Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Taraszewska, Joanna and Rosłonek, Grzegorz(1997) 'Kinetic and Thermodynamic Stability of Ni(III) Polyazacyclotetradecane Complexes', Supramolecular Chemistry, 8: 4, 369 — 377

To link to this Article: DOI: 10.1080/10610279708034956

URL: http://dx.doi.org/10.1080/10610279708034956

SUPRAMOLECULAR CHEMISTRY, 1997, Vol. 8, pp. 369–377
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Gordon and Breach Science Publishers imprint
Printed in Malaysia

Kinetic and Thermodynamic Stability of Ni(III) Polyazacyclotetradecane Complexes

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(Received 29 July 1996)

The thermodynamic and kinetic stability of Ni(III) in polyazacyclotetradecane complexes **1–4** was studied as a function of pH, concentration of indifferent electrolyte (sodium perchlorate), and solvent basicity. The thermodynamic stability was estimated from the changes in formal potentials of the Ni(II)/Ni(III) redox couple as determined by cyclic voltammetry. Complexes of Ni(III) were produced by controlled potential electrolysis. Their kinetic stability was studied by UV-Vis spectrophotometry. In every solution investigated the decay of Ni(III) followed first order kinetics. The stability of Ni(III) cyclam decreased with increasing pH and electrolyte concentration. As the basicity of the solvent increased, the thermodynamic stability of Ni(III) increased in the series: complex **3** > complex **1** > complex **4** > complex **2**. The kinetic stability did not parallel the thermodynamic trend. It is suggested that the rate determining step in the Ni(III) decomposition process is the deprotonation of the NH group in the macrocyclic ring. The mechanism of decomposition is discussed.

INTRODUCTION

Since the discovery that the tetraazamacrocyclic ligands facilitate the generation of the nickel third oxidation state[1], there has been interest in the thermodynamic and kinetic stability of these complexes.

Information concerning the thermodynamic stability of Ni(III) complexes relative to the corresponding Ni(II) species depending on the kind of solvent and salt concentration were obtained by Buttafava *et al.*[2] from redox potential values. Also, in our previous work[3] the dependence of the thermodynamic stability of Ni(III) on solvent donor number in two tetraazamacrocyclic complexes having pendant amino groups and in a cyclam was studied.

Numerous tetraazamacrocyclic Ni(III) complexes have been prepared by chemical, radiolytic, or electrochemical oxidation of the corresponding Ni(II) species and their decay characterised by UV-Vis and ESR techniques.[4,5] In general Ni(III)

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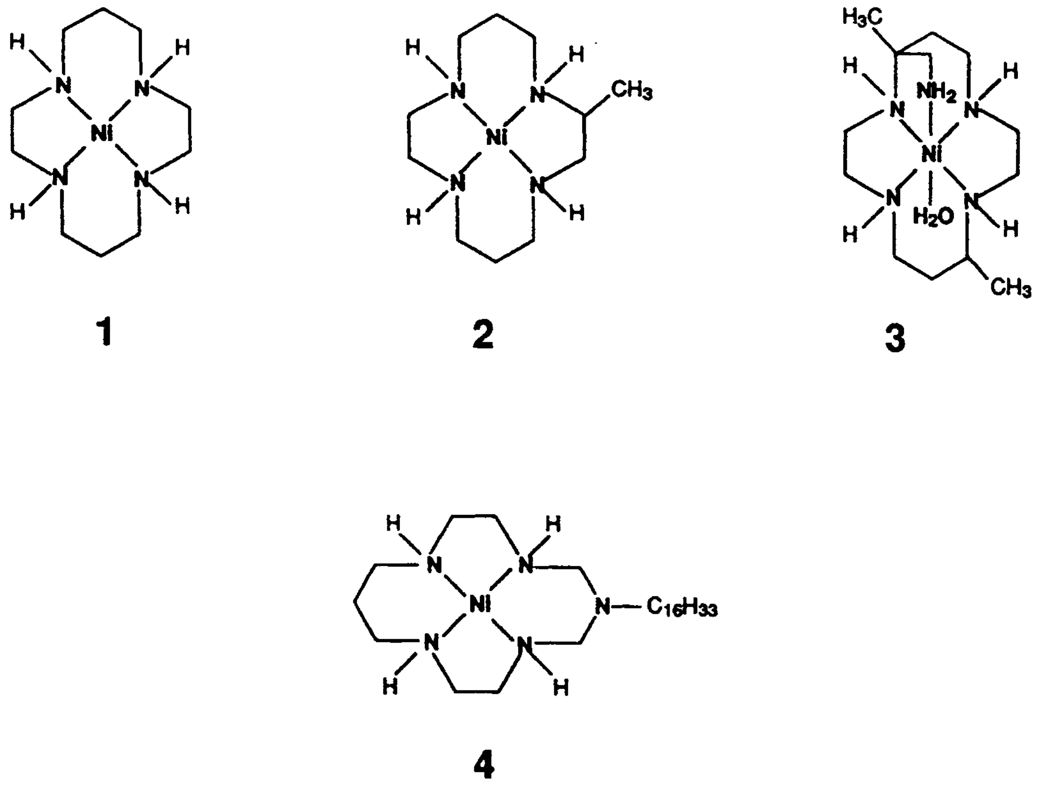
complexes are indefinitely stable in the solid state when they are preserved in a dry atmosphere.[4] However, in solutions their kinetic stability depends considerably on the presence of coordinating anions, the ligand structure, the kind of solvent, and pH.

