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Kinetics and Thermodynamics of Dissociation of Nickel(II)–Isoquinoline Complexes in Water, Ethanol, and 1-Propanol

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Rate constants and associated activation parameters for the dissociation of $(solv)_5Ni(isoquin)^{2+}$ (solv = solvent, isoquin = isoquinoline) in ethanol, 1-propanol, and water and of $(solv)_5NiSCN^+$ in 1-propanol have been measured kinetically by stopped-flow spectrophotometry using H_3O^+ as the decomposing ion for $(solv)_5Ni(isoquin)^{2+}$ and copper(II) for $(solv)_5NiSCN^+$. These data are compared with previously reported results on dissociation of $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in several donor solvents. Pathways for dissociation of both $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in the solvents studied are accommodated within an I_d-type mechanism.

Introduction

An improved understanding of solvent properties can be obtained from studies of reactions in which solvent molecules are direct participants, such as in the solvolysis of ligand-substituted complexes. It has been shown[1,2] that measurements of dissociation rates of $(solv)_5Ni(isoquin)^{2+}$ (solv = solvent, isoquin = isoquinoline) in water, methanol, acetonitrile, and dimethyl sulfoxide and of $(solv)_5NiSCN^+$ in water, methanol, acetonitrile, dimethyl sulfoxide, and dimethylformamide can be interpreted through an I_d-type mechanism represented by eq 1, where solv is a solvent molecule and L is either iso-

$$LNi(solv)_5 + solv \rightleftarrows solv,(solv)_5Ni\text{–}L \rightleftarrows solv\text{–}Ni(solv)_5,L \qquad (1)$$

quinoline or thiocyanate ion (charges omitted). It has also been shown that dissociation rate constants at a single temperature do not bear a systematic relation to the donor properties of the solvent, but enthalpies of activation for dissociation of both $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ bear an inverse linear relation to solvent donor properties as expressed by the Gutmann donor number.[3]

We report in this work studies of the dissociation of $(solv)_5Ni(isoquin)^{2+}$ in water, ethanol, and 1-propanol and of $(solv)_5NiSCN^+$ in 1-propanol over a range of temperatures. Enthalpies and entropies of activation for dissociation in these solvents have been calculated; the results, in conjunction with previous work on these systems in other solvents,[1,2] are discussed in terms of mechanisms and solvent donor properties.

Experimental Section

Solvents. Commercial 1-propanol (Baker Analyzed, assay 99%) was refluxed for 12 h over BaO and fractionally distilled in the absence of air. The middle fraction, collected over alumina previously baked 24 h at 550 °C, was shaken for 12 h and then fractionally distilled. The middle cut from the second distillation was fractionally distilled twice more from metallic sodium in the absence of air. The purified solvent was used within 24 h of the final distillation. Pure ethanol, USP (U.S. Industrial Chemicals), was used as obtained without further treatment. Singly distilled water was redistilled from alkaline $KMnO_4$ before use.

Reagents. Nickel(II) was introduced as the perchlorate salt. In all solvents, nickel(II) perchlorate monohydrate, prepared as previously described,[4] was used. Copper(II) was introduced as hexakis(acetonitrile)copper(II) perchlorate and was prepared as before.[5] Perchloric acid (Mallinckrodt, analytical reagent, 70%) was used as received. Isoquinoline (Aldrich, mp 26–28 °C, bp 252 °C) was purified as described before.[4] Potassium thiocyanate (J. T. Baker, Baker Analyzed, assay 100%) was dried at 60 °C under vacuum for 3 days.

