for the addition of OH^- to the hexafluoroacetylacetonato (hfac) ligand in $Co(en)_2(hfac)^{2+}$ to produce $Co(en)_2(hfac{\cdot}OH)^+$; viz., $\Delta \bar{V} = +10.7$ cm^3 mol^{-1}. $\Delta V^{*}(k_i)$ is usually small for an interchange step (I_a or I_d).[30] The overall $\Delta V^{*}_{\text{exptl}}$ value can again not be as large as found in this study. A final possibility is the recently suggested E2 mechanism,[9,10] which consists of a concerted process for the formation of the five-coordinate intermediate, thus basically S_N1, in which deprotonation immediately leads to loss of Cl^- as indicated in (10). It is realistic to expect $\Delta V^{*}_{\text{exptl}}$ for this process

$$Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \rightarrow Co(NH_3)_3(NH_2)(NH_2X)^{2+} + Cl^- + H_2O \quad (10)$$

to be smaller than $\Delta \bar{V}(K)$, since the latter quantity also contains a positive contribution resulting from the recombination of water with the conjugate base species (see (2)). Thus we conclude that the significantly higher $\Delta V^{*}_{\text{exptl}}$ value found in this study can only be interpreted in terms of the suggested S_N1CB mechanism.

Acknowledgments. The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Y.K. acknowledges support from the Japanese Ministry of Education, which enabled him to participate in this study. The authors wish to thank Prof. S. Balt (Free University of Amsterdam) for drawing their attention to the series of complexes investigated and for providing the samples.

Registry No. *cis*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$, 91383-91-4; *trans*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$, 36527-86-3; *trans*-$Co(NH_3)_4(C_2H_5NH_2)Cl^{2+}$, 91321-37-8; *cis*-$Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl^{2+}$, 91321-39-0; *trans*-$Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl^{2+}$, 91384-21-3; *trans*-$Co(NH_3)_4(n\text{-}C_4H_9NH_2)Cl^{2+}$, 91321-41-4; *trans*-$Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl^{2+}$, 91321-43-6.

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Università di Pavia, 27100 Pavia, Italy

Thermodynamic Aspects of the Nickel(III/II) Redox Change in Polyaza Macrocyclic Complexes

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The reaction entropies ΔS°_{rc} of the Ni^{III}/Ni^{II} redox couple for some polyaza macrocyclic complexes in aqueous solution have been determined by measuring $E_{1/2}(Ni^{III}/Ni^{II})$ values through voltammetry experiments at varying temperatures using a nonisothermal cell. ΔS°_{rc} values are in any case positive, and their magnitudes decrease with the increasing number of nitrogen atoms of the coordinating system (from four to six): this is ascribed to the release of water molecules from the coordination sphere and/or the hydration sphere during the Ni^{III}/Ni^{II} redox change. The presence of negative charges on the coordinating system (deprotonated amido or carboxylate groups) makes the $\Delta S^\circ_{rc}(Ni^{III}/Ni^{II})$ values substantially less positive. Redox equilibria of the type $M^{III}L_1 + M^{II}L_2 \rightleftharpoons M^{II}L_1 + M^{III}L_2$ have been considered and the corresponding values of the enthalpy term (ΔH°) evaluated for chosen pairs of ligating systems L_1 and L_2. Inspection of the above values indicates that the enthalpy contribution (which includes bond energy terms) favors the attainment of trivalent nickel along the sequence N(amine) > N(deprotonated amido groups) $\simeq$ $-COO^-$ and that a square arrangement of four nitrogen atoms (cyclam) is the very most favorable coordinative situation (from the enthalpic point of view).

