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Registry No. $\text{Ni}(\text{H}_3\text{G}_4)^{2-}$, 39016-92-7; $\text{Ni}^{\text{III}}(\text{H}_3\text{G}_4)^-$, 60165-88-0; $\text{G}_3\text{aCH}_2\text{OH}$, 65621-94-5.

References and Notes

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Microcalorimetric Determination of the Enthalpy of a Slow Reaction: Destruction with Cyanide of the Macrocyclic (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Ion

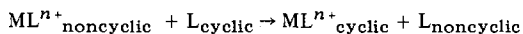
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The calorimetric determination of the enthalpy of formation of (1,4,8,11-tetraazacyclotetradecane)nickel(II) has been made by displacing the macrocyclic ligand with cyanide and following the reaction to completion (5 h) in a batch microcalorimeter of the heat-flow type. The ΔH° value found ($-20.3 \text{ kcal mol}^{-1}$) is 11 kcal mol^{-1} less than that previously reported. Thermodynamic parameters of both octahedral and square-planar forms of the complex have been calculated. The macrocyclic effect in Ni(II) complexes has been rationalized with that already established for Cu(II) complexes.

Introduction

The term "macrocyclic effect" was first introduced in 1969 by Cabbiness and Margerum² to highlight the large increase in stability constants which they had found for the macrocyclic complex $[\text{Cu}(\text{tet-a})]^{2+}$ when compared to that of the equivalent complex with a noncyclic ligand in which the chelate rings were present in the same alternating ring sequence (5,6,5), namely, $[\text{Cu}(2,3,2\text{-tet})]^{2+}$. In general terms, the "macrocyclic effect" refers to the decrease in Gibbs energy for the metathetic reaction



and, as for the chelate effect before it, considerable attention has been directed toward separating ΔG° into its component enthalpic and entropic parts in order to understand the origins of the enhanced stability of macrocyclic complexes, which play an important role in many naturally occurring systems.

However, macrocyclic complexes also display an enhanced kinetic inertness, with respect to either their formation in aqueous solution or their degradation, and, until recently, it has not been possible to determine ΔH° directly by calorimetry. Thus, the first attempts to separate ΔG° involved ΔH° values which had been obtained empirically or indirectly, and these are summarized below together with more recent calorimetric determinations of ΔH° .

(1) ΔH° for $[\text{Cu}(\text{tet-a})]^{2+}$ was obtained³ by extrapolating the empirical ΔH° vs. $\nu(\text{d-d})$ relationship already established for Cu(II) polyamine complexes, and the authors concluded that the enhanced stability of the macrocyclic complex could be attributed equally to both enthalpy and entropy terms arising from a stronger Cu-N interaction and a smaller loss in configurational entropy, respectively.

(2) ΔH° for $[\text{Ni}[14]\text{aneN}_4]^{2+}$ and $[\text{Ni}(\text{tet-a})]^{2+}$ were obtained⁴ from temperature-dependent stability constant

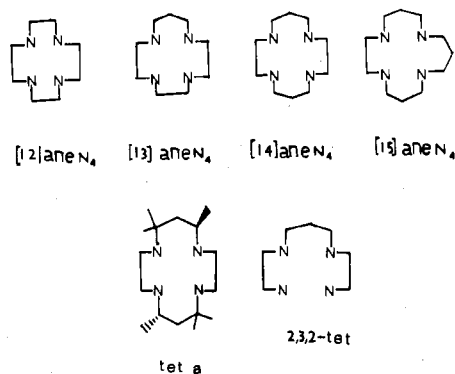


Figure 1. Macrocyclic and noncyclic ligands.

measurements, essentially determined spectroscopically, and the authors concluded that the macrocyclic effect was due to an extremely large enthalpy term (12–14 kcal mol⁻¹) and an unfavorable entropy term and interpreted this in terms of the different degrees of solvation of the cyclic and noncyclic ligands.