Instruments and Experimental Procedure. All nonaqueous solutions were prepared and dispensed in a drybox (Kewaunee Scientific) under dry nitrogen by using glassware that had been oven-dried at 100 °C for several days. All standard procedures for handling nonaqueous solutions were followed. The first-order dissociation rate constant of $(solv)_5Ni(isoquin)^{2+}$ in perchloric acid was determined by measuring the rate of formation of $isoquinH^+$ by following the rate of change of transmittance upon mixing of a solution of $(solv)_5Ni(isoquin)^{2+}$ with $HClO_4$ at a wavelength where $isoquinH^+$ absorbs strongly and $(solv)_5Ni(isoquin)^{2+}$ and $HClO_4$ absorb but little. A stopped-flow spectrophotometer (Durrum Instrument Co., Model D110) was used for all kinetic measurements. A description of the instrument along with modifications for better temperature control has been given.[6] Solutions of $(solv)_5Ni(isoquin)^{2+}$ were prepared in dry volumetric flasks by adding measured volumes of a standard nickel(II) solution to a known volume of a stock isoquinoline solution and diluting to volume with solvent. In all solutions, the concentration of nickel(II) was in 50- to 100-fold excess of the isoquinoline concentration to ensure the formation of the mono complex only. The total concentration of perchloric acid in the final mixed solution was held higher than the total concentration of nickel(II) by a ratio of 2 to 1 in water and 1-propanol and 6 to 1 in ethanol. In 1-propanol, kinetic measurements were done in both the presence and absence of acetic anhydride, the concentration of acetic anhydride being held equal to the concentration of perchloric acid or held at double the concentration of perchloric acid. Absorbance measurements were made at 332 nm in water and 1-propanol and at 334 nm in ethanol. Dissociation rate constants of

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Table I. Dissociation Rate Constants k_{obsd} (s^{-1}) of Ni(isoquin)$^{2+}$ in Perchloric Acid[a]

$10^2 \times$ [$HClO_4$], M	$10^2 \times$ [Ac_2O], M	*t*, °C								
		5	10	15	20	25	30	35	40	45
In Ethanol										
2[b]						17.9				
3[b]						17.7				
4[b]						17.9				
5[b]						17.9				
3[b]		1.76	3.26	6.03	10.4	17.9	29.2	48.7		105.5_5
In 1-Propanol										
1[c]						20.0				
2[c]						20.1				
3[c]						20.1				
4[c]						20.1				
1[c]	1					20.1				
2[c]	2					19.3				
3[c]	3					20.3				
1[b]	2	1.95	3.65	6.60	11.5	19.5	30.7	47.6	71.4	102
In Water										
20[c]		3.83	6.44_7	10.9_1	18.2_4	29.7_4	47.7_2			

[a] All concentrations refer to final values after mixing in a stopped-flow cell. The uncertainty in k_{obsd} is ±3% or less. [b] [Ni^{2+}] = 5×10^{-3} M, [isoquin] = 1×10^{-4} M. [c] [Ni^{2+}] = 1×10^{-2} M, [isoquin] = 2×10^{-4} M.

Table II. Dissociation Rate Constants k_{obsd} (s^{-1}) of $NiSCN^+$ in 1-Propanol[a]

10^2[Cu^{2+}], M	*I*, M	*t*, °C				
		5	10	15	20	25
0.5	0.0167					10.2_3
1	0.0317					10.2_7
1.5	0.0467					10.3
2.0	0.0617					10.2_7
0.5	0.0167	0.98	1.83	3.38	6.19	10.3_4[b]

[a] Concentrations of nickel(II) perchlorate and potassium thiocyanate held constant at 5×10^{-4} M. All concentrations refer to final values after mixing in a stopped-flow cell. [b] At 25 °C, k_b = 10.34 s^{-1}, $\Delta H_b{}^{\ddagger}$ = 19.0 ± 0.2 kcal, and $\Delta S_b{}^{\ddagger}$ = 9.6 ± 0.8 eu.

Table III. Comparison of Rate Constants and Associated Activation Parameters for Dissociation of the Mono Complex of Nickel(II) with Isoquinoline[a,b]

solvent	k_b, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	donicity[c]
H_2O	29.7_4 (29.9)[d]	16.4 ± 0.1 (16.1 ± 0.6)[d]	+2.9 ± 0.4 (+2.2)[d]	18.0
CH_3OH	1.91	19.3 ± 0.2	+7.5 ± 0.7	9[e]
EtOH	17.9	18.6 ± 0.1_5	+9.5 ± 0.5	
n-PrOH	19.5	18.4 ± 0.1_5	+8.9 ± 0.5	
$(CH_3)_2SO$	109	13.5 ± 0.4	−4 ± 1	29.6
CH_3CN	0.135	17.2 ± 0.5	−5 ± 2	14.1
propylene carbonate	0.275	17.7 ± 0.5	−6 ± 2	15.1
DMF	26.5	13.9 ± 0.4	−5 ± 1	26.8

[a] Temperature 25 °C. [b] Data from ref 2, except for water, ethanol, and 1-propanol. [c] Data from ref 3. [d] Data from ref 2. [e] Data from ref 1.