Introduction

Transition-metal complexes very often display one-electron or multielectron redox activity to give species that are stable in solution at least on the time scale of electrochemical perturbation techniques such as cyclic voltammetry. As a consequence, a lot of $E_{1/2}$ values, associated to redox changes of metal complexes, have been determined by conventional voltammetric methods. It should be noted that in the case of electrochemical reversibility the $E_{1/2}$ value approaches the standard electrode potential value, E°; thus, it has a thermodynamic significance. In general, for a given class of coordination compounds displaying redox reactivity, the trend of $E_{1/2}$ values has been interpreted in terms of bonding quantities, such as ligand field stabilization effects, intensity of the coordinative interactions, etc. However, one could argue that above quantities are all enthalpy terms, whereas the electrode potential E° is proportional to the ΔG° value associated to the redox change and therefore it should be more correctly considered as "made" by two distinct contributions, enthalpic and entropic in nature. Whereas the ΔH° term is expected to include bonding quantities, i.e. the energies of the metal-donor atom interactions in the oxidized and in the reduced species, the ΔS° term should be mainly related to the solute–solvent interactions and to the order/disorder variations associated to the redox change.

In 1979 Weaver[1] pioneered the use of the voltammetric investigation at varying temperatures using a nonisothermal cell for the determination of ΔS°_{rc}, the difference of the standard entropies of the reduced and oxidized forms, $S^\circ_{red} - S^\circ_{ox}$, for simple metal complexes in aqueous solution. Since then, a lot of papers reporting entropy data on coordination compounds of varying nature and complexity have appeared.[2]

We report here a temperature-dependent electrochemical study using a nonisothermal cell on the Ni^{III}/Ni^{II} redox change for metal complexes with polyaza macrocycles, a topic to which we have devoted some interest in past years.[3]

Trapping of the metal center by a cyclic coordinating framework permits the attainment of the usually unstable Ni^{III} oxidation state. The solution stability of the trivalent complex, relative to the divalent one, is expressed by the value of the $E_{1/2}(Ni^{III}/Ni^{II})$, a quantity that can be modulated over a substantial range of potentials through structural modifications on the ligand (nature and number of the donor atoms,[4] size of the macrocyclic cavity,[5] degree of unsaturation,[6] presence of substituents on the nitrogen atoms[7] or on the carbon backbone).[8]

We wish to report here a temperature-dependent electrochemical investigation on the Ni^{III}/Ni^{II} redox couple in aqueous solution for some fully saturated polyaza systems of varying denticity: the

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(1) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131-1137.

(2) Hupp, J.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639-3644 and references therein.

(3) Fabbrizzi, L. *Comments Inorg. Chem.* **1985**, *4*, 33-54.

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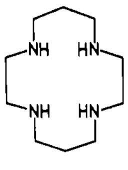

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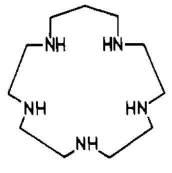

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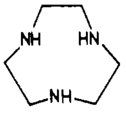

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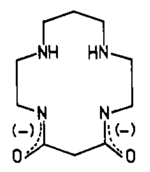

4

14-membered tetraaza macrocycle cyclam (**1**), the 16-membered pentaaza macrocycle [16]aneN_5 (**2**), and the six-coordinating system obtained through the coordination of two molecules of the 9-membered macrocycle [9]aneN_3 (**3**), which have been found to form stable trivalent species in aqueous solution. In particular, we have chosen the ligands that, among each class of *n*-dentate macrocycles, give the most stable Ni^{III} complexes from either a thermodynamic or a kinetic point of view.

Moreover, in order to evaluate the effect of the electrical charge of the redox-active species on $\Delta S°_{rc}(Ni^{III}/Ni^{II})$, ligating systems bringing a double-negative charge (e.g. dioxocyclamato(2–) (**4**))[9] have been investigated.

As anticipated, the purpose of this work is to separately consider the enthalpy and entropy contributions that contribute to the potential of the Ni^{III}/Ni^{II} redox change and to further clarify the factors that govern access to the Ni^{III} oxidation state. The very final goal of our work remains the finding of further pieces of information that can give useful suggestions for the synthesis of a tailor-made ligand for the Ni^{III} metal ion.

