

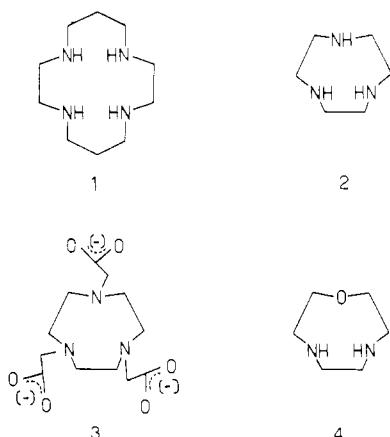
Entropy Contribution to the Ni^{III}/Ni^{II} Redox Change in Six-Coordinating Systems. Investigation of the Role of the Negative Charge of the Ligand in the Stabilization of High Oxidation States of the Metal Center

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Received February 1, 1989

Entropy changes ΔS°_{rc} associated with the two half-reactions (i) $[\text{Ni}^{\text{III}}\text{L}_2]^{3+} + e^- = [\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ and (ii) $[\text{Ni}^{\text{III}}\text{Y}]^0 + e^- = [\text{Ni}^{\text{II}}\text{Y}]^-$ (L = 1,4,7-triazacyclononane (2); Y³⁻ = 1,4,7-triazacyclononane-*N,N',N''*-triacetate (3)) have been determined through the investigation of the temperature dependence of the $E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}})$ parameter over the 0.1–3.5 M concentration range of the background electrolyte (NaCl). ΔS°_{rc} for half-reaction i is positive, and its value decreases with an increasing concentration of the background electrolyte, whereas ΔS°_{rc} for half-reaction ii is negative and its value increases (becoming less negative) with an increasing concentration of NaCl. The above results have been interpreted in terms of variation in the size of the hydration sphere of the electroactive species, which are related to changes of the electrical charge on the complexes. In particular, it is demonstrated that such polynegatively charged ligands as Y³⁻ favor access to unusually high oxidation states of the metal center due to a very favorable entropy term: this reflects a substantial increase of translational entropy, associated with the release of water molecules from the hydration sphere of the complex during the $[\text{Ni}^{\text{II}}\text{Y}]^-/[\text{Ni}^{\text{III}}\text{Y}]^0$ oxidation process.

Coordination of a 3d metal center by a cyclic polyamine system favors the attainment of high oxidation states. This unique property was first recognized in the case of nickel, for which preparation and characterization of a Ni^{III} complex¹ was carried out only a few years after the Ni^{II}-assisted synthesis of the 14-membered unsaturated tetraaza macrocycle 2,2,3,9,9,10-hexamethyl-1,4,8,11-tetraazacyclotetradeca-3,10-diene.² Advances in the synthetic procedures in the 1970s made available quite a large choice of polyaza macromolecules,^{3,4} and the solution chemistry of corresponding Ni^{II} and Ni^{III} complexes was extensively studied by using electrochemical⁵⁻⁷ and ESR techniques (to characterize the trivalent, d⁷, low-spin cation).⁷ Further studies have demonstrated that the greatest stabilization on the trivalent state (which is expressed by a less positive value of the Ni^{III/II} redox potential) is exerted by two different classes of cyclic polyamines: (i) a 14-membered symmetric tetraaza ring (cyclam (1) and derivatives), which chelates the metal center in a coplanar



fashion to produce a tetragonal stereochemistry, the axial positions being occupied by solvent molecules or coordinating anions;⁸ (ii)

a nine-membered triaza ring ([9]aneN₃ (2)) that, through a 1:2 metal to ligand ratio, complexes the nickel center according to a slightly distorted octahedral stereochemistry.⁹ In particular, the potential values associated with the $[\text{Ni}^{\text{III/II}}(\text{cyclam})]^{3+/2+}$ and $[\text{Ni}^{\text{III/II}}([\text{9]aneN}_3)_2]^{3+/2+}$ redox couples in aqueous solution or in other polar media are almost the same, whereas even slight modifications of the ligand framework (e.g. expansion of the 14-membered ring of cyclam or of the nine-membered ring of [9]aneN₃ by a -CH₂- group) make the potential considerably more positive and the attainment of the trivalent state much more difficult.^{8,9} Thus, it is not surprising that the very few X-ray structural investigations on Ni^{III} macrocyclic complexes refer to a complex of cyclam,¹⁰ to a complex of a hexamethyl-substituted cyclam ligand,¹¹ and to a 1:2 complex with [9]aneN₃.¹² Moreover, a further Ni^{III} complex with a functionalized triaza macrocycle has been obtained in the crystalline state and investigated by X-ray analysis: it is a neutral complex with 1,4,7-triazacyclononane-*N,N',N''*-triacetate (TCTA³⁻ (Y³⁻, 3)), in which the three tertiary amine nitrogen atoms of the ring and three oxygen atoms of the pendant acetate groups bind the metal center, according to a distorted-octahedral arrangement.¹³ Stabilization of trivalent nickel by the latter ligand may be unexpected: in fact, it has been observed that formation of metal complexes in unusually high oxidation states takes place in the presence of coordinating systems of especially high strength.¹⁴ This is the case for cyclam, which is able to exert particularly intense interactions in the equatorial plane, and it is also the case for the system made by two molecules of [9]aneN₃, which present six amine nitrogen atoms at the corners of an octahedron, the preferred arrangement by the d⁷, low-spin, Ni^{III} center. On the other hand, Y³⁻, which exhibits a N₃O₃ donor set, does not exert very strong coordinative interactions and is not expected, on a simple ligand field basis, to favor the attainment of the Ni^{III} state. On the basis of X-ray structural data, Hancock¹³ suggested that the unusual stability of the $[\text{Ni}^{\text{III}}\text{Y}]^0$ complex derives from the very efficient "packing" of the Y³⁻ ligand around the Ni^{III} metal center: this makes the average Ni^{III}-N distance