Table IV. Rate Constants k_b (s^{-1}) for Dissociation of Ni(isoquin)$^{2+}$ in Water

method	*t*, °C						
	5	10	15	20	25	30	35
I[a]	3.83	6.44_7	10.9_1	18.2_4	29.7_4	47.7_2	
II[b]			12.2	21.0	29.6	52.3	78.4
III[c]			11.8_7	20.9_6	29.9	52.9_5	78.0_2

[a] This work. [b] Obtained from intercepts of pseudo-first-order plots for formation of $(solv)_5Ni(isoquin)^{2+}$ in water in ref 4. [c] Calculated from equilibrium constant and formation rate constant data for $(solv)_5Ni(isoquin)^{2+}$ in ref 2.

$(solv)_5Ni(isoquin)^{2+}$ were measured at temperatures over the range of 5–45 °C at 5 °C intervals.

The procedure for measuring the dissociation rate constant of $(solv)_5NiSCN^+$ using copper(II) as the decomposing ion was as described before.[2] In $(solv)_5NiSCN^+$ solutions, concentrations of nickel(II) and thiocyanate ion were kept constant at 1×10^{-3} and 4×10^{-4} M. Potassium thiocyanate was used as the source of thiocyanate ion. Copper(II) concentrations were varied from 1×10^{-2} to 4×10^{-2} M in four increments. The first-order dissociation rate constant of $(solv)_5NiSCN^+$ was determined by following at 400 nm the rate of formation of $(solv)_5CuSCN^+$ upon mixing of solutions of copper(II) and $(solv)_5NiSCN^+$. The procedure for preparation of $(solv)_5NiSCN^+$ solutions was the same as for $(solv)_5Ni(isoquin)^{2+}$ solutions. In 1-propanol, a solution of $(solv)_5NiSCN^+$, 1×10^{-3} M in nickel(II) and 4×10^{-4} M in thiocyanate, became slightly hazy with time, and when the solution was stored in a stoppered flask in a drybox filled with dry nitrogen gas, a trace amount of finely crystalline white precipitate appeared in the bottom of the flask. The precipitate was removed by vacuum filtration through a 10–20-μm glass frit under nitrogen in the drybox, and the clear solution was used for kinetic measurements. All measurements were repeated several times with different batches of reagents and solvents; results were reproducible within ±2–3% or better in all cases.

Results and Discussion

Experimental conditions in this work were chosen so as to observe only dissociation of the mono complex of nickel(II) with isoquinoline and thiocyanate.[4,7] Table I lists dissociation rate constants of $(solv)_5Ni(isoquin)^{2+}$ in ethanol, 1-propanol, and water at several temperatures over a range of concentrations of acetic anhydride and perchloric acid. Dissociation rate constants of $(solv)_5NiSCN^+$ in 1-propanol at various temperatures, ionic strengths, and concentrations of copper(II) are shown in Table II. In Table III dissociation rate constants and associated activation parameters for dissociation of $(solv)_5Ni(isoquin)^{2+}$ in different solvents are tabulated. The dissociation rate constants of $(solv)_5Ni(isoquin)^{2+}$ in water at various temperatures, as calculated by different methods, are tabulated for comparison in Table IV. The major features of the results are the following.

1. Dissociation of $(solv)_5Ni(isoquin)^{2+}$ by H_3O^+ in all solvents studied in this work is independent of the concentration of H_3O^+ as long as [H_3O^+] is equal to or greater than the concentration of nickel(II) (Table I).

2. Ionic strength variations do not influence the dissociation of $(solv)_5Ni(isoquin)^{2+}$ in any of the solvents studied (Table I).