Experimental Section

Ligands and Complexes. Cyclam (**1**),[10] [16]aneN_5 (**2**),[4] [9]aneN_3 (**3**),[11] and dioxocyclamate (**4**)[12] were prepared according to the reported procedures. Metal complexes with polyamine macrocycles 1–3 were obtained by mixing hot ethanolic solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ and of the ligand in appropriate molar ratios and refluxing for 1 h. Cooling of the solutions gave the nickel(II) complex perchlorate salts, which were satisfactorily analyzed. *Caution*! Perchlorate salts of metal–polyamine complexes can be explosive and must be handled with care: such compounds should not be heated as solids. The $[Ni(O_2cyclam)]^0$ (O_2cyclam = dioxocyclamato(2–)) complex was obtained on mixing an aqueous solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ with an equimolar ethanolic solution of dioxocyclam at room temperature. When the mixture was allowed to stand, gold platelets of the Ni^{II} complex formed.

Temperature-Dependent Electrochemistry. A nonisothermal cell assembly based on the design of Weaver[1] was employed. In particular, a calomel electrode, filled with a 3.5 M NaCl solution, was dipped in a compartment made 3.5 M in $NaClO_4$ and thermostated by a jacket of flowing water circulating at 18 °C. This reference compartment was separated by a fine-porosity glass frit from the working compartment, containing the working electrode and the counter electrode thermostated at the chosen temperature, which typically varied in the range 5–50 °C (controlled within 0.05 °C). For measurements in 0.5 M KNO_3 the reference compartment was filled with a 3.5 M NH_4Cl solution. A carbon-paste electrode was used as a working electrode and a platinum foil as counter electrode.

Nickel(II) perchlorate complexes were dissolved in the aqueous $NaClO_4$ solution of the working cell in (1–5) × 10^{-4} M concentration, and the occurrence of the Ni^{II}/Ni^{III} redox change was monitored using either cyclic voltammetry (50–100 mV s^{-1}) or AC_1 voltammetry (1 mV s^{-1}). The latter technique was preferred for the determination of $E_{1/2}$ values since it gives peak potentials with a better precision (±1–2 mV). To prevent hydrolysis of the Ni^{III} complex, solutions of the cyclam (**1**) complex were acidified to pH 2 by using standard $HClO_4$. In the case of complexes with amine macrocycles **2** and **3**, the Ni^{III}/Ni^{II} half-wave potential and its temperature coefficient displayed the same values in either neutral or acidified solution, indicating that hydrolysis of the divalent species does not occur with these coordinating systems.

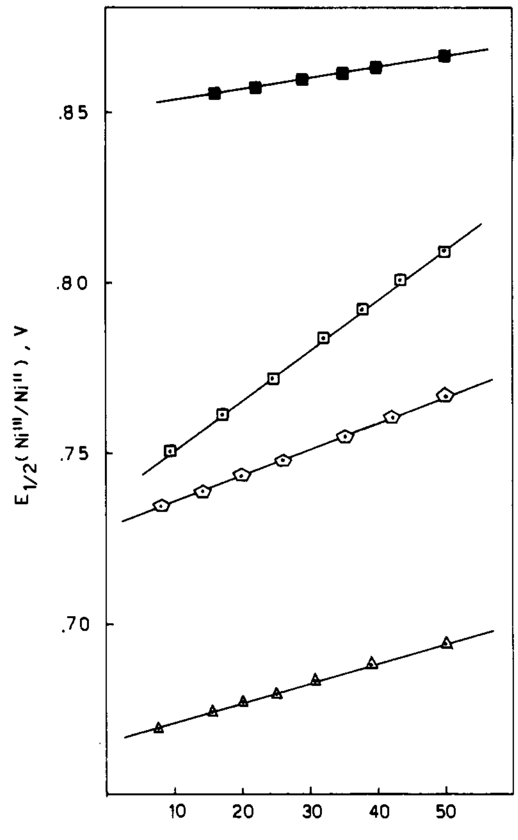

Figure 1. Dependence of $E_{1/2}$ for the Ni^{III}/Ni^{II} redox change in polyaza macrocyclic complexes upon temperature at 3.5 M ionic strength ($NaClO_4$): △, $[Ni(3)_2]^{3+/2+}$; □, $[Ni(1)]^{3+/2+}$; ⬠, $[Ni(2)]^{3+/2+}$; ■, $[Ni(4)]^{+/0}$.