(3) ΔH° for $[\text{Cu}[12]\text{aneN}_4]^{2+}$, $[\text{Cu}[13]\text{aneN}_4]^{2+}$, and $[\text{Cu}[15]\text{aneN}_4]^{2+}$ were obtained^{5,6} from temperature-dependent stability constant measurements determined polarographically and showed the macrocyclic effect to be due to a small enthalpy term and a large entropy term.

(4) The first direct calorimetric determination of ΔH° ,⁷ for $[\text{Cu}[14]\text{aneN}_4]^{2+}$, demonstrated that for this complex the enthalpy contribution to the macrocyclic effect was 4.7 kcal mol⁻¹. The entropy contribution could not be assessed since no stability constant data were available.

(5) Other calorimetric determinations for $[\text{Cu}[12]\text{aneN}_4]^{2+}$ and $[\text{Cu}[15]\text{aneN}_4]^{2+}$,⁸ for which stability constant data were available, essentially confirmed the indirect ΔH° values and thus a small enthalpy but larger entropy contribution to the macrocyclic effect.

At this point, the very unusual result for the Ni(II) complexes where the entire extra stability of the cyclic complexes seemed to arise in an enthalpy term, causing ΔH° for these complexes to be as high as ΔH° for equivalent copper complexes, in contrast to the complexes with noncyclic ligands ($\Delta H^\circ(\text{Ni}) \approx 2/3\Delta H^\circ(\text{Cu})$), prompted us to question the validity of the previous indirect determination and to attempt to see if a method could be found to make a direct calorimetric determination. The formation of macrocyclic nickel(II) complexes is too slow to be determined calorimetrically using the conditions developed for the Cu(II) complexes at pH 14. We therefore decided to study the destruction of the macrocyclic complex with cyanide⁴ in strongly alkaline solutions and found that this reaction is complete within 5 h and that we were able to record the total thermal output by using a Batch microcalorimeter of the heat-flow type by increasing the sensitivity during the course of the reaction.

Furthermore, we had previously found,⁹ contrary to a report⁴ that $[\text{Ni}[14]\text{aneN}_4]^{2+}$ existed solely as the yellow, square-planar form in aqueous solution, that a square-planar/octahedral equilibrium is present, and at 25 °C the percentages of the square-planar and octahedral species present are 71% and 29%, respectively.

In this work, we are reporting ΔH° values for both the square-planar and octahedral forms of $[\text{Ni}[14]\text{aneN}_4]^{2+}$, which are drastically lower than the original value and which make two separate interpretations of the macrocyclic effect unnecessary.

Experimental Section

Reagents. $[\text{Ni}[14]\text{aneN}_4](\text{ClO}_4)_2$ and $[\text{Ni}(2,3,2\text{-tet})](\text{ClO}_4)_2$ were prepared by mixing equimolar solutions of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the ligand in hot ethanol or butanol. $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ was prepared

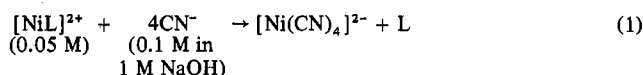
by a previously described method¹⁰ and dehydrated to constant weight at 100 °C to give anhydrous $\text{K}_2[\text{Ni}(\text{CN})_4]$. Elemental analyses were as follows.

	% calcd			% found		
	C	H	N	C	H	N
$[\text{Ni}[14]\text{aneN}_4](\text{ClO}_4)_2$	26.2	5.3	12.2	26.1	5.2	12.4
$[\text{Ni}(2,3,2\text{-tet})](\text{ClO}_4)_2$	20.1	4.8	13.4	20.2	4.9	13.5
$\text{K}_2[\text{Ni}(\text{CN})_4]$	19.9		23.3	19.8		23.3

The nickel content of an aqueous solution of $\text{Ni}(\text{ClO}_4)_2$ (~0.25 M) was determined gravimetrically as the dimethylglyoximate, and this solution was accurately diluted to provide the necessary solutions of Ni^{2+} (aq) for calorimetry. The solution of alkaline cyanide was prepared by adding appropriate quantities of NaOH (Erba RP) and NaCN (Erba RP) to CO_2 -free, twice distilled water, and the same solution was used throughout the duration of this work. Fresh solutions of the metal complexes were prepared before each calorimetric measurement, since it was observed that slight precipitation occurred after several days if the solutions were allowed to stand.