3. Water was introduced as a result of using perchloric acid dihydrate as acid in the work in dry ethanol and 1-propanol. As a result, water concentrations of 0.10 M in ethanol and

0.08 M in 1-propanol were present in these solvents, but this level had no influence on the dissociation of $(solv)_5Ni(isoquin)^{2+}$ in these solvents (Table I). Dissociation rates of $(solv)_5Ni(isoquin)^{2+}$ in 1-propanol are unaffected by the addition of acetic anhydride to remove water introduced as perchloric acid dihydrate.

4. Dissociation of $(solv)_5NiSCN^+$ in 1-propanol is unaffected by either the ionic concentration of the solution or the total concentration of copper(II) if the copper(II) concentration is kept at least ten times greater than the total concentration of nickel(II) (Table II).

5. Direct measurements of the dissociation of $(solv)_5Ni(isoquin)^{2+}$ in water with H_3O^+ as the decomposing ion agree within experimental uncertainty with previously reported data either (a) calculated from the equilibrium constant and formation rate constant of the complex or (b) measured by intercepts of kinetic plots of observed pseudo-first-order rate constants against total concentration of nickel(II) (Tables III and IV).

6. Values of the enthalpy of activation for dissociation of $(solv)_5Ni(isoquin)^{2+}$ in ethanol and 1-propanol are larger than for any of the solvents studied thus far except methanol (Table III).

Previous measurements on the $(solv)_5Ni(isoquin)^{2+}$ system in water were repeated here to verify previously reported results and to check the procedure; the mechanistic pathways for dissociation of this complex in water are well established.[2] As shown in Table I, the influence of concentration of the decomposing ion along with the effect of ionic strength on the dissociation of both $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ indicates that in both ethanol and 1-propanol the dissociation process can be represented by eq 2 and 3. When $[A] \gg [L]$,

$$NiL^{(2-n)+} + solv \underset{k_f}{\overset{k_b}{\rightleftharpoons}} Ni^{2+} + L^{n-} \qquad (2)$$

$$A^{y+} + L^{n-} \xrightarrow{k_1} AL^{(y-n)+} \qquad (3)$$

as used in this work, k_{obsd}, the experimentally determined observed pseudo-first-order rate constant, is given by eq 4.

$$k_{obsd} = k_b k_1[A^{y+}]/(k_f[Ni^{2-}] + k_1[A^{y+}]) \qquad (4)$$

When $k_1[A^{y+}] \gg k_f[Ni^{2+}]$, and the ionic concentration of the medium does not change, k_{obsd}, the first-order dissociation constant of the complex $(solv)_5NiL^{(2-x)+}$, is equal to k_b. Here L may be either isoquinoline or thiocyanate ion, x is the charge on L, A may be either H_3O^+ or copper(II), and y is the charge on A. Solvent molecules associated with nickel(II), A^{y+} and $NiL^{(2-x)+}$ have been omitted for simplicity.