Table I. Half-Wave Potentials, $E_{1/2}$ (V, at 25 °C), and Entropy Changes, $\Delta S°_{rc}$ (cal mol^{-1} K^{-1}), for the Ni^{III}/Ni^{II} Redox Couple of Polyaza Macrocyclic Complexes in 3.5 M $NaClO_4$ Aqueous Solution

redox couple	$E_{1/2}$[a]	$\Delta S°_{rc}$[b]	redox couple	$E_{1/2}$[a]	$\Delta S°_{rc}$[b]
$[Ni(3)_2]^{3+/2+}$	0.679	14.0	$[Ni(1)]^{3+/2+}$	0.772	34.3
$[Ni(2)]^{3+/2+}$	0.747	17.5	$[Ni(4)]^{3+/2+}$	0.858	7.2

[a] Vs. a 3.5 M NaCl calomel electrode, ±2 mV. [b] ±0.5 cal mol^{-1} K^{-1}.

Electrochemical measurements were performed with an AMEL apparatus connected to a Hewlett-Packard 7045A fast X-Y recorder (CV) and a Polarecord E 502 (Metrohm) machine (AC_1).

Results and Discussion

Ni^{III}/Ni^{II} Redox Change in 6-, 5-, and 4-Coordinating Macrocyclic Systems. Figure 1 shows the temperature-dependent behavior of the $E_{1/2}$ values for the Ni(III)/Ni(II) redox change in 3.5 M $NaClO_4$ solution for 1:1 complexes of **1** and **2** and the 1:2 complex of **3**. $E_{1/2}$ values were the peak potentials of the reversible AC_1 profiles obtained by performing voltammetric investigations using a carbon-paste working electrode in a nonisothermal cell. Entropy changes for the Ni^{III}/Ni^{II} half-reaction, $\Delta S°_{rc}$, were obtained from the slope of the $E_{1/2}$ vs. *T* straight lines (obtained through least-squares analysis) drawn in Figure 1 and are reported in Table I.

The 3.5 M $NaClO_4$ concentration has been chosen for reasons of homogeneous comparison. In fact, the Ni^{II} cyclam complex is present in dilute solution as a mixture of two species:[13] the blue,

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[12] Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807–813.

high-spin six-coordinate complex and the yellow, low-spin four-coordinate complex, according to the equilibrium

$$\underset{\text{octahedral, high-spin}}{[\mathrm{Ni(cyclam)(H_2O)_2}]^{2+}} \rightleftharpoons \underset{\text{square, low-spin}}{[\mathrm{Ni(cyclam)}]^{2+}} + 2\mathrm{H_2O} \quad (1)$$

At 25 °C in 0.1 M $NaClO_4$ solution 29% of the high-spin and 71% of the low-spin species are present. Equilibrium 1 is displaced to the right by an increase in either the temperature or the supporting electrolyte concentration. It is evident that the temperature dependence of equilibrium 1 superimposes with the temperature dependence of $E_{1/2}(\mathrm{Ni^{III}/Ni^{II}})$ values and complicates the interpretation of data. On the other hand, titration of an aqueous solution of $[\mathrm{Ni(cyclam)}](\mathrm{ClO_4})_2$ with $NaClO_4$ has shown that the absorption band of the yellow low-spin species (at 445 nm) reaches its limiting value (64.5 dm^3 mol^{-1} cm^{-1}) for electrolyte concentration ≥3.0 M, indicating the presence of the 100% of the square complex. Therefore, the concentration of 3.5 M supporting electrolyte $NaClO_4$ has been chosen in order to avoid exotic temperature-dependent effects and to define an unambiguous reference state for the Ni^{II} cyclam complex (the low-spin, square species).