Apparatus. For all calorimetric measurements an LKB Batch microcalorimeter (10700-2) was used. The thermal output was amplified by a Keithley 150B microvolt amplifier and recorded as a trace on a potentiometric recorder. The heat output was determined by comparison of the area under the heat curve with a similar area produced by electrical calibration. During the course of the reactions, the sensitivity of the amplifier was increased in order to measure accurately the small heat output produced as the reactions neared completion, and different calibration experiments were performed for each sensitivity range used. During the initial stages of the reactions, when the thermal curve showed considerable curvature, the areas were determined as the mean of six measurements made with an accurate planimeter. In the latter stages, when the thermal curve became essentially linear, the areas were calculated as successive trapezoids. Glass reaction cells were used, and to prevent the reactants from "creeping" over the partition wall into the cells,¹¹ the insides of the cells were coated with a thin layer of paraffin wax. Solutions were introduced into the cells by weight with hypodermic syringes, and the volumes of the reactants were kept constant throughout (0.4 cm³ of Ni(II) solution and 3.0 cm³ of NaOH/NaCN). The reference cell was empty throughout all measurements. The calorimeter was checked for absolute accuracy by determining the enthalpy of formation of water ($\Delta H^\circ = -13.2$ kcal mol⁻¹). UV spectral measurements were made on a Beckman DK2A spectrophotometer equipped with 1-cm quartz cells.

Calorimetric Procedure. The reactions for which ΔH° has been determined can be represented as



where L = aq, 2,3,2-tet, and [14]aneN₄. However, in aqueous solutions containing Ni^{2+} , CN^- , and OH^- ions, other species exist than the ones represented in eq 1, the most important being $[\text{NiL}(\text{CN})]^{+}$ and $[\text{Ni}(\text{CN})_5]^{3-}$. Under the exact reaction conditions used and by employing previously determined stability constant values, the percentage of the species present at equilibrium was calculated by means of the DISPOL computer program¹² and is given in Table I. It can be seen that in each case the final equilibrium should contain ~98% of the species $[\text{Ni}(\text{CN})_4]^{2-}$.

In the calorimetric experiments, 0.4 cm³ of the nickel-containing solution (0.05 M) was introduced into one side of the mixing cell and 3.0 cm³ of the NaOH/NaCN solution (1 M NaOH, 0.1 M NaCN) into the other. The cell was now allowed to equilibrate overnight until a steady baseline on the most sensitive range to be used was established. The sensitivity was now decreased and the reactants were mixed. As the reaction proceeded and the heat output became less, the sensitivity was increased; the reaction was judged to be complete when no further heat output on the original high-sensitivity range could be detected and the baseline had returned to its prereaction value. For different ligands the time involved varied as follows:

$\text{Ni}(\text{aq})^{2+}$	0.5 h
$[\text{Ni}(2,3,2\text{-tet})]^{2+}$	1.5 h
$[\text{Ni}[14]\text{aneN}_4]^{2+}$	5 h

the kinetic inertness of the macrocyclic complex is clearly demonstrated.

Table I. Percent Species at Equilibrium^a

L	[NiLCN] ⁺	[NiLOH] ⁺	[Ni(CN) ₄] ²⁻	[Ni(CN) ₅] ³⁻	[Ni(CN) ₆] ⁴⁻	[NiL] ²⁺
[14]aneN ₄	0.2	0	97.9	1.9	0	0
2,3,2-tet	b	b	98.1	1.9	0	0
aq	b	b	98.1	1.9	0	0

^a log β values: [NiL⁺CN]⁺, 26.5;⁴ [NiL⁺OH]⁺, 23.0;⁴ [Ni(CN)₄]²⁻,²¹ 30.5; [Ni(CN)₅]³⁻, 30.0;²² [Ni(CN)₆]⁴⁻, 28.9;²² [NiL⁺]²⁺, 22.2;⁴ [NiL²⁺]²⁺, 15.8.⁴ L¹ = [14]aneN₄ and L² = 2,3,2-tet. ^b These species were not taken into account since there is no evidence that they contribute significantly.