Zeigerson *et al.*[6–10] studied the influence of inorganic anions on the stability of trivalent nickel complexes with *meso*-$Me_6[14]aneN_4$, cyclam and $Me_6[14]$-4,11-dieneN_4 ligands. A significant influence of SO_4^{2-} anions on complex stability was found in acidic ($pH = 1.6$) aqueous solution. In this medium the above authors demonstrated the dependence of the half life $t_{1/2}$ of Ni(III) on the ligand type. The influence of anion type and pH on the stability of Ni(III) cyclam has been studied recently by Lampeka and Rosokha.[11]

As a rule Ni(III) tetraazamacrocyclic complexes are much more stable in acidic than in alkaline solutions.[8,9,12] The effect of basic, non-aqueous solvents such as pyridine and triethylamine on the decomposition of Ni(III) complexes was studied by Barefield and Mocella[13], mainly from the mechanistic point of view.

The aim of the present studies was to characterise the thermodynamic and kinetic stability of chosen Ni(III) polyazacyclotetradecane complexes in function of pH, electrolyte concentration ($NaClO_4$) and kind of non-aqueous solvent. The complexes studied in this work were: (Ni(II)cyclam]$(ClO_4)_2$ (**1**), 2-methyl-1,4,8,11-tetraazacyclotetradecane nickel(II) diperchlorate (**2**), *trans*-aquo-5-aminomethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) diperchlorate (**3**), and 3-hexadecyl-1,3,5,8,12-pentaazacyclotetradecane nickel(II) diperchlorate (**4**). The structures of complexes are shown in Figure 1. As an example of a weakly basic solvent,



1 **2** **3**

4

FIGURE 1 Structures of the studied complexes acetonitrile (ACN) was used; dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were chosen as solvents more basic than water.

We undertook these studies to increase understanding of the role of high valent nickel species in catalytic oxidation reactions[14–20] and in biological systems.[21,22]

EXPERIMENTAL

Materials

Complexes 1–4 were prepared as described in papers[23–26], respectively. All chemicals were p.a. grade reagents. Merck $NaClO_4$ used in non-aqueous solvents was dried at 60°C in vacuum and kept in dry box. The solvents used were dried and purified for electrochemical use.[27] Triply distilled water was used. The third distillation was carried out from an all-quartz still.

Instrumentation

Voltammetric experiments were carried out in a three-electrode cell at 25 ± 0.5°C using EG&G Princeton Applied Research Model 273 potentiostat/galvanostat, driven by a personal computer. A glassy carbon (GC-30) electrode (Tokai Carbon Co., Japan) sealed in a Teflon tube was used as the working electrode. The counter electrode was a platinum coil, and the 1M NaCl calomel electrode (MCE) was used as the reference electrode. In the controlled-potential electrolysis (CPE) experiments the working electrode was a platinum gauze. In both kinds of experiments the reference electrode was connected to the electrolytic cell via an intermediate vessel filled with the solution under investigation. Additionally, the voltammetric curves of the ferrocene-ferricinium system (Fc) were recorded and in non-aqueous solvents all potentials were referred to this internal reference system. The UV-VIS spectra were measured by using both HP8452A (Hewlett Packard) and Cary 1E (Varian) spectrophotometers. The second apparatus had the cell compartments thermostated to the desired temperature. Measurements were made at 25 ± 0.2°C.