For the three investigated complexes ΔS°_{rc} values associated with the Ni^{III}/Ni^{II} redox change are all cases positive, the smallest value being observed in the case of bis(triaza macrocyclic) complexes, whose half-reaction is

$$\underset{\text{low-spin}}{[\mathrm{Ni([9]aneN_3)_2}]^{3+}} + e^- \rightleftharpoons \underset{\text{high-spin}}{[\mathrm{Ni([9]aneN_3)_2}]^{2+}} \quad (2)$$

The stereochemistry of the complexes involved in the half-reaction (2) has been elucidated through X-ray diffraction studies: in the trivalent complex, the Ni^{III} ion is six-coordinated according to an elongated octahedral arrangment (Ni–N(equatorial) = 1.97 Å; Ni–N(axial) = 2.11 Å).[11] On the other hand, the six-coordinated Ni^{II} complex presents a nearly regular octahedral stereochemistry (Ni–N (average) = 2.10 Å).[14] The measured ΔS°_{rc} value (14.0 cal mol^{-1} K^{-1}) should be corrected for the spin state change (from 1 unpaired electron for Ni^{III} to 2 unpaired electrons on the Ni^{II}) for the (Rln3–Rln2) term to give 13.2 cal mol^{-1} K^{-1}. Since there are no serious variations in the stereochemistry, the ΔS°_{rc} value must be mainly ascribed to a change in solute–solvent interactions during the +3/+2 redox change.

In a very qualitative way, decrease of the electrical charge on the metal centers reduces the acidity of the coordinated NH groups and their ability to bind water molecules through hydrogen bonding. The values found for the $[\mathrm{Ni(3)_2}]^{3+/2+}$ redox change can be compared to that found for the $[\mathrm{Ru(en)_3}]^{3+/2+}$ redox couple (13 cal mol^{-1} K^{-1}).[1]

The Ni^{III}/Ni^{II} redox change for the complex with the quinquedentate macrocycle **2**, which involves a more positive ΔS°_{rc} value, can be represented by

$$\underset{\text{low-spin}}{[\mathrm{Ni([16]aneN_5)(H_2O)}]^{3+}} + e^- \rightleftharpoons \underset{\text{high-spin}}{[\mathrm{Ni([16]aneN_5)(H_2O)}]^{2+}} \quad (3)$$

ESR (for Ni^{III}) and electronic spectra (for Ni^{II}) indicate an octahedral stereochemistry for both the oxidized and reduced forms, with a solvent molecule occupying a coordination site.[4] Also in this case, the experimental ΔS°_{rc} value must be corrected for spin-state expansion, giving the value of 14.7 cal mol^{-1} K^{-1}. The more positive value, compared to that for the fully saturated bis(triaza macrocyclic) complex, can be ascribed to the presence of a H_2O molecule instead of a NH group in the coordinative sphere. A coordinated water molecule is much more effective than an amine group (primary or secondary) in orientating through hydrogen-bonding water molecules of the first hydration sphere, and as a consequence, the 3+ to 2+ reduction of the electrical charge on the metal center involves the release of a greater number of solvent molecules, which justifies the more positive value of ΔS°_{rc} (see for instance ΔS°_{rc} (cal mol^{-1} K^{-1}) along the series $[\mathrm{Ru(H_2O)_6}]^{3+/2+}$, 36; $[\mathrm{Ru(NH_3)_6}]^{3+/2+}$, 19; $[\mathrm{Ru(en)_3}]^{3+/2+}$, 13; $[\mathrm{Ru(NH_3)_5(H_2O)}]^{3+/2+}$, 25).[1]

The most positive ΔS°_{rc} value is exhibited by the half-reaction of the cyclam complex, which is represented by

$$\underset{\text{low-spin}}{[\mathrm{Ni(cyclam)(H_2O)_2}]^{3+}} + e^- \rightleftharpoons \underset{\text{low-spin}}{[\mathrm{Ni(cyclam)}]^{2+}} + 2\ \mathrm{H_2O} \quad (4)$$