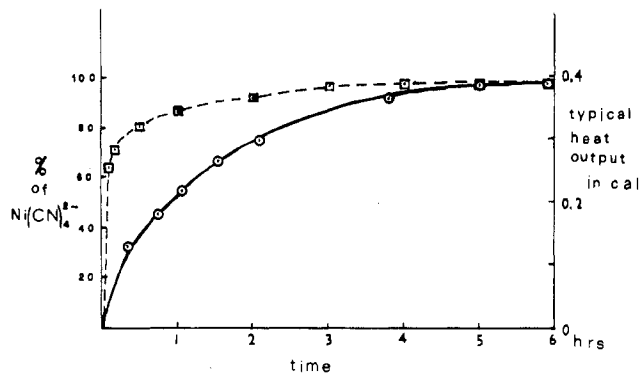
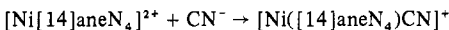


Figure 2. Formation of [Ni(CN)₄]²⁻ (—○—) and the typical heat output from the calorimeter (---□---) during the course of the reaction [Ni[14]aneN₄]²⁺ + 4CN⁻ → [Ni(CN)₄]²⁻ + [14]aneN₄.

In the case of [Ni[14]aneN₄]²⁺, in order to demonstrate that the equilibrium 98% [Ni(CN)₄]²⁻ had been formed after 5 h, a parallel reaction using the same concentrations of reactants was followed spectrophotometrically using the absorption band at 268 nm in the spectrum of [Ni(CN)₄]²⁻. The extinction coefficient of this band was determined directly from the spectrum of a solution of K₂[Ni(CN)₄] to be 1.21 × 10⁴ L cm⁻¹ mol⁻¹. The concentration of [Ni(CN)₄]²⁻ in the reaction mixture after 5 h was found to be 97%, and the rate of increase in concentration of this species, calculated from the spectroscopic measurements, is shown in Figure 2, together with the thermal output from the calorimeter. Because of the exceptionally high extinction coefficient of [Ni(CN)₄]²⁻, it was necessary to dilute the solution of reactants by a factor of 50 with water before measuring the molar absorption. The dilution causes a change in the theoretical equilibrium concentrations reducing the [Ni(CN)₄]²⁻ percentage to 42%. Great care was therefore taken to make sure that the spectral measurements were made within 5 min of this dilution to minimize the change in concentration of the [Ni(CN)₄]²⁻ due to the slow shift in the equilibrium toward the new conditions.

A correction was made to each measurement for the enthalpy of dilution of the NaOH/NaCN solution which was determined separately (0.4 cm³ of H₂O + 3.0 cm³ of NaOH/NaCN). This was endothermic (+0.033 cal) and remained constant throughout, since the same volumes of reactants were used. This correction amounted to between 4% and 6% of the total heat output, depending on the particular system.

The experimental results were now corrected for the presence of the species [Ni(CN)₅]³⁻ and [Ni[14]aneN₄]CN⁺ as indicated in Table I. ΔH° for the fast reaction



was calculated from the temperature dependence of the equilibrium constant⁴ to be -4.7 kcal mol⁻¹, and the ΔH° value of +3.1 kcal mol⁻¹ for the fast reaction



had been previously reported.¹³ These corrections proved to be less than 0.2% and so the uncertainty in the ΔH° values of the above reactions was not important.