The absence of an ionic strength effect on dissociation of $(solv)_5Ni(isoquin)^{2+}$ in the solvents studied is expected because the charge does not change upon interaction between nickel(II) and isoquinoline. But the absence of any effect of ionic strength on the dissociation of $(solv)_5NiSCN^+$ in 1-propanol is contrary to previous observations on dissociation of $(solv)_5NiSCN^+$ in methanol. In methanol the influence of ionic concentration on dissociation of $(solv)_5NiSCN^+$ was thought to be linearly related to the extent of ionic association between $(solv)_5NiSCN^+$ and ClO_4^-. 1-Propanol, with a lower dielectric constant than methanol, might be expected to show greater ion association effects than methanol under the same experimental conditions, and the dissociation rate of $(solv)_5NiSCN^+$ might be expected to be influenced more in 1-propanol than in methanol. However, in 1-propanol, even at the lowest concentration of $[(solv)_5NiSCN^+][ClO_4^-]$ used in this work, 0.0167 M, ion association is so great that a further small change in ionic strength does not affect ion association greatly, and due to the labeling effect on ion association, the dissociation rate remains unaffected. A similar labeling effect on the degree of ion association between $(solv)_5NiSCN^+$ and ClO_4^- in methanol, with a corresponding absence of any influence of further increase of ionic strength on the dissociation rate of $(solv)_5NiSCN^+$, has been observed before.[1] An alternative explanation for the absence of an ionic strength effect on the rate of dissociation of $(solv)_5NiSCN^+$ in 1-propanol may stem from the presence of trace amounts of water in the solvent. This assumption seems likely to be ruled out, however, because different batches of solvent, purified with care and used within 12 h of final distillation, gave the same results. Also, any water present in the system would likely replace one or more solvent molecules in $(solv)_5NiSCN^+$. The enthalpy of activation for dissociation of the resulting complex would be expected to be lower than for $(solv)_5NiSCN^+$ in 1-propanol, and since the donicities of 1-propanol predicted from the results of the dissociation of $(solv)_5Ni(isoquin)^{2+}$, where no water was present, and $(solv)_5NiSCN^+$ are identical, we believe that the 1-propanol used in the studies of dissociation of $(solv)_5NiSCN^+$ was not contaminated with water. Therefore we conclude that the low dielectric constant of 1-propanol gives rise to a high degree of association between $(solv)_5NiSCN^+$ and ClO_4^- in 1-propanol at the concentrations used in this work, and the degree of association is not substantially affected over the range of ionic strengths used.

As observed before[1,2] in other solvents, the rate constants for dissociation of $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in ethanol and 1-propanol at a given temperature do not show any systematic relation with solvent donicity. The scheme that fits the results on dissociation of $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in ethanol and 1-propanol can also be represented by an I_d-type interchange mechanism as represented by eq 1.

Donor numbers of alcohols cannot be measured directly owing to solvolysis of $SbCl_5$. Extrapolating the linear inverse relation between enthalpy of activation ($\Delta H_b^‡$) for dissociation of the complex and the donor number of solvent to results for dissociation of complexes in alcohols, we estimated donor numbers for methanol, ethanol, and 1-propanol to be 9, 11, and 12. The significance of these low values is not clear. The order of the enthalpies of activation for dissociation among solvents with nickel(II) as the Lewis acid is not changed when isoquinoline is replaced by thiocyanate or 4-phenylpyridine.[9] However, whether this relative order is the same for other Lewis acids is not known; further work is needed to establish this point.

In summary, we conclude that the values of the enthalpy of activation for dissociation of $(solv)_5Ni(Isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in ethanol and 1-propanol follow the trends observed for nickel complexes in other solvents and that the mechanism for the dissociation of the complexes in both ethanol and 1-propanol is of an I_d type. Fine details of the mechanism can be more readily understood by consideration of thermodynamic parameters rather than rate constants at a single temperature. Also, directly measured dissociation rate constants and associated activation parameters are more precise than values calculated either from measured equilibrium constants and forward formation rate constants or from intercepts obtained in plots of pseudo-first-order formation rate constants against concentrations of the coordinating cation.

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Registry No. $(n\text{-}PrOH)_5NiSCN^+$, 71155-91-4; $(H_2O)_5Ni(isoquinoline)^{2+}$, 60489-00-1; $(EtOH)_5Ni(isoquinoline)^{2+}$, 71155-92-5; $(n\text{-}PrOH)_5Ni(isoquinoline)^{2+}$, 71155-93-6.

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Thermodynamic and Spectroscopic Properties in Aqueous Solutions of Pentadentate Macrocyclic Complexes