The trivalent species presents a trans octahedral stereochemistry,[6,13] whereas the divalent, diamagnetic, complex is square planar. The ΔS°_{rc} value is the most positive among the investigated polyaza macrocyclic complexes and also becomes more positive after correction for the spin-state variation (Rln1–Rln2 = 1.4 cal mol^{-1} K^{-1}). The especially large value of ΔS°_{rc} seems to be ascribed to the fact that the Ni^{III}/Ni^{II} reduction process, in addition to the liberation of hydration sphere water molecules typically associated to the +3/+2 electrical charge reduction, involves the neat release of the two water molecules apically coordianted.

Present results may permit one to rationalize the stabilization of trivalent nickel through coordination by polyaza macrocycles. $E_{1/2}(\mathrm{Ni^{III}/Ni^{II}})$ values reported in Table I indicate that $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$, which is formed at a considerably less negative potential, is more stable than $[\mathrm{Ni(cyclam)}]^{3+}$. This could be reasonably ascribed to the fact that the Ni^{III} ion prefers six-coordination, and, therefore, it should profit from the strain-free quasi-octahedral coordination by two molecules of $[9]aneN_3$ rather than from the in-plane coordination by quadridentate cyclam, even if it is especially strong. Let us now consider the metathetic equilibrium

$$[\mathrm{Ni(cyclam)(H_2O)_2}]^{3+} + [\mathrm{Ni([9]aneN_3)_2}]^{2+} \rightleftharpoons [\mathrm{Ni(cyclam)}]^{2+} + [\mathrm{Ni([9]aneN_3)_2}]^{3+} + 2\mathrm{H_2O} \quad (5)$$

Equation 5 is displaced to the right (at 25 °C, E° = 93 mV, $K = 10^{1.5}$). The combination of ΔG° and ΔS° values permits the determination of the enthalpy change ΔH° associated with redox process 5. Thermodynamic quantities ($\Delta G^\circ = -2.1$ kcal mol^{-1}, $\Delta H^\circ = +3.9$ kcal mol^{-1}, $T\Delta S^\circ = +6.0$ kcal mol^{-1}) indicate that the greater stabilization of $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ results from the particularly favorable entropy term, which more than compensates the enthalpy term, which, on the contrary, is strongly favorable to the formation of $[\mathrm{Ni(cyclam)(H_2O)_2}]^{3+}$. It should be considered that since the ΔH° term essentially expresses the ligand field effects, in-plane four-coordination by cyclam favors access to trivalent nickel much better than six-coordination by the two molecules of $[9]aneN_3$. Thus, the highest oxidation power and the lower stability of $[\mathrm{Ni(cyclam)(H_2O)_2}]^{3+}$ in aqueous solution compared to the case of $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ simply results from the especially large entropy gain associated to the reduction half-reaction due to the liberation of the two coordiated water molecules, which more than compensates an unfavorable enthalpy contribution.

Effect of the Overall Electrical Charge of the Complex on the Ni^{III}/Ni^{II} Redox Change. A further macrocyclic tetraaza system that is able to stabilize trivalent nickel in aqueous solution is represented by dioxocyclamato(2–) (**4**). This ligand exhibits the same 14-membered framework as cyclam (**1**) but contains two deprotonated amido groups in the donor set. The negative charge of each deprotonated amido group must be considered as delocalized on the enrtire NCO group (see formula **4**), as indicated by the sharp decrease of the C=O stretching frequency of the Ni^{II} complex (1650 cm^{-1}) compared to that of the neutral diamine–diamide macrocycle dioxocyclam (1675 cm^{-1}). Due to the dinegative charge of the ligand, the Ni^{III}/Ni^{II} redox change in the dioxocyclamato system involves a neat +/0 process. Stereochemical aspects of the Ni^{III}/Ni^{II} redox change are the same as found in the case of the cyclam system: the ESR spectrum of the $[\mathrm{Ni^{III}(O_2cyclam)}]^+$ species is that expected for a d^7, low-spin, cation in an elongated octahedral coordinative environment, with two water molecules occupying the axial sites; the Ni^{II} complex exists as 100% of the low-spin, square-planar form, even at low concentration of supporting electrolyte.[15]

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[13] Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438–444.