In summary, the reaction conditions used were selected with several objectives in mind. The strongly alkaline solution (pH 14) was necessary to ensure that the ligands liberated during the course of the reaction did not form protonated species (for [14]aneN₄,¹⁴ pK₁ = 11.6 and pK₂ = 10.6; for 2,3,2-tet,¹⁵ pK₁ = 10.2 and pK₂ = 9.5) and to obtain the best possible speed of reaction for the macrocyclic complexes, while the concentration of cyanide was selected to maximize

Table II. Experimental Results

Reaction	ΔH° (25 °C), kcal mol ⁻¹
[Ni[14]aneN ₄] ²⁺ + 4CN ⁻ → [Ni(CN) ₄] ²⁻ + [14]aneN ₄	22.35 22.54 22.46 22.56 Mean 22.48 ± 0.14 ^a
[Ni(2,3,2-tet)] ²⁺ + 4CN ⁻ → [Ni(CN) ₄] ²⁻ + 2,3,2-tet	24.28 24.32 24.06 24.04 Mean 24.22 ± 0.16 ^a
Ni(aq) ²⁺ + 4CN ⁻ → [Ni(CN) ₄] ²⁻	42.99 42.67 42.64 43.13 42.56 Mean 42.80 ± 0.42 ^a

^a Uncertainties are expressed as twice the average deviation from the mean.

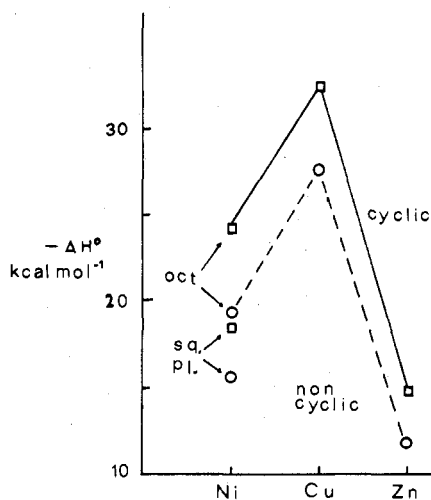
the [Ni(CN)₄]²⁻ percentage at equilibrium without incurring an unduly high [Ni(CN)₅]³⁻ percentage.

Results and Discussion

The experimental results are given in Table II. Using these values ΔH° for [Ni[14]aneN₄]²⁺ and [Ni(2,3,2-tet)]²⁺ was calculated to be -20.3 ± 0.6 and -18.6 ± 0.6 kcal mol⁻¹, respectively. The error limits, the sum of the uncertainties of the experimental values, are probably pessimistic. Both of these quantities have previously been determined. For [Ni(2,3,2-tet)]²⁺, ΔH° values of -17.9 (from the reaction of the nickel complex with HCl in 0.5 M KCl)¹⁶ and -19.4 kcal mol⁻¹ (from the cyanide displacement method)⁴ have been reported. With regard to the latter, the difference of 0.8 kcal mol⁻¹ from our result lies in the choice of ΔH° for [Ni(CN)₄]²⁻. We have preferred to measure this directly under experimental conditions identical with those of the other reactions to avoid problems of differing ionic strengths, whereas the previous authors have interpolated the results of Christensen et al.¹⁷ to their own experimental conditions. Our result for ΔH° of [Ni(CN)₄]²⁻ agrees satisfactorily with that of Christensen at low ionic strength. It is comforting that we have obtained exactly the same ΔH° for the reaction of [Ni(2,3,2-tet)]²⁺ with cyanide as that obtained by Margerum et al.⁴ (-24.2 kcal mol⁻¹). It is more difficult to reconcile the difference between the value obtained by reaction of [Ni(2,3,2-tet)]²⁺ with HCl in 0.5 M KCl¹⁶ and our present value, but the answer may lie in the fact that a relatively high inert electrolyte concentration will shift the blue-yellow equilibrium toward the yellow form, and since the blue-to-yellow conversion is endothermic,⁹ ΔH° will appear lower than the present value obtained in the absence of inert electrolyte. The most serious discrepancy, however, occurs between our value for ΔH° of [Ni[14]aneN₄]²⁺ (-20.3 kcal mol⁻¹) and the value originally determined by Margerum from the temperature dependence of stability constant data (-31.0 ± 0.6 kcal mol⁻¹).⁴ We have no reason to distrust our present direct value outside the error limits and can only conclude that this gross discrepancy emphasizes the inherent unreliability of determining ΔH° from