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The complexes of two pentadentate macrocycles containing N, S, and O (A = 1-oxa-7,10-dithia-4,13-diazacyclopentadecane and B = 1-oxa-4,13-dithia-7,10-diazacyclopentadecane) and the open-chain analogue of B (L = 8-oxa-2,14-diaza-5,11-dithiapentadecane) with the cations Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, and Pb^{2+} have been studied in aqueous 0.1 M $NaClO_4$ solutions at 25 °C, by potentiometry, calorimetry, and UV–visible spectroscopy. The three ligands form 1:1 complexes with all the cations studied. The protonation constants of the ligands and the overall stability constants of the 1:1 complexes are given, together with the complexation enthalpies and entropies of some of the 1:1 complexes of B and L. The stability constants of the protonated and binuclear species, when they are formed, are also given. It is found that the following occur: (i) Selectivity corresponding to the general Irving–Williams rule is displayed by both macrocycles. (ii) The magnitude of the macrocyclic effect, displayed by B with respect to L, is strongly dependent on the nature of the cation. (iii) In the case of Cu^{2+}, for which there is a strong macrocyclic effect, the thermodynamic origin of the macrocyclic effect is equally enthalpic and entropic. For Pb^{2+}, which displays no macrocyclic effect, the enthalpic and entropic contributions are both zero. (iv) The difference in the heteroatom positions in the macrocycles A and B leads to nonnegligible variations of the complex stabilities, which also depend upon the nature of the cation. The molecular structures in the solid state, as well as the electronic spectra in the solid state and in aqueous solution of the nickel, copper, and silver complexes of A and B, suggest a possible correlation between structure and stability. The ligand field parameters *Dq* for the octahedral Ni(II) complexes are found equal to 1740 cm^{-1} for A and 1800 cm^{-1} for B. The nephelauxetic ratio is very low for both macrocycles (β = 0.50) as could be expected for sulfur donor ligands.

Introduction

Thermodynamics in solution of macrocyclic complexes has received continuously increasing interest during the last 10 years and has been extensively studied, principally with respect to macrocyclic polyethers[2] and polyamines.[3–18] But "mixed" macrocycles, containing nitrogen, oxygen, and/or sulfur donor atoms have been considerably less investigated. No data on the stability of macrocyclic complexes containing three different heteroatoms N, S, and O could be found in the literature before our work.

We report here the results of our potentiometric, spectrophotometric, and calorimetric studies in aqueous solution of the complexes of a new class of mixed N, S, and O pentadentate macrocycles. These were synthesized for the first time by one of us[19] and we have already published preliminary results,[20–23] as well as some crystal structure determinations.[22–26]

The two macrocycles investigated, A = 1-oxa-7,10-dithia-4,13-diazacyclopentadecane and B = 1-oxa-4,13-dithia-7,10-diazacyclopentadecane, are represented in Figure 1, together with the linear secondary diamine L = 8-oxa-2,14-diaza-5,11-dithiapentadecane, which is the open-chain homologue of the macrocycle B. The stabilities of the complexes of these three ligands with the transition- and heavy-metal cations Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, and Pb^{2+} have been investigated potentiometrically, in aqueous 0.1 M $NaClO_4$ media, at 25 °C.

Our interests in the study consisted mainly in the search for eventual complexation selectivities and in the investigation of the influence of the heteroatom positions in the cycle upon the complex structures and stabilities. We also wished to investigate the so-called "macrocyclic effect", the enhancement of stability of a metallic macrocyclic complex with respect to the corresponding noncyclic chelate,[3] by comparing the stabilities of the various complexes of the macrocycle B to those of its acyclic analogue. The enthalpies of formation of some of the complexes were determined calorimetrically, in order to evaluate the relative contributions of the enthalpic and entropic origins of the macrocyclic effect. These are much debated and seem to vary with the nature of both the cation and the ligand.[3–18] Moreover, the electronic spectra of the nickel(II) octahedral complexes in solution enabled us to determine the ligand field parameters *Dq* and the nephelauxetic ratios β.

The results reported here are brought together for comparison with the recent thermodynamic studies of the complexes of two other pentadentate macrocyclic ligands: the pentaamine 1,4,7,10,13-pentaazacyclopentadecane or [15]-aneN_5[17] and the 1,7,10-trioxa-4,13-diazacyclopentadecane or [2.1] (Figure 2). The latter has been studied by two of us in the general framework of the study of the stability in various solvents of polyoxadiaza macrocycles.[27,28] It is analogous to A but with the S(7) and S(10) atoms replaced by oxygen atoms.

Experimental Section

Reagents. The macrocycles A and B were prepared and purified as described elsewhere.[19] The aqueous solutions of ligand perchlorate, obtained by adding a slight excess of $HClO_4$ to the free ligand, were

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