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In 3.5 M $NaClO_4$ solution, the $E_{1/2}(Ni^{III}/Ni^{II})$ value is more positive than for the cyclam complex (see Table I), and its linear increase with temperature corresponds to a $\Delta S°_{rc}$ value of 7.2 cal mol^{-1} K^{-1}, a quantity much less positive than observed for the cyclam analogue. This behavior should be ascribed to the fact that the Ni^{III} dioxocyclamato complex, due to its reduced overall electrical charge (+1), is able to orient a smaller number of water molecules in its hydration sphere, and the number of particles released in the process of charge reduction is consequently lower than in the case of cyclam.

Let us consider now the thermodynamic quantities associated to the redox equilibrium

$$[N^{III}(O_2cyclam)(H_2O)_2]^+ + [Ni^{II}(cyclam)]^{2+} \rightleftharpoons [Ni^{II}(O_2cyclam)]^0 + [Ni^{III}(cyclam)]^{3+} + 2H_2O \quad (6)$$

($E° = 0.086$ V; $\Delta G° = -2.0$ kcal mol^{-1}; $\Delta H° = -8.1$ kcal mol^{-1}; $T\Delta S° = -6.1$ kcal mol^{-1}). Redox equilibrium 6 is displaced to the right ($K = 10^{1.5}$); i.e., formation of Ni^{III} is easier in the case of coordination by cyclam rather than by the dioxocyclamato(2−) ligand. Above thermodynamic quantities indicate that stabilization of Ni^{III} by cyclam rather than by dioxocyclamato(2−) originates from an extremely favorable enthalpy term that overwhelms an unfavorable entropy term. In other words, the quenching of the electrical charge by dioxocyclamato(2−) favors the attainment of the Ni^{III} state through an entropy-driven mechanism, but this contribution is more than compensated by the ligand field effects (enthalpy term) associated with cyclam coordination, which operates in favor of Ni^{III} stabilization.

We have approached the study of the effect of the overall electrical charge of the complex also from a different side. In particular, we wanted to consider the charge reduction effect also in the case of six-coordination. To do that, we were interested in generating a ternary species containing a rigid coordinating moiety (the triaza macrocycle $[9]aneN_3$) and a flexible dinegative moiety (e.g. the iminodiacetate anion, IDA^{2-}). Zompa,[16] performing pH titration measurements on the Ni^{2+}–$[9]aneN_3$ system in a 1:1 molar ratio, evidenced the formation of the sole $[Ni([9]aneN_3)]^{2+}$ species and determined its formation constant. This 1:1 complex exhibits the typical macrocyclic inertness toward demetalation and persists even in acidic solution.[17] We have prepared a standard $[Ni([9]aneN_3)]^{2+}$ solution by dissolving equimolar amounts of $Ni(ClO_4)_2$ and $[9]aneN_3$ in 0.5 M KNO_3. The solution was refluxed for 1 h to accelerate the formation of the $[Ni([9]aneN_3)]^{2+}$ species, which is slow at room temperature.[16] To this solution was added 1 equiv of iminodiacetic acid. The solution was then thermostated at 25 °C and was titrated with standard NaOH. Features of the titration curve (presence of a buffer zone followed by a sharp pH jump after the addition of 2 equiv of standard base) are indicative of the binding of the iminodiacetate anion to the $[Ni([9]aneN_3)]^{2+}$ complex, according to a 1:1 stoichiometry. Least-squares curve fitting of titration data[18] gave a log *K* value of 7.63 for complexation equilibrium 7. The solution obtained from the pH titration studies, adjusted

$$[Ni([9]aneN_3)]^{2+} + IDA \rightleftharpoons [Ni([9]aneN_3)(IDA^{2-})]^0 + 2H^+ \quad (7)$$

to the minimum pH value at which the ternary species is present at 100% (i.e., 7.5), was investigated for the oxidation behavior with a carbon-paste electrode. Voltammetric studies disclosed a reversible one-electron oxidation profile (for both CV and AC responses) centered at an $E_{1/2}$ value of 0.800 V vs. SCE (0.5 M KNO_3, 25 °C).

