ground states observed in the Eu dihalides.

Summary and Conclusions

The structural, electronic, and magnetic properties of europium dihalides are established from the combination of X-ray diffraction, magnetic susceptibility, and ^{151}Eu Mössbauer spectrometry results. The bonding properties, i.e. the charge and spin densities at the Eu nucleus, are inferred from the isomer shift and hyperfine field, respectively. The evolution of these parameters along the series of compounds reveals a correlated dependence, which indicates

covalency effects involving primarily the Eu 6s valence orbital being populated by charge transfer from the ligand s (or p) orbitals. The relatively large Eu interatomic distances and the low symmetry of the Eu sites account qualitatively for the low ordering temperatures (in comparison to other Eu^{2+} insulators) measured for $EuCl_2$ and EuI_2 ($T_t \le 1.8$ K) and the paramagnetism of $EuBr_2$ down to 1.1 K.

Ultrasonic Relaxation and Variable-Pressure Spectrophotometric Study of the Planar ⇌ Octahedral Equilibrium in Aqueous Solutions of [[1R,4S,8S,11R]-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Perchlorate, Ni(Me4cyclam)(ClO4)2 (trans-III Isomer)

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A single relaxation curve describes the excess ultrasound adsorption in aqueous solutions of the title compound, Ni(Me4-cyclam)(ClO4)2. The relaxation time at 25 °C of 16.8 ± 0.1 ns is identified as arising from perturbation of the equilibrium between the diamagnetic planar complex and the paramagnetic octahedral complex formed by trans addition of two water molecules. From equilibrium constants K_{46} determined by the Evans NMR method, rate parameters at 25 °C were calculated: $k_{46} = 3.10 \times 10^7$ s^{-1}, $\Delta H_{46}^* = 2.44$ (2) kcal mol^{-1}, $\Delta S_{46}^* = -16.06$ (3) cal deg^{-1} mol^{-1}; $k_{64} = 2.85 \times 10^7$ s^{-1}, $\Delta H_{64}^* = 9.31$ (2) kcal mol^{-1}, $\Delta S_{64}^* = 6.79$ (1) cal deg^{-1} mol^{-1}. From the relaxation amplitude, the volume difference ΔV_{46}° is found to be -10.1 (2) cm^3 mol^{-1}. An independent measurement from the pressure dependence of the electronic absorption spectrum gives -8.6 (3) cm^3 mol^{-1}. For Ni(cyclam)$^{2+}$, the analogous relaxation time is somewhat longer and the volume change measured from the pressure dependence of the electronic spectrum only -3.5 (1) cm^3 mol^{-1}.

Introduction

The existence of a diamagnetic–paramagnetic equilibrium in aqueous solutions of the *trans*-III isomer of the tetramethylcyclam complex of nickel(II) [[1R,4S,8S,11R]-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II), Ni(Me4cyclam)$^{2+}$ (*trans*-III isomer)) was suggested when the complex was first prepared.[2] Recently, the thermodynamics of the equilibrium have been measured with visible electronic absorption spectra,[3] solution magnetic susceptibility (Evans method),[3] and proton NMR contact shifts.[4] From the solution electronic spectrum it has been inferred[3] that the paramagnetic form is octahedrally coordinated with two solvent molecules:

$$Ni(Me_4cyclam)^{2+} + 2H_2O \underset{K_{46}}{\rightleftharpoons} Ni(Me_4cyclam)(H_2O)_2^{2+} \quad (1)$$
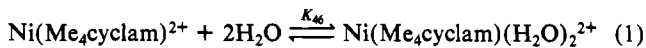
The dynamics of this equilibrium have not been described for aqueous solutions, although related processes in acetonitrile have been studied in detail.[5,6]