Table III. Thermodynamic Parameters at 25 °C

	$[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$			$[\text{Ni}(2,3,2\text{-tet})]^{2+}$		
	$\log K_{\text{ML}}$	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ K ⁻¹	$\log K_{\text{ML}}$	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ K ⁻¹
Equilibrium mixture	22.2	-20.3	+33.6	15.8	-18.6	+10.4
Blue (octahedral) form	21.9	-24.1	+19.5	16.0	-19.2	+8.7
Yellow (square-planar) form	22.3	-18.7	+39.5	15.4	-15.8	+17.4

Figure 3. ΔH° values for metal complexes with $[\text{14}] \text{aneN}_4$ (cyclic) and 2,3,2-tet (noncyclic) ligands

only three stability constant values over a limited range of temperature particularly when the required linear relationship is not conclusively established.

Both $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$ and $[\text{Ni}(2,3,2\text{-tet})]^{2+}$ exist in aqueous solution as a mixture of the blue (octahedral) and yellow (square-planar) forms, and the relative amounts of the blue form present in solutions containing a small quantity of inert electrolyte (0.1 M NaClO_4) are 29% and 78%, while ΔH° values for the blue-to-yellow conversion are +5.4 and +3.4 kcal mol⁻¹, respectively.⁹ We have repeated our earlier work in pure water and have found that the percentages of the forms present are identical with those found in 0.1 M NaClO_4 solutions. Assuming that Margerum's value of $\log K_{\text{ML}}$ for $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$ is reliable at 25 °C (the values at 10 and 40 °C are more suspect since they depend directly on calculated values of $\log \beta_4$ for $[\text{Ni}(\text{CN})_4]^{2-}$ whereas the value of $\log \beta_4$ used at 25 °C is an experimental value), we have calculated the thermodynamic parameters at 25 °C for the formation of the blue and yellow forms of both $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$ and $[\text{Ni}(2,3,2\text{-tet})]^{2+}$ (Table III).

ΔH° values for the octahedral forms of $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$ and $[\text{Ni}(2,3,2\text{-tet})]^{2+}$ are compared in Figure 3, and the usual Irving-Williams order $\text{Cu} > \text{Ni} > \text{Zn}$ is confirmed in both series. The contribution of the enthalpy term to the extra stability of the macrocyclic complexes is the difference between the two curves shown in Figure 3. These macrocyclic enthalpies (kcal mol⁻¹) are as follows: Ni(octahedral), 4.9; Cu, 4.7; Zn, 2.9; Ni(square planar), 2.9.

We have previously shown that in a series of Cu(II) complexes with macrocyclic ligands of differing ring size the ΔH° value of the macrocyclic complex reaches a maximum at $[\text{Cu}[\text{14}] \text{aneN}_4]^{2+}$,^{8,18} falling off sharply on either side (complexes with [12]-, [13]-, and [15]aneN₄ as ligands). We have interpreted this to mean that in order to maximize the ΔH° value, while maintaining the planar arrangement of the metal atom and the four donor atoms in the macrocyclic complex, the size of the metal ion must match closely the size

of the aperture in the macrocyclic ligand in its minimum-strain conformation (all four donor atoms planar).¹⁹ The normal Cu-N distance observed in tetramine complexes (2.03–2.10 Å) gives the best matching of sizes in the above series with $[\text{14}] \text{aneN}_4$ as the ligand. Since in octahedral coordination the Ni²⁺ ion has almost exactly the same size as Cu²⁺, a maximum in ΔH° would also be expected for octahedral $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$. In square-planar coordination the size of the Ni²⁺ ion is drastically reduced and observed Ni-N bond distances in diamagnetic amine complexes are around 1.9 Å. Thus the nickel ion is now too small for the macrocyclic ligand which must expend conformational energy in contracting itself to the requirements of the metal ion, resulting in a lowering of ΔH° . Moreover, this contraction will be more difficult for the comparatively rigid macrocyclic ligand than for the noncyclic 2,3,2-tet ligand, and this is manifest in the lower macrocyclic enthalpy of the square-planar system.