Procedure

The CPE experiments were carried out to produce the amounts of Ni(III) complexes sufficient for spectrophotometric measurments. Concentrations of Ni(II) complexes taken for electrolysis changed in the range $5 \times 10^{-4} - 5 \times 10^{-3}$M. To avoid the possibility of secondary products formation the electrolysis times did not exceed 20 min. Experiments were performed in non deareated solutions. The absorbance changes of the green solution of Ni(III) complex which formed at a potential ca. 0.150V above the anodic peak potential were monitored at the wavelength 308nm. Plots of the absorbance changes vs. time were approximated by the relationship $A(t) = A_0\exp(-kt)$ up to 3 half-times which means that the decay of Ni(III) followed a first-order kinetics. Due to the slow rates of this reaction and observed increase in acidity of studied solutions (especially as high concentrations of Ni(II) complexes were taken for electrolysis) longer times were difficult to follow. Each experiment was repeated several times. The values of $t_{1/2}$ were estimated with an accuracy of ±12%.

RESULTS

pH Dependent Stability of Ni(III) Cyclam

Cyclic voltammetric (CV) curves were recorded at different pH values in solutions containing complex 1 in 0.1M $NaClO_4$. The pH value was adjusted by $HClO_4$ or NaOH. Changes in the formal potential of the Ni(II)/Ni(III) redox couple expressed as $E_f = 1/2(E_{pa} - E_{pc})$ [where E_{pa} and E_{pc} represent the potentials of the anodic and cathodic peaks, respectively] are shown in Figure 2 curve 1. Over the pH range 2–7, the value of E_f was practically

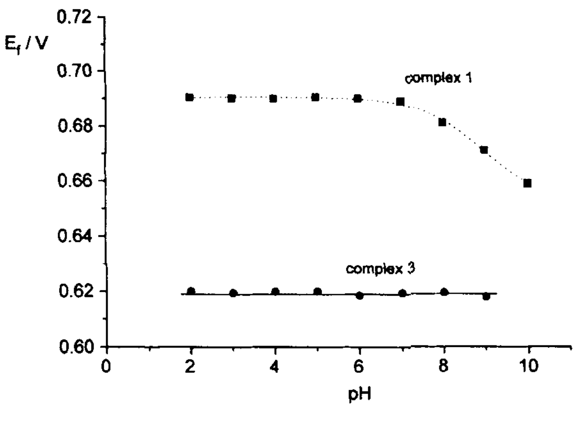


FIGURE 2 Formal potentials E_f of the Ni(II)/Ni(III) redox couple in complex **1** (■) and in complex 3 (●) as a function of pH; supporting electrolyte 0.1M $NaClO_4$.

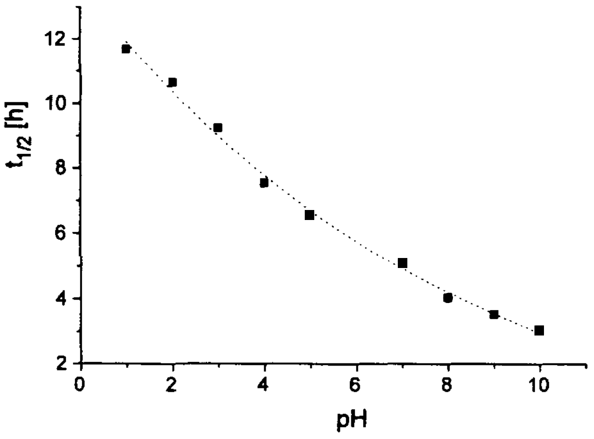


FIGURE 3 Half-life times $t_{1/2}$ of the $[Ni(III)cyclam]^{3+}$ as a function of pH in solution of 0.1M $NaClO_4$.

constant (about 0.69V) and characteristic for a one electron reversible process. With further increase in pH, the E_f moved toward less positive values and the process lost its reversibility (for pH ≥ 8 $\Delta E_p \approx 0.080V$). A similar change of E_f with pH has been recently observed for Ni-cyclam by De Santis *et al.*[12]

For complex **3**, in the whole pH range studied, the redox process was reversible and E_f had a constant value of about 0.62V (Figure 2, curve 2).