A temperature-dependent investigation in the 5–50 °C range using the nonisothermal cell showed that $E_{1/2}(Ni^{III}/Ni^{II})$ for the ternary complex remained constant, corresponding to $\Delta S°_{rc} = 0$. For both $[Ni^{II}([9]aneN_3)(IDA^{2-})]^0$ and $[Ni^{III}([9]aneN_3)(IDA^{2-})]^+$ complexes, a more or less distorted octahedral stereochemistry can be hypothesized with a facially coordinated iminodiacetate anion, in analogy with the chelating mode of the corresponding bis(triaza macrocyclic) complex. The much smaller value of $\Delta S°_{rc}$ compared to that of the bis(triaza macrocyclic) system $[Ni(3)_2]^{3+,2+}$ (15 cal mol^{-1} K^{-1}, in 0.5 M KNO_3) should be ascribed to the fact that the electrical charge of the metal ions is shielded by the negative charge of the acetate groups. As a consequence, the $[Ni^{III}([9]aneN_3)(IDA^{2-})]^+$ complex is poorly hydrated and its reduction to Ni^{II} involves the release of a number of water molecules much lower than for the reduction of the tripositive $[Ni^{III}([9]aneN_3)_2]^{3+}$ species.

Also, for this type of complex it may be useful to consider the thermodynamic quantities associated with the redox equilibrium

$$[N^{III}([9]aneN_3)(IDA^{2-})]^+ + [Ni([9]aneN_3)_2]^{2+} \rightleftharpoons [Ni^{II}([9]aneN_3)(IDA^{2-})]^0 + [Ni([9]aneN_3)_2]^{3+} \quad (8)$$

($E° = 0.109$ V; $\Delta G° = -2.5$ kcal mol^{-1}; $\Delta H° = -7.0$ kcal mol^{-1}; $T\Delta S° = -4.5$ kcal mol^{-1}).

The situation is qualitatively similar to that observed for the cyclam/dioxocyclam redox equilibrium (7). In fact, also in this case, the entropy term favors the formation of the trivalent ternary species due to the charge-quenching effect, but this contribution is more than compensated by an enthalpy term very favorable to the formation of the trivalent bis(triaza macrocyclic) complex. This latter term reflects the stronger donor ability toward Ni^{III} (compared to Ni^{II}) of the amine nitrogen atom with respect to the oxygen atoms of the carboxylate group.

Conclusion

Present investigations on the thermodynamic aspects of the Ni^{III}/Ni^{II} redox change in some representative complexes with polyaza macrocycles throw light on the factors that control the attainment of trivalent nickel in aqueous solution. In particular:

(i) Solute–solvent interactions control the access to the Ni^{III} state according to an entropy-driven mechanism. Attainment of the trivalent complex is favored in processes that involve the less pronounced uptake of water molecules (to be accomodated in the coordination and/or hydration sphere). In particular, reduction of the overall electrical charge favors the Ni^{II}/Ni^{III} oxidation process.

(ii) Ligand field effects are expressed by the enthalpy term; in particular, $\Delta H°$ reflects the ligand field stabilization energy gain from which the Ni^{II} to Ni^{III} oxidation process profits. This investigation has shown that the Ni^{III} stabilizing effect decreases in the order N(amine) > N^-(amide) $\simeq$ $-COO^-$. Among polyamine macrocyclic complexes, solely considering metal ligand interactions, the square four-coordinating arrangement offered by cyclam remains the most favorable one, exerting a stabilization effect on Ni^{III} even greater than that exerted by coordinating systems of higher denticity.

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