It therefore seems that the macrocyclic enthalpies can be rationalized on the following basis. The noncyclic ligands must expend energy in arranging their donor atoms around the metal ion and will experience steric resistance during this process. However, the synthetically preoriented macrocyclic ligand already has its donor atoms in approximately the correct positions for coordination and is able to exert the strongest and most effective metal-donor interactions, particularly if the size of the metal ion is matched to that of the aperture in the macrocyclic ligand. This ability of the macrocyclic ligand to form the strongest interactions is demonstrated by spectrochemical data; Ni(II) (octahedral) and Cu(II) complexes with $[\text{14}] \text{aneN}_4$ have larger $Dq(xy)$ values than do the corresponding complexes with 2,3,2-tet ($\Delta Dq(xy) = 1000$ and 800 cm⁻¹, respectively).²⁰

It is difficult to assess the entropy contribution accurately because of the uncertainty in the $\log K_{\text{ML}}$ value for $[\text{Ni}[\text{14}] \text{aneN}_4]^{2+}$ and the lack of the stability constant for the Cu(II) complex with the same ligand. We have previously estimated¹⁸ ΔS° for $[\text{Cu}[\text{14}] \text{aneN}_4]^{2+}$ to be +29 cal K⁻¹ mol⁻¹, and using the data in Table III and ΔS° for $[\text{Cu}(2,3,2\text{-tet})]^{2+}$ (+16.5 cal K⁻¹ mol⁻¹)¹⁶ the entropy contribution to the macrocyclic effect in these two comparable systems is calculated to be +12.5 cal K⁻¹ mol⁻¹ for Cu(II) and +10.8 cal K⁻¹ mol⁻¹ for Ni(II) (octahedral). This confirms our belief that there will always be a positive entropy contribution to the macrocyclic effect, arising from the relative gain in conformational entropy of the noncyclic ligand upon decomplexation. When the ligands and the geometries of the complexes are the same, this entropy should be the same. It will, however, vary slightly from ligand to ligand.

For octahedral complexes of Ni(II) with $[\text{14}] \text{aneN}_4$ and 2,3,2-tet the extra stability of the macrocyclic complex ($\Delta G^\circ = -8.1$ kcal mol⁻¹) is made up of two almost equal contributions, an enthalpy term ($\Delta H^\circ = -4.9$ kcal mol⁻¹) and an entropy term ($-T\Delta S = -3.2$ kcal mol⁻¹), while for the comparable complexes with Cu(II) the contributions are $\Delta G^\circ = -8.4$, $\Delta H^\circ = -4.7$, and $-T\Delta S = -3.7$ kcal mol⁻¹, although in this case the ΔG° and $T\Delta S^\circ$ terms have been estimated.

We now must consider whether the fact that the macrocyclic enthalpies of the Cu(II) and octahedral Ni(II) complexes with $[\text{14}] \text{aneN}_4$ and 2,3,2-tet are almost identical is significant. It must be admitted that this equality would support the original hypothesis of Margerum that the macrocyclic enthalpy arises from a difference in the degree of hydration of the macrocyclic and noncyclic ligands in aqueous solution,⁴ which would mean that for metal complexes with comparable geometries and the same ligand the same macrocyclic enthalpy would be expected. However, the magnitude of the macrocyclic enthalpy (~5 kcal mol⁻¹) falls far short of the amount calculated by Margerum (14 kcal mol⁻¹) which would result from the breaking of

hydrogen bonds consistent with two more water molecules being bound to the noncyclic ligand. Most significantly, however, in all cases we have found a favorable entropy contribution to the macrocyclic effect. In order for Margerum's original hypothesis to be viable a negative entropy contribution must be expected since it is highly improbable that the relative gain in configurational entropy of the noncyclic ligand on decomplexation could outweigh the loss in translational entropy associated with two extra water molecules being bound to the noncyclic ligand. The present results confirm our view that this original hypothesis is no longer tenable and the equality of the macrocyclic enthalpies of the Cu(II) and octahedral Ni(II) complexes with [14]aneN₄ and 2,3,2-tet is to some extent fortuitous, both macrocyclic complexes benefiting from similar increases in M-N interaction over their noncyclic counterparts.