Figure 3 shows the change in $t_{1/2}$ of $[Ni(III)cyclam]^{3+}$ in solutions of 0.1M $NaClO_4$ as a function of pH. In agreement with literature data, the stability of $[Ni(III)cyclam]^{3+}$ significantly decreases with increase in pH, however even at the highest pH studied the $t_{1/2}$ value is about 3h. The value of $t_{1/2}$ estimated by us at pH = 1 is about twice as high as that reported[11], however it is similar to the value of $t_{1/2}$ ($\approx$10 h) reported for $[Ni(III)cyclam]^{3+}$ in 0.3M $NaClO_4$ at pH = 1.6 by Zeigerson *et al.*[7]

Stability of Ni(III)cyclam in $NaClO_4$ Solutions

The kinetic stability of $[Ni(III)cyclam]^{3+}$ was studied in $NaClO_4$ solutions in the concentration range 0.1–7M. The voltammetric studies of the influence of the $NaClO_4$ concentration on the value of the redox potential of the Ni(II)/Ni(III) in cyclam carried out by Buttafava *et al.*[2] indicated that an increase in the salt concentration from 0.1 to 7M caused a shift of E_f by about 0.080V toward more positive values.

Figure 4 shows the change in $t_{1/2}$ of $[Ni(III)cyclam]^{3+}$ as a function of $NaClO_4$ concentration. The results presented show that a progressive increase in $NaClO_4$ concentration generates a significant destabilization effect on Ni(III) species.

Stability of Ni(III) in Dependence on the Kind of Complex and Solvent

The kinetic stability of Ni(III) in complexes **1–3** was studied in water and in three aprotic solvents: ACN, DMF, and DMSO, all containing anhydrous 0.1M $NaClO_4$. The stability of Ni(III) in complex **4** was measured only in aprotic solvents because it was insoluble in water.

In all complexes, the Ni(II)/Ni(III) redox process was reversible. Changes of E_f expressed *vs.* the ferrocene (Fc) redox system depend on the donor number (DN) of the solvent as shown in Figure 5. Under our experimental conditions, potentials of Fc vs. 1 MCE were 0.275V, 0.425V and 0.370V in

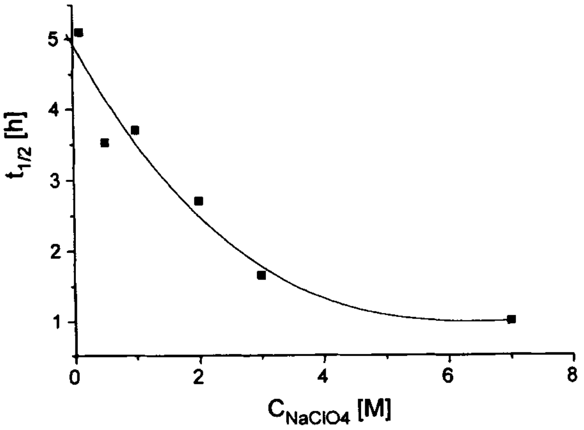


FIGURE 4 Half-life times $t_{1/2}$ of the $[Ni(III)cyclam]^{3+}$ as a function of $NaClO_4$ concentration.