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(1.93 Å) remarkably shorter than that observed in the [Ni^{III}L₂]³⁺ complex (1.97 Å).

The above considerations prompted us to perform a comparative investigation on the formation of [Ni^{III}Y]⁰ and [Ni^{III}L₂]³⁺ complexes in aqueous solution. In particular, the Ni^{III}/Ni^{II} redox change was investigated by means of voltammetric techniques: due to the reversible nature of the electrochemical response measured, $E_{1/2}$ values were considered to satisfactorily approximate E° values. The two considered coordinating systems present substantially different donating tendencies toward metal centers: L₂ utilizes six secondary amine nitrogen donors, whereas Y³⁻ has three tertiary amine nitrogen atoms (which are slightly more basic) and three much less donating oxygen donors. Therefore, in order to discriminate *ligand field* and *solute-solvent interaction* contributions to the solution stability, we wished to evaluate separately the entropy and enthalpy contributions to the redox potential values of triazacyclononanetriacetate (3) and bis(triazacyclononane) (2) complexes. This goal was accomplished by studying the temperature dependence of the Ni^{III}/Ni^{II} redox potential, which allowed us to determine directly the entropy change ΔS°_{rc} , associated with each reduction half-reaction. Finally, it was observed that redox potential values for the [Ni^{III}Y]^{0/-} and [Ni^{III}L₂]^{3+/2+} systems display a substantially different dependence upon the concentration of the background electrolyte (e.g. NaCl). Once again, electrochemical investigations at varying temperatures allowed us to have a deeper insight into the effect of solvation and of ion-pair interactions on the redox behavior of six-coordinate complexes in aqueous solution.

This work further demonstrates that the interpretation of the relative stability of oxidation states in solution on the simple basis of electrode potential values may not be correct and that, in particular, a direct correlation of redox potential values with ligand field parameters can be misleading. The temperature-dependent electrochemical approach¹⁵ opens the route to a more thorough evaluation of redox processes in solution, which takes into account both metal-ligand effects and solvation terms.

Experimental Section

Materials. The ligand 1,4,7-triazacyclononane (2, L) and 1,4,7-triazacyclononane-*N,N,N'*-triacetate (3, Y³⁻) and the corresponding Ni^{II} complexes [NiL₂](ClO₄)₂⁹ and Na[NiY]¹⁶ were obtained through literature methods.

Electrochemistry. Cyclic voltammetry and alternating current profiles were recorded with Amel Electrochemlab equipment, which included the Model 552 potentiostat-galvanostat and the Model 563 function generator. Voltammograms were recorded at scan rates of 50–200 mV s⁻¹ (CV) and of 2 mV s⁻¹ (ac) on a Hewlett-Packard Model 7040A X-Y recorder. A nonisothermal cell,¹⁷ designed by following the principles outlined by Weaver,¹⁵ was used. The working cell, containing a platinum microsphere as a working electrode and a platinum coil as an auxiliary electrode, was jacketed by circulating thermostated water, and the temperature in the half-cell, controlled within ± 0.05 °C, was varied over the 0–50 °C range. The reference cell, containing a sodium saturated calomel electrode (SSCE) dipped in a 3.5 M NaCl solution, was jacketed by circulating water, thermostated at 18 °C. Reversible CV and ac profiles were obtained. $E_{1/2}$ values, at a given temperature and ionic strength, obtained by both CV and ac techniques were the same, but ac values were taken for temperature-dependent potential determination, since they were found to be affected by a lower standard deviation (± 2 mV). Potential vs temperature plots were linear, and $dE_{1/2}/dT$ values were obtained through least-squares treatment. Two typical potential/temperature plots are reported in Figure 1.