We have used an ultrasonic relaxation technique to obtain the relaxation time for equilibrium 1 and have independently measured

the equilibrium constant by using the Evans NMR method. With these data, the rate constants k_{46} and k_{64} have been calculated, along with a value for the volume change associated with the equilibrium. Good agreement was found with the volume change measured directly with high-pressure spectrophotometry and also with that reported[4] from high-pressure NMR measurements. Some observations were also made on the analogous equilibrium of the cyclam complex of nickel(II) ([1,4,8,11-tetraazacyclotetradecane]nickel(II), Ni(cyclam)$^{2+}$).[3,7–9]

Experimental Section

The perchlorate salts of the complexes were prepared by methods described in the literature[2,10,11] from cyclam ligand purchased from Strem Chemicals Inc. Ultrasonic absorption measurements were made as described previously.[12,13] Solution magnetic susceptibility measurements of 0.020 g mL^{-1} of Ni(Me4cyclam)(ClO4)2 in H2O by the Evans method were made at 90 MHz (Bruker HX-90). An internal reference of 5% v/v t-BuOH was used. A capillary of ethylene glycol was used as an internal temperature probe. The data were corrected for changes in density and, hence, concentration with changes in temperature.[13]

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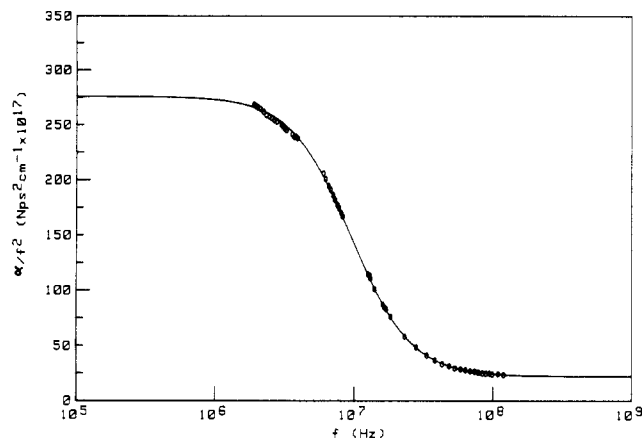(13) Binstead, R. A.; Beattie, J. K.; Dewey, T. G.; Turner, D. H. *J. Am. Chem. Soc.* 1980, 102, 6442.

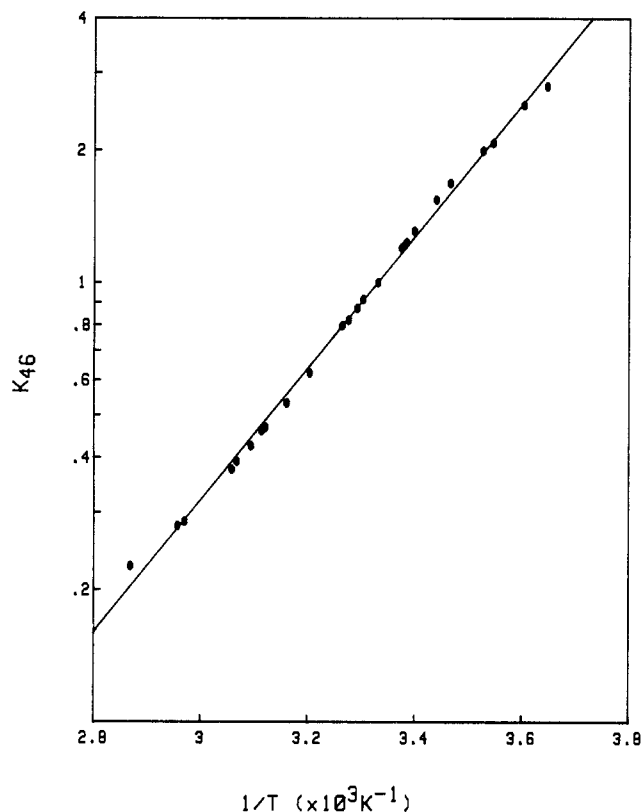**Figure 1.** Ultrasonic relaxation curve for 0.070 M solutions of Ni-(Me$_4$cyclam)(ClO$_4$)$_2$ at 25 °C.

Figure 2. Temperature dependence of the equilibrium constant K_{46} determined by the Evans NMR method.