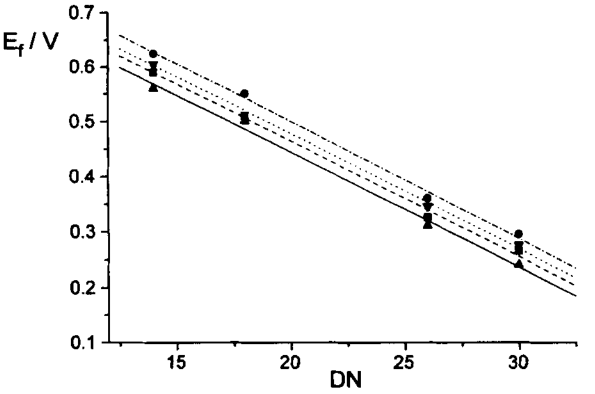


FIGURE 5 Formal potentials E_f of the Ni(II)/Ni(III) redox couple in complex **1** (■), in complex **2** (●), in complex **3** (▲), and in complex **4** (▼) as a function of solvent donor number; supporting electrolyte 0.1M $NaClO_4$.

ACN, DMF and DMSO, respectively. Results presented in Figure 5 indicate that the thermodynamic stability of Ni(III) increases in the series: complex **3** > complex **1** > complex **4** > complex **2**.

For all complexes in the solvents under investigation, the decay of Ni(III) species followed first order kinetics; similarly as for $[Ni(III)cyclam]^{3+}$ in aqueous solutions. However, the wavelength of the absorption band characteristic of Ni(III) species depended on the kind of complex and solvent. The data are presented in Table I.

TABLE I The dependence of the wave length of absorption band characteristic for Ni(III) species on the kind of complex and solvent.

Complex	l [nm]			
	ACN	H_2O	DMF	DMSO
1	308	308	284	298
2	308	312	286	298
3	300	298	284	298
4	305	—	284	298

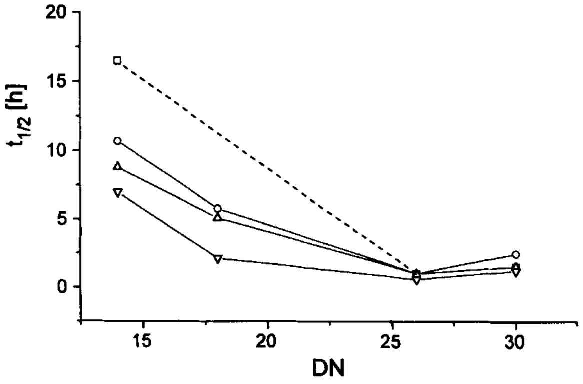


FIGURE 6 Half-life times $t_{1/2}$ of Ni(III) in complex **1** (Δ), in complex **2** (∇), in complex **3** (O), and in complex **4** (■) as a function of the solvent donor number; electrolyte 0.1M $NaClO_4$.

Figure 6 shows the change in $t_{1/2}$ of Ni(III) in complexes **1–4** vs. DN of the solvent. The stability of all complexes is the highest in the least basic solvent (ACN) and it decreases with increasing basicity of the solvent. However, in aqueous solutions the stability of Ni(III) also depends on the kind of complex.

DISCUSSION

The presented investigations have shown a significant influence of pH, concentration of indifferent electrolyte ($NaClO_4$), kind of complex, and solvent on the thermodynamic and kinetic stability of Ni(III).

The shift of E_f and the loss of reversibility of the Ni(II)/Ni(III) redox process in cyclam with an increase in the basicity of the solution (Figure 2, curve 1) may be due to the interaction of the central ion with OH^- anions in the axial position. Taking into account a high positive potential of the redox couple Ni(II)/Ni(III) the concentration of OH^- anions in the double layer region may be significant although their bulk concentrations are rather low.

The coordinating influence of the OH^- anions to the Ni(II) and Ni(III) centers in some tetraazacyclotetradecane complexes has been postulated.[8,28] Also in our previous paper[19] the coordination of the OH^- ions to $[Ni(II)cyclam]^{2+}$ in alkaline solutions has been reported. The OH^- anions can directly coordinate to the nickel center in Ni(II)-cyclam which exists in the square-planar form or may be produced by deprotonation of the apically coordinated water molecules in Ni(II)-cyclam which exists in the octahedral form. The apical coordination of Ni(II) by one OH group and by one H_2O molecule seems to be the most probable situation. However, in the case of Ni(III) complexes one should expect axial coordination by two OH^- anions.