Results and Discussion

1. Ni^{III}/Ni^{II} Redox Couple Potential and Corresponding Entropy Change. Both [Ni^{II}L₂]²⁺ and [Ni^{III}L₂]³⁺ and [Ni^{II}Y]⁻ in aqueous solution undergo a reversible one-electron-oxidation process at the platinum microsphere electrode, as indicated by cyclic voltammetry investigations. In 0.5 M NaCl, at 25 °C, $E_{1/2}$ -

(Ni^{III}/Ni^{II}) is 0.69 V vs SCE for the bis(triazacyclononane) system (2) and 0.92 V for the triazacyclononanetriacetate ligand (3): thus, the [Ni^{III}L₂]³⁺ species exhibits a greater relative stability in solution than the [Ni^{III}Y]⁰ complex. However, the difference in $E_{1/2}$ values seems quite moderate and, in any case, lower than expected on the basis of simple ligand field arguments. In fact, it has been documented for a considerable number of redox changes involving transition-metal complexes, and in particular for the Ni^{III}/Ni^{II} couple, that the attainment of the higher oxidation state is favored by stronger donating arrangements.¹⁴ For example, the 1:2 complex with the tridentate macrocycle 1-oxa-4,7-diazacyclononane ([9]aneN₂O, 4), which exhibits octahedral stereochemistry, with an N₄O₂ donor set, is formed at a potential which is considerably more positive than that for the N₆ complex [Ni^{III}L₂]³⁺ ($E_{1/2}$ values, in MeCN with 0.1 M Et₄NBF₄, at 25 °C, are 0.56 and 1.08 V vs Fc^{+/0}, respectively).¹⁸ This is consistent with the fact that the $10Dq$ value for [Ni^{II}L₂]²⁺ is much greater than that observed for the [Ni^{II}([9]aneN₂O)₂]²⁺ species, in which two amine nitrogen atoms are replaced by two less donating ethereal oxygen atoms (12700 and 11770 cm⁻¹, respectively).¹⁹ The current explanation is that a tripositive cation will profit from crystal field stabilization to a larger extent than a dipositive one: thus, the greater the donor tendencies of the ligand, the easier the attainment of the higher oxidation state. Therefore, it may be surprising that formation of the Ni^{III} complex with the ligand Y³⁻, which has an N₃O₃ donor set and exerts the weakest coordinative interactions ($Dq(\text{Ni}^{\text{II}}) = 10800 \text{ cm}^{-1}$),¹⁹ is less disfavored, compared to the [Ni^{III}L₂]³⁺ reference system, than formation of [Ni^{III}([9]aneN₂O)₂]³⁺ (donor set N₄O₂, higher $Dq(\text{Ni}^{\text{II}})$). It is possible that this apparent paradox does not originate from crystal field arguments but derives from different effects, for instance purely electrostatic ones: the oxidation of [Ni^{II}Y]⁻ is relatively easier since the electron is abstracted from a negative species; the oxidation of [Ni^{II}L₂]²⁺ is relatively more difficult since the electron is taken away from an already positively charged species. To verify this hypothesis and to define its thermodynamic nature, we have determined the entropy changes associated with the Ni^{III}/Ni^{II} redox couple in the coordinating systems under investigation. ΔS°_{rc} values have been obtained by measuring $E_{1/2}$ values over the 0–50 °C temperature range with use of a nonisothermal cell. This technique, pioneered by Weaver in 1979,¹⁵ has been widely employed in coordination chemistry during the last decade to explore the redox behavior of metal centers in aqueous and nonaqueous solutions.

Figure 1 displays the variation of the half-wave potential with temperature for the [Ni^{III}L₂]³⁺/[Ni^{II}L₂]²⁺ and [Ni^{III}Y]⁰/[Ni^{II}Y]⁻ redox couples in aqueous 0.5 M NaCl: for both systems $E_{1/2}$ values show a regular and distinctly defined straight-line dependence upon temperature, but slopes present the *opposite* sign: for the bis(triazacyclononane) system potential values increase with temperature (positive entropy term), for the triazacyclononanetriacetate complex potential values decrease with temperature (negative entropy change). The stoichiometries of the considered half-reactions and pertinent ΔS°_{rc} values are reported in Table I.

