand-radical species.[26]

The lack of a stabilizing of effect SO_4^{2-} on Cu^{III} might be due to the inability of the low-spin d^8 configuration to form strong axial bonds as are observed with (d^7) tervalent nickel macrocycles.[11,12]

Conclusions.—The results of both the electrochemical and pulse-radiolysis studies indicate that while SO_4^{2-} ion does have an effect on the oxidation of [Cu(cyclam)]$^{2+}$, this effect does not result in the kinetic stabilization of the III oxidation state. Lack of stable axial complexation for [Cu(cyclam)]$^{3+}$ seems reasonable since it is a low-spin d^8 system. The effect of SO_4^{2-} on the electrochemical oxidation of [Cu(cyclam)]$^{2+}$ does seem to involve stabilization of an intermediate product as indicated by the shoulder in the cyclic voltammogram (Figure 2) at *ca.* 990 mV. In addition, a decrease in overpotential in SO_4^{2-} compared to ClO_4^- has been found for the oxidation of [Ni(*meso*-Me$_6$cyclam)]$^{2+}$ and may also be a contributing factor in this case.[13b]

The pulse-radiolysis results indicate that [Cu(cyclam)]$^{3+}$, when formed, has a lifetime of several seconds even at pH 3. Thus the observation that no stable copper(III) complexes are formed during the electrochemical oxidation cannot be attributed to the instability of [Cu(cyclam)]$^{3+}$. This behaviour is apparently due to the fact that at the potential required for the oxidation of copper, or perhaps at even lower potentials, the bound ligand can be oxidized by two-electron processes. These results demonstrate that, whereas electrochemical oxidation results in the thermodynamically more favourable two-electron ligand oxidation, the oxidation by free radicals, which are strong single-electron oxidants, causes the less favourable oxidation of the central cation. It should be noted that in the nickel cyclam system no further wave was observed up to 1.4 V. Thus, it seems that Ni^{III} stabilizes the ligand relative to copper(II) towards electrochemical oxidation as does H^+ in the free ligand. This order is consistent with the relative inductive effects of H^+, Ni^{III}, and Cu^{II}.

Finally, it is of interest to note that although the stability constants for complexation by sulphate are similar for [Ni(cyclam)]$^{3+}$ and [Ni(*meso*-Me$_6$cyclam)]$^{3+}$,[12] the effect of SO_4^{2-} on the kinetic stability of the two products differs considerably. Thus the half-life for decomposition of [Ni(cyclam)]$^{3+}$ is increased from *ca.* 10 h in 0.3 mol dm^{-3} ClO_4^- to 5 d in 0.1 mol dm^{-3} SO_4^{2-} at pH 1.6 while the half-life of [Ni(*meso*-Me$_6$cyclam)]$^{3+}$ increases from *ca.* 1 min to over 1 year under the same conditions. The higher stability of the uncomplexed [Ni(cyclam)]$^{3+}$ is apparently due to the lower redox potential (0.75 V) for [Ni(cyclam)]$^{3+/2+}$ *versus ca.* 1 V for [Ni(*meso*-Me$_6$cyclam)]$^{3+/2+}$.[13b] However, the large difference in stabilization due to SO_4^{2-} clearly does not originate from thermodynamic factors {$E = 0.46$ and *ca.* 0.64 V for [Ni(cyclam)(SO_4)]$^{+/0}$ and [Ni(*meso*-Me$_6$cyclam)]$^{+/0}$ respectively}. This difference must, therefore, stem from kinetic factors perhaps resulting from conformational differences. This point is under further study.

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