This conclusion seems to be supported by the experiment with complex 3. In this complex, due to the axial binding of the NH_2 group, the nickel centre is less acidic than in cyclam, and the apically coordinated water molecule does not deprotonate. This may explain the constant value of E_f as a function of pH (Figure 2, curve 2) obtained for this complex.

A shift in potential of the Ni(II)/Ni(III) redox couple in cyclam to more positive values with an increase in $NaClO_4$ concentration observed by Buttafava *et al.*[2] indicates the less thermodynamic stability of Ni(III) which according to the above mentioned authors may be connected with a decrease in H_2O activity. This may also be the reason for the decreasing kinetic stability observed by us (Figure 4). As the solvating properties of the medium change a competition for H_2O molecules between Ni(III) center and electrolyte ions begins. Decrease of H_2O activity weakness it's coordination to Ni(III) center and second-sphere complex solvent interactions facilitating Ni(III) decomposition.

The values of E_f for all complexes studied shifted toward less positive values with the change in DN, (Figure 5) used as a measure of solvent basicity according to the Lewis interpretation. This indicates that the formation of Ni(III) is favoured by an increase in DN.

The thermodynamic stability of Ni(III) is highest in complex **3**. In this complex the axially coordinated H_2O molecule is substituted by a molecule of the organic solvent in non-aqueous systems. We proved this in a series of experiments in which the content of H_2O released after the dissolution of complex in a given solvent was determined by the Karl-Fischer method. The presence of the NH_2 group as the second axial substituent may be the reason that in this complex the molecule of solvent is more strongly coordinated to the Ni(III) center making it thermodynamically more stable than in other complexes.

The lowest thermodynamic stability of Ni(III) was found in complex **2**. This may be due to the presence of the methyl substituent in the chelate ring which makes coordination of a solvent molecule more difficult. This is consistent with the observation of Lovecchio *et al.*[29] Also we have previously shown[30] that in ACN containing 0.1M $NaClO_4$ the potential of the Ni(II)/Ni(III) redox couple was more positive in dimethylated cyclam in comparison with unsubstituted species.

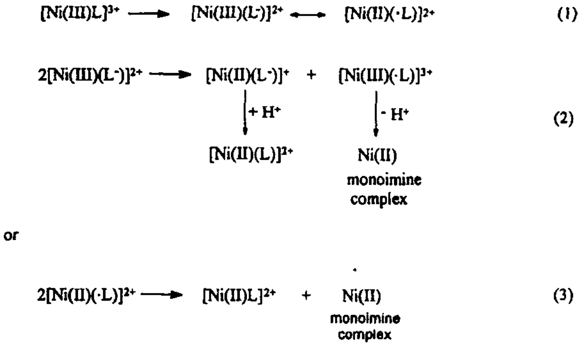
However, the kinetic stability of Ni(III) does not parallel the thermodynamic stability (Figure 6). The stability of Ni(III) complexes was the highest in ACN and, as found in aqueous solutions, it depended on the kind of complex. We have no explanation for the high stability of Ni(III) in complex **4** in ACN. In the case of the other complexes, their kinetic stability in ACN as well as in water paralleled their thermodynamic stability.

However, in DMF and DMSO stability was low and practically independent of the kind of complex.

Among the factors which can influence the kinetics of Ni(III) decay the most important are: the particular ligand type, the nature of the axial substituents, and the basicity of the solution. For instance Zeigerson *et al.*[7] have found that $[Ni(III)cyclam]^{3+}$ prepared by electrolysis in 0.3M $NaClO_4$ at pH = 1.6 had $t_{1/2}$ *ca.* 10 h and the Ni(III) complex of *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in the same solution only *ca.* 1.2 min.[9] However, for $[Ni(III)cyclam]^{3+}$ at the same pH in 0.5M Na_2SO_4 the value of $t_{1/2}$ was *ca.* 5 days.[6] Also Fabbrizzi and Proserprio[33] in the case of Ni(III) complexes with cyclic terdenate ligands containing NH, O, and S, respectively, found significant differences in $t_{1/2}$ of Ni(III).

Solvent basicity is also essential for the stability of Ni(III) tetraazamacrocyclic complexes however, we have found no literature data concerning kinetic parameters. The problem is a complex one because in addition to solvation processes, the effect of intramolecular (chelation) must also be considered.