The sign and magnitude of half-reaction entropies can be accounted for on the basis of the variation of solute-solvent interactions that accompanies each reduction process: in the case of the bis(triazacyclononane) system, the Ni^{III}/Ni^{II} reduction process involves a net decrease of the electrical charge from 3+ to 2+ (see reaction 1 in Table I). Since the hydration sphere of a tripositive cation is larger than that of a dipositive cation, half-reaction 1 should involve a substantial release of water molecules. The corresponding increase of translational entropy is reflected in the distinctly positive value of ΔS°_{rc} . On the other hand, on reduction, a negative charge is created on the neutral triazacy-

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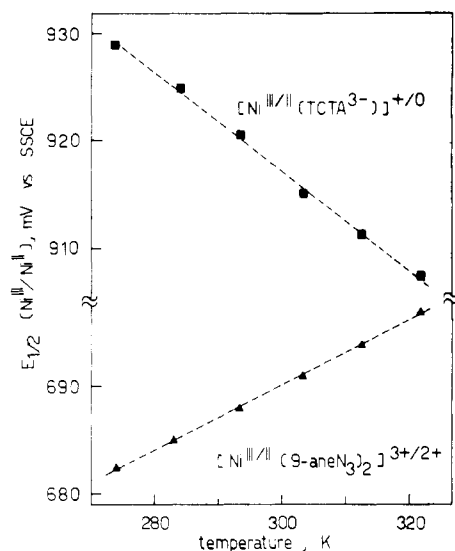


Figure 1. Temperature dependence of the half-wave potentials $E_{1/2}$ associated with the half-reactions $[\text{Ni}^{\text{III}}\text{Y}] + e^- = [\text{Ni}^{\text{II}}\text{Y}]^-$ (\blacksquare ; $Y = 3$) and $[\text{Ni}^{\text{III}}\text{L}_2]^{3+} + e^- = [\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ (\blacktriangle ; $L = 2$). Slopes of the least-squares straight lines indicate the entropy change $\Delta S^\circ_{\text{rc}}$ associated with the first redox couple is *negative*, whereas that for the second redox couple is *positive*.

Table I. Half-Wave Potentials ($E_{1/2}$), Temperature Coefficients ($dE_{1/2}/dT$), and Entropy Changes ($\Delta S^\circ_{\text{rc}}$) for the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ Redox Couple in Six-Coordinate Complexes in Aqueous 0.5 M NaCl

eq no.	half-reacn	$E_{1/2}$, V ^a	$dE_{1/2}/dT$, mV K ⁻¹ ^b	$\Delta S^\circ_{\text{rc}}$, cal mol ⁻¹ K ⁻¹ ^c
1	$[\text{Ni}^{\text{III}}\text{L}_2]^{3+} + e^- = [\text{Ni}^{\text{II}}\text{L}_2]^{2+}$	0.690	0.31	7.1
2	$[\text{Ni}^{\text{III}}\text{Y}]^0 + e^- = [\text{Ni}^{\text{II}}\text{Y}]^-$	0.918	-0.47	-10.8

^a At 25 °C, vs SSCE, ± 0.002 . ^b Slopes of the least-squares straight lines in Figure 1; ± 0.02 . ^c ± 0.5 .

clononacetate complex (see half-reaction 2 in Table I). This should cause an aggregation of water molecules on the complex and a decrease of the translational entropy of the system. This solvent ordering effect would explain the very negative value of $\Delta S^\circ_{\text{rc}}$ for half-reaction 2. The above results indicate that the entropy change operates in opposite directions for the stabilization of six-coordinate trivalent nickel complexes in solution: it favors the formation of the $[\text{Ni}^{\text{III}}\text{Y}]^0$ complex and disfavors the formation of the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$ species. This behavior is strictly related to the variation in electrical charge that occurs during the redox change and is in particular connected to the ability of each electroactive species to aggregate and organize water molecules through hydrogen bonding.

2. Enthalpy Contribution to the Relative Stability of $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$ and $[\text{Ni}^{\text{III}}\text{Y}]^0$ Complexes. It may be useful to consider the metathetic reaction



The ΔG° value associated with reaction 3 is related to the difference in redox electrode potentials of reactions 2 and 1 in Table I: $\Delta G^\circ = -F[E^\circ(2) - E^\circ(1)]$; ΔS° for equilibrium 3 is obtained from the difference in $\Delta S^\circ_{\text{rc}}$ values of half-reactions 2 and 1. Finally, from the difference of ΔG° and $T\Delta S^\circ$ it is possible to obtain ΔH° for reaction 3: $\Delta G^\circ = -5.3$ kcal mol⁻¹, $\Delta H^\circ = -10.6$ kcal mol⁻¹, and $T\Delta S^\circ = -5.3$ kcal mol⁻¹. The moderately negative value of ΔG° indicates that the formation of the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$ complex is favored with respect to that of the $[\text{Ni}^{\text{III}}\text{Y}]^0$ species. This is due to a very favorable enthalpy contribution, which is compensated in part (about 50%) by an unfavorable entropy term. The very exothermic enthalpy change should reflect the much more favorable ligand field contribution that is associated with the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ oxidation process inside the more coordinating bis(triazacyclononane) system (in potential units, it corresponds to 0.5 V). On the other hand, the entropy contribution would shift