In conclusion, the most significant consequence of this study is to bring the interpretation of the macrocyclic effect for Ni(II) within the same framework as that already established for other metal complexes and to reemphasize that this effect has its origins in both enthalpic and entropic terms.

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Registry No. [Ni[14]aneN₄(H₂O)₂]²⁺ (octahedral), 64616-26-8; [Ni[14]aneN₄]²⁺ (square-planar), 46365-93-9; [Ni(2,3,2-tet)(H₂O)₂]²⁺ (octahedral), 23236-28-4; [Ni(2,3,2-tet)]²⁺ (square-planar), 25669-75-4.

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Mechanism of the Quenching of the Emission of Substituted Poly(pyridine)ruthenium(II) Complexes by Europium(II)

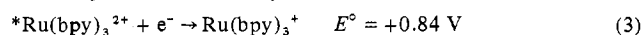
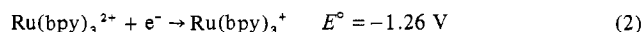
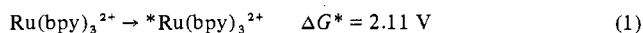
CAROL CREUTZ

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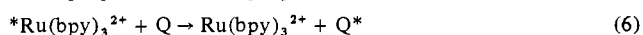
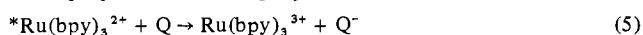
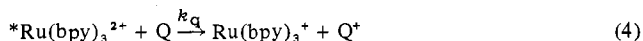
The emission from the charge-transfer excited states of poly(pyridine)ruthenium(II) complexes (RuL₃²⁺, L = a 2,2'-bipyridine or 1,10-phenanthroline derivative) is quenched by aqueous europium(II) at rate constants ranging from 1.5 × 10⁶ to 1.0 × 10⁸ M⁻¹ s⁻¹ (25 °C, 0.5 M ionic strength) depending on the identity of L. The quenching gives rise to the electron-transfer products RuL₃⁺ and Eu(III) which undergo back-reaction to form RuL₃²⁺ and Eu(II) at rate constants ranging from 2 to 6 × 10⁷ M⁻¹ s⁻¹. Energy-transfer and electron-transfer mechanisms are considered for the Eu(II) quenching process and the free energy dependences observed in europium outer-sphere electron-transfer reactions are reviewed.

Introduction

The emitting state of tris(2,2'-bipyridine)ruthenium(II) (*Ru(bpy)₃²⁺) is a stronger oxidant than the ground-state molecule by ~2.1 V as a consequence of its excitation energy (eq 1-3).^{1,2} Since the excited state is a rather strong oxidant,



its emission may be quenched by reducing agents according to eq 4; oxidative (eq 5)³⁻⁵ and energy transfer (eq 6)^{3,6}



mechanisms also provide pathways for the emission quenching.

Evidence for reductive quenching according to eq 4 has been provided by studies of the emission quenching by such diverse reductants as Ru(NH₃)₆²⁺,¹ S₂O₄²⁻,¹ Eu_{aq}²⁺,^{1,2} Os(CN)₆⁴⁻,⁷ and Fe(CN)₅L³⁻,⁸ and by organic amines.⁹ More direct evidence for the operation of this pathway has been provided by flash-photolysis studies of the Eu_{aq}²⁺ and the organic amine⁹ systems in which the low oxidation state Ru(bpy)₃⁺ was observed spectrally. The present study extends the use of Eu_{aq}²⁺ as a quencher to other poly(pyridine)ruthenium(II) complexes. The results of cyclic voltammetric, steady-state emission quenching, and flash-photolysis experiments with these complexes are reported below.

Experimental Section

Materials. Tris(2,2'-bipyridine)ruthenium(II) chloride (Ru(bpy)₃Cl₂) purchased from G. F. Smith was recrystallized from hot water at least twice before use. This was necessary in order to remove an insoluble dark brown impurity present in some lots. The other RuL₃²⁺ complexes used (L = 4,4'-(CH₃)₂bpy, 4,4'-dimethyl-2,2'-