The mechanism of decomposition of Ni(III) macrocyclic tetraamine complexes and the nature of the products is an area of active investigation.[12,13,31,32] Barefield and Mocella[13] claimed that the intermediate product of decomposition was a Ni(II) ligand radical complex ($[Ni(II)(\cdot L)]^{2+}$). They identified it on the basis of flow experiments performed in the cavity of an ESR spectrophotometer. Recently De Santis *et al.*[12] studied the decay of $[Ni(III)cyclam]^{3+}$ by pH change using a high speed diode array spectrophotometer coupled to a stopped-flow system. They assumed that the first decomposition product, absorbing at $\lambda = 539$ nm was a $[Ni(III)(L^-)]^{3+}$ anion (where L denotes cyclam and L^- its deprotonated form). This assumption was based on analogy with decomposition of an Fe(III)-bis(1,3,7-triazacyclonate) complex studied by Pohl *et al.*[34] who unambiguously characterised the deprotonated complex as an Fe(III) species. In fact the $[Ni(III)(L^-)]^{2+}$ anion and the $[Ni(II)(\cdot L)]^{2+}$ radical may be treated as resonance structures. Therefore, we suggest that there is no essential contradiction between the mechanistic approach presented in ref. 12 and ref. 13. Then, the unified mechanism of decomposition may be described by scheme 1.



SCHEME 1

The pathways (2) and (3) are experimentally indistinguishable.

In both cases, the first step of decomposition of Ni(III) complexes is connected with dehydrogenation of one of the four equivalent amine groups in the macrocyclic ligand. The nature of the intermediate products is a matter of hypothesis. However, in the spectrum of the final solution $[Ni(II)cyclam]^{2+}$ and its monoimine complex were found by De Santis *et al.*[12] Also Korybut-Daszkiewicz[35] decomposed the samples of $[Ni(III)cyclam]^{3+}$ by addition of carbonate solution of pH = 8 and isolated as final decomposition products $[Ni(II)cyclam](ClO_4)_2$ and its monoimine analog, although not in quantitative amounts.

In the case of complexes studied by us the decay of Ni(III) species followed the first order kinetics independent of the solvent, electrolyte concentration and pH. This situation has been observed by other authors. This fact implies that the rate-determining step in the overall decomposition process should be first order.

The acidity of protons at the NH groups of the macrocyclic ring markedly depends on the medium and kind of complex. Therefore, the formation rate of $[Ni(III)(L^-)]^{2+}$ anion may strongly depend on the experimental conditions. In the experiments of De Santis *et al.*[12] the formation of $[Ni(III)(L^-)]^{2+}$ anion in a measurable quantity was forced by a rapid change of pH. We could also observe the transient red-violet color if we suddenly basified a Ni(III) complex produced by electrolysis at much lower pH. However, under our experimental conditions Ni(III) complexes decomposed spontaneously in solutions in which they have been produced. This may be the reason that deprotonation of the NH group may not always be a rapid process.

Deprotonation of one of the NH groups in the tetraazamacrocyclic complex is strongly base promoted. This may explain the solvent dependent differences in the kinetic stability of Ni(III) in complexes we studied. Since DMSO and DMF are much stronger bases than ACN and H_2O, they may significantly facilitate the abstraction of a proton in spite of the fact that their apical coordination to the Ni center is stronger than the latter two solvents. This may also be a reason that the stability of Ni(III) does not depend on the kind of complex.

Some explanation is required for the rather slow decay of Ni(III) complexes in alkaline solutions. As the Ni(III) complexes are produced electrochemically the concentration of OH^- anions in the diffuse layer is much greater than in the bulk of solution. In these conditions, a water molecule apically coordinated to the Ni center may be deprotonated with formation of a Ni(III)-OH bond. The presence of an axially coordinated anion may significantly increase the rate of Ni(III) decay.

Acknowledgements

Part of this work was supported by the grant of the European Community ERB 3510 PL 922911 No. 4076 for J.T. and No. 4077 for G.R. The authors thank to Prof. L. Fabbrizzi from Pavia University, Italy, where part of the work was done, for helpful discussion.

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