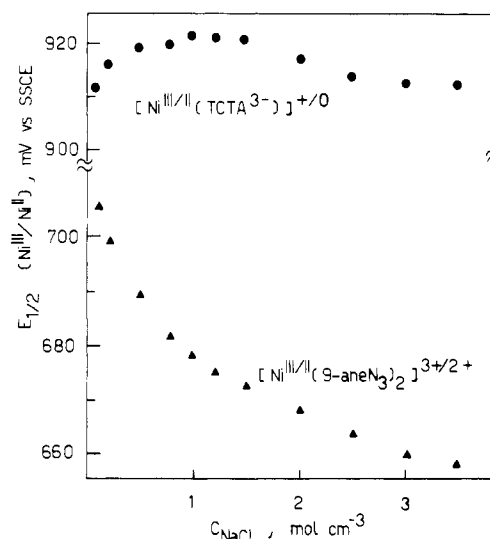


Figure 2. Variation of the half-wave potentials $E_{1/2}$ associated with the half-reactions $[\text{Ni}^{\text{III}}\text{Y}] + e^- = [\text{Ni}^{\text{II}}\text{Y}]^-$ (\bullet ; $Y = 3$) and $[\text{Ni}^{\text{III}}\text{L}_2]^{3+} + e^- = [\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ (\blacktriangle ; $L = 2$) with the concentration of the supporting electrolyte (NaCl), at 25 °C.

equilibrium 3 to the left: as outlined in the previous paragraph, this should be considered essentially a solute–solvent effect.²¹ As one goes from right to left, electrical charges on complexes are reduced in absolute value, inducing the liberation of water molecules from the hydration sphere of the complexes.

3. Dependence of the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ Redox Couple Potential upon the Concentration of the Background Electrolyte: Ion-Pair Formation. Entropy investigations have shown that hydration/dehydration phenomena may affect to a remarkable extent the redox behavior of Ni^{II} and Ni^{III} coordinatively saturated complexes (vide supra). On the other hand, it is well-known that the background electrolyte, when present in a relatively high concentration, may alter substantially the nature and intensity of solute–solvent interactions. The above considerations suggest an investigation of the $[\text{Ni}^{\text{III}}\text{Y}]^0/[\text{Ni}^{\text{II}}\text{Y}]^-$ and the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}/[\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ redox changes over a substantial range of background electrolyte concentration (0.1–3.5 M NaCl).

Figure 2 displays the dependence of the $E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}})$ values for bis(triazacyclononane) and triazacyclononaneacetate complexes upon the NaCl concentration. It can be seen that the potential for the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}/[\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ redox couple remarkably decreases with an increasing concentration of NaCl (i.e. the relative stability of the trivalent species increases). On the other hand, the $[\text{Ni}^{\text{III}}\text{Y}]^0/[\text{Ni}^{\text{II}}\text{Y}]^-$ redox couple potential, in the same concentration range, remains almost constant. Moreover, at chosen values of the NaCl concentration, the temperature dependence of $E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}})$ was investigated in the range 0–50 °C, and corresponding $\Delta S^\circ_{\text{rc}}$ values were determined. The plot of $\Delta S^\circ_{\text{rc}}$ vs NaCl concentration for the two investigated redox changes is reported in Figure 3.

It can be seen that $\Delta S^\circ_{\text{rc}}$ for the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}/[\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ redox change decreases with the increasing NaCl concentration to reach a plateau value of about 3 cal mol⁻¹ K⁻¹. For the $[\text{Ni}^{\text{III}}\text{Y}]^0/[\text{Ni}^{\text{II}}\text{Y}]^-$ redox couple the opposite trend is observed: $\Delta S^\circ_{\text{rc}}$ steeply increases with the concentration of the background electrolyte, to reach a constant value (–7 cal mol⁻¹ K⁻¹). It has been hypothesized before that the distinctly positive value of $\Delta S^\circ_{\text{rc}}$ for the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}/[\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ redox couple has to be ascribed to the liberation of water molecules that accompanies the reduction of the electrical charge on the complex. The background electrolyte competes for the solvent and should reduce the number of water molecules available for the hydration of the electroactive species: thus, the decrease of $\Delta S^\circ_{\text{rc}}$ with the increasing NaCl concentration

(21) Notice that the concept of favorable packing of Y^{3-} around the Ni^{III} metal center and the consequent shortening of the $\text{Ni}^{\text{III}}\text{--N}$ distances, put forward in ref 20, should be an *enthalpy* effect, also.

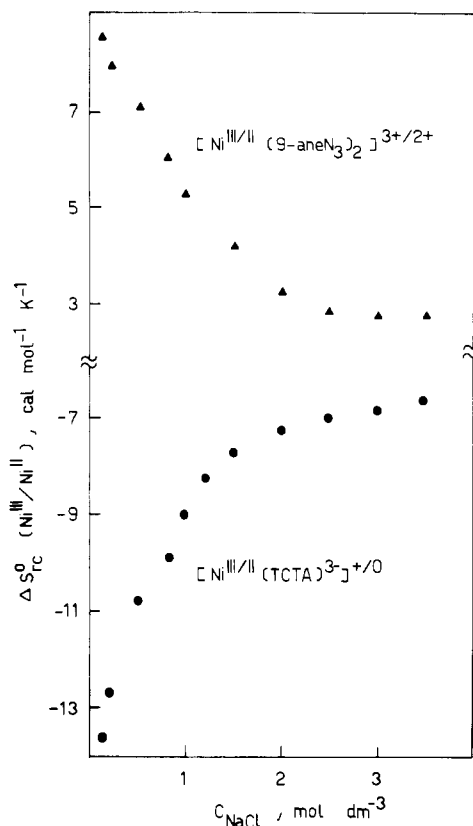
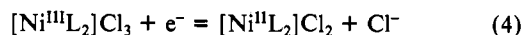
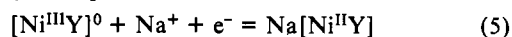


Figure 3. Variation of the entropy changes ΔS°_{rc} associated with the half-reactions $[\text{Ni}^{\text{III}}\text{Y}] + e^- = [\text{Ni}^{\text{II}}\text{Y}]^-$ (\bullet ; $\text{Y} = 3$) and $[\text{Ni}^{\text{III}}\text{L}_2]^{3+} + e^- = [\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ (\blacktriangle ; $\text{L} = 2$) with the concentration of the supporting electrolyte (NaCl).

should reflect the liberation of a lower number of particles during the half-reaction. At an electrolyte concentration of 2.5 M or higher, ΔS°_{rc} takes the constant value of about $+3 \text{ cal mol}^{-1} \text{ K}^{-1}$. It is possible that at these levels of NaCl concentration neutral complex-chloride ion aggregates are formed. Thus, the redox change for the triazacyclononane system should be better described as



The $[\text{Ni}^{\text{III}}\text{L}_2]\text{Cl}_3$ and $[\text{Ni}^{\text{II}}\text{L}_2]\text{Cl}_2$ neutral aggregates should be poorly solvated, and in any case, the contribution to the translational entropy due to the release of water molecules from the hydration shell should be very small. Thus, the ΔS°_{rc} value of $3 \text{ cal mol}^{-1} \text{ K}^{-1}$ should correspond to the entropy contribution due to the liberation of a chloride ion in aqueous solution. It should be noted that eq 4 represents an *idealized* situation: aggregates of the type $[\text{Ni}^{\text{III}}\text{L}_2]\text{Cl}_2^+$ and $[\text{Ni}^{\text{II}}\text{L}_2]\text{Cl}^+$ could also be present. In any case, due to the formation of these aggregates, the number of water molecules released during the redox half-reaction should be drastically reduced. Similar arguments can be used to explain the increase of ΔS°_{rc} with increasing NaCl concentration (see Figure 3) in the case of the $[\text{Ni}^{\text{III}}\text{Y}]^0/[\text{Ni}^{\text{II}}\text{Y}]^-$ redox change: a less pronounced hydration of the $[\text{Ni}^{\text{II}}\text{Y}]^-$ complex can account for the less negative value of the entropy change. The limiting value of ΔS°_{rc} could correspond to an *idealized* situation in which the divalent complex exists as an ion pair and the half-reaction is described by the equation



Thus, if it is admitted that at high concentrations of the background electrolyte the species involved in half-reaction 5 are poorly solvated, no aggregation/liberation of water molecules should occur and the value of $-7 \text{ cal mol}^{-1} \text{ K}^{-1}$, according to eq 5, should be simply ascribed to the disappearance of a Na^+ ion in aqueous solution. Also in this case, the existence of the unique species $\text{Na}[\text{Ni}^{\text{II}}\text{Y}]$ is only postulated and should be considered as a limiting situation.

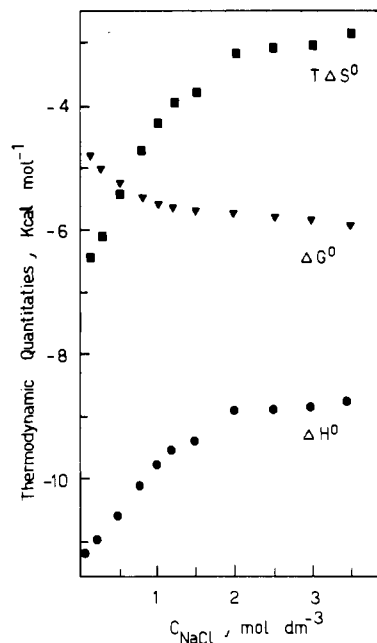
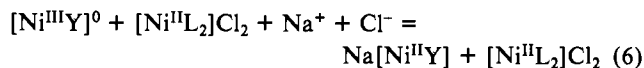


Figure 4. Effect of the variation of the concentration of the supporting electrolyte (NaCl) on the thermodynamic quantities ΔG° , ΔH° , and $T\Delta S^{\circ}$ (in kcal mol^{-1}) associated with the metathetic reaction $[\text{Ni}^{\text{III}}\text{Y}]^0 + [\text{Ni}^{\text{II}}\text{L}_2]^{2+} = [\text{Ni}^{\text{II}}\text{Y}]^- + [\text{Ni}^{\text{III}}\text{L}_2]^{3+}$. At the highest concentration of sodium chloride the metathetic reaction should be better described by eq 6.

Finally, Figure 4 illustrates the effect of the variation of NaCl concentration on the thermodynamic functions associated with the metathetic reaction (3): it is seen that the ΔG° value is only moderately affected by an increase of the background electrolyte concentration. In particular, it takes slightly more negative values, which indicates that increasing the electrolyte concentration slightly favors the formation of $[\text{Ni}^{\text{III}}\text{L}]^{3+}$ compared to that of $[\text{Ni}^{\text{III}}\text{Y}]^0$. However, Figure 4 shows that this very moderate electrolyte effect on the relative stability of trivalent complexes results from the compensation of pronounced and opposite enthalpy and entropy contributions. In particular the enthalpy term becomes progressively less negative with increasing electrolyte concentration, to reach a constant value of about -8 kcal mol^{-1} . On the other hand, the $T\Delta S^{\circ}$ term becomes less negative until a *plateau* value of about -3 kcal mol^{-1} . On the basis of the previous considerations on the NaCl dependence of ΔS°_{rc} the metathetic reaction (3) should be written in the form



Equation 6 indicates that, at high electrolyte concentrations, 1 mol of aqueous chloride disappears: this produces a distinctly negative entropy effect ($T\Delta S^{\circ} = -3 \text{ kcal mol}^{-1}$), but much less negative than that observed in dilute solution (eq 3), where a substantial aggregation of water molecules around charged species on the right-hand member was hypothesized ($T\Delta S^{\circ} = -6.5 \text{ kcal mol}^{-1}$ in 0.1 M NaCl). It has been suggested before that the substantially negative enthalpy term associated with reaction 3 has to be ascribed to a favorable ligand field effect. The extreme sensitivity of the ΔH° term to the electrolyte concentration, as indicated in Figure 4, indicates that also the solute-solvent interaction term is important. Under dilute conditions (metathetic reaction described by eq 3), where ions of the inert electrolyte do not seriously compete for the solvent, the $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$ and $[\text{Ni}^{\text{II}}\text{Y}]^-$ species are able to aggregate water molecules to a greater extent than the $[\text{Ni}^{\text{II}}\text{L}_2]^{2+}$ and $[\text{Ni}^{\text{III}}\text{Y}]^0$ species; thus, a further exothermic contribution to the metathetic reaction (3) (and to the relative stability of the trivalent nickel bis(triazacyclononane) complex) is given by solute-solvent effects. This effect decreases with increasing electrolyte concentration, which reduces the size of the hydration spheres of the electroactive species. At NaCl

concentrations higher than 2.5 M, where the metathetic reaction is probably better described by eq 6, solvation effects should be minimized and the enthalpy change of -8 kcal mol^{-1} should result from the balance of the exothermic ligand field contribution and the endothermic contribution due to the disappearance of 1 mol of aqueous Na^+ and Cl^- ions.

Conclusions

The general suggestion to the synthetic chemist wishing a design ligands that stabilize high oxidation states of transition-metal ions is to look at strongly coordinating systems. This tip arises from the consideration that a $\text{M}^{(n+1)+}$ metal center will profit from ligand field stabilization energy effects to a greater extent than the corresponding M^{n+} cation. Considering things from a thermodynamic standpoint, this should be defined as a pure *enthalpy* effect. Another reasonable tip could be to put several negative charges on the coordinating system: intuitively, the energy to be

spent to increase the positive charge of the metal center should be lower in a negatively charged coordinative environment. The present investigation has demonstrated that this latter effect is not a ligand field enthalpy effect but is essentially an *entropy* effect and, in particular, it arises from the gain in translational entropy that occurs when the overall negative charge of the metal complex decreases in absolute value and water molecules are released from the hydration sphere. It is reasonable to predict that the ligand's negative charge effect on the stabilization of metal centers in unusually high oxidation states, being strictly related to solute-solvent interactions, should vary significantly with the nature of the solvent employed.

Acknowledgment. We are indebted to the Ministry of Public Education of Italy for financial support (MPI 40%).

Registry No. $[\text{Ni}^{\text{III}}\text{Y}]$, 87306-48-7; $[\text{Ni}^{\text{II}}\text{Y}]^-$, 82980-33-4; $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$, 86709-81-1; $[\text{Ni}^{\text{III}}\text{L}_2]^{2+}$, 59034-11-6; NaCl , 7647-14-5; Ni , 7440-02-0.

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Water Exchange of *trans*-Dichlorodiaquaplatinum(II) and Tetraaquaplatinum(II) Studied by an Oxidative-Addition Quenching Technique. Isotopic Shifts and Platinum-195 NMR Chemical Shifts for Mixed Chloro-Aqua Complexes of Platinum(II) and Platinum(IV)

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Received January 17, 1989

Water exchange on $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ has been studied by means of a new ^{18}O -tracing technique. The exchange between a platinum(II) complex and ^{18}O -enriched water has been rapidly quenched by addition of excess chlorine, which gives a substitution-inert platinum(IV) complex. The time-dependent $^{16}\text{O}/^{18}\text{O}$ distributions of the platinum(II) complexes are obtained from the ^{195}Pt NMR spectra of the corresponding oxidized complexes, which display well-resolved oxygen isotopic shifts in the 78-MHz signal. Product identification based on the isotopic splitting of the NMR signal due to both $^{16}\text{O}/^{18}\text{O}$ and $^{35}\text{Cl}/^{37}\text{Cl}$ shows that the oxidation takes place without scrambling and involves the formation of a Cl-Pt-OH_2 axis perpendicular to the original coordination plane of platinum(II). The oxidation products of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, and PtCl_4^{2-} are thus found to be $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$, *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$, and $\text{PtCl}_5\text{H}_2\text{O}^-$, respectively. There is no observable exchange of *trans*- and *cis*-aqua ligands in those platinum(IV) complexes during the time required to accumulate the spectra. Water exchange of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ is slower than that of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ by a factor of 30. The statistically corrected rate constants are $k_{\text{ex}}^{298} = (1.58 \pm 0.03) \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{ex}}^{298} = (4.8 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, respectively. Variable-temperature measurements (278–303 K) gave $\Delta H^\ddagger = (92 \pm 2) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = (0 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$ for exchange on $\text{Pt}(\text{H}_2\text{O})_4^{2+}$. The effect of the nonreacting ligands is basically the same as that previously reported for the chloride anation reactions of these two substrates. The chemical shifts of the complexes $\text{PtCl}_{4-n}(\text{H}_2\text{O})_n^{2-n}$, $n = 0-4$, have been measured in a 1.00 M HClO_4 medium. The increment in the chemical shift for substitution of water by chloride is smaller *trans* to water than *trans* to chloride but increases with the number of chloride ligands in a *cis* position to the replaced water molecule. This might be consistent with a large ground-state *trans* influence of chloride compared to water and a negligible relative *cis* influence.

Introduction

Rate data for exchange of water on square-planar metal complexes were hitherto only available for the tetraqua ions of platinum(II)^{1,2} and palladium(II).³ Volumes of activation have been determined to be $-4.6 \text{ cm}^3 \text{ mol}^{-1}$ and $-2.2 \text{ cm}^3 \text{ mol}^{-1}$, respectively.^{2,3} The mechanistic interpretation of these volume changes is still an open question.^{2,3}

Halide anation of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ is more than 2 orders of magnitude faster than that of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$.⁴ The former reaction is favored thermodynamically and by the 2+ ionic charge of the complex. Neutral as well as anionic ligands react rather rapidly with the *trans* complex, replacing one of the chloride ligands,⁵ but there are no data for the replacement of the aqua

ligands, except for the chloride anation. It was therefore of interest to study the water exchange on *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ in order to evaluate the effect of the two *cis* chlorides. The exchange reaction occurs with $\Delta G^\circ = 0$ and with conservation of ionic charge, and the data are therefore of particular interest in relation to previous data for halide anation.^{4,6,7}

The small chemical shift range in oxygen-17 NMR makes the conventional isotopic dilution technique unsuitable for study of water exchange in mixtures of aqua complexes. Evaluation of rate constants from the absolute oxygen-17 signal intensity is difficult when the complexes are not stable with time due to side reactions or when the accumulation of spectra is time consuming compared to the half-life of exchange.

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