Figure 3. Temperature dependence of the calculated rate constants.
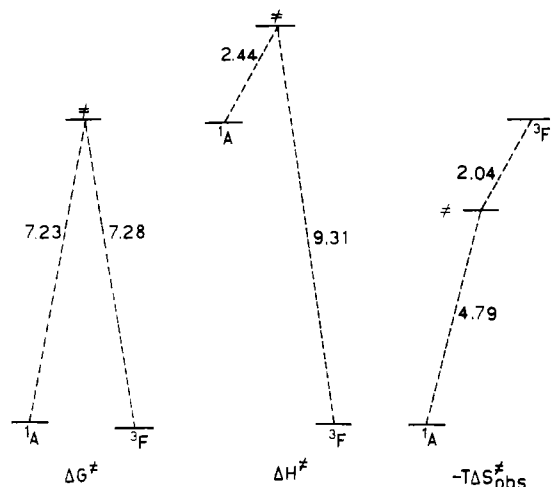
Figure 4. Profile of the reaction coordinate (kcal mol^{-1}).

Variable-pressure spectrophotometric measurements were made with a high-pressure cell[14] in a Varian Techtron 635D spectrophotometer interfaced with a PDP-11 minicomputer. Corrections were made to allow for the compressibility of the solution over the pressure range 1–1500 bar from the bulk compressibility of water, 4.6 × 10^{-5} bar^{-1} at 1 bar.[15]

Results

[[1R,4S,8S,11R]-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Perchlorate. Aqueous solutions of this complex exhibit excess ultrasound adsorption, as illustrated in Figure 1. The data are adequately described by a curve for a single relaxation process (eq 2), where α is the absorption coef-

$$\alpha/f^2 = A(1 + \omega^2\tau^2)^{-1} + B \qquad (2)$$

ficient (Np cm^{-1}), f is the frequency (Hz), ω is the angular frequency ($\omega = 2\pi f$), τ is the relaxation time (s), and A and B are
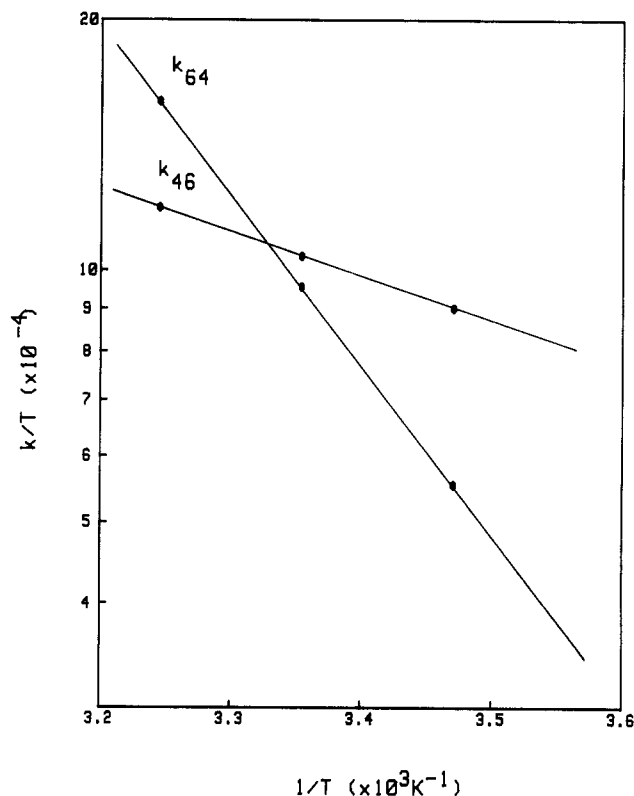
constants for a particular relaxation curve.[16]

The parameters obtained by nonlinear least-squares analysis of measurements at three temperatures are given in Table I.

To interpret the relaxation times the equilibrium constants at the various temperatures must be known. These were obtained with the Evans ^{1}H NMR method. The temperature dependence of the solution magnetic moment could be described by an equilibrium between a diamagnetic singlet state with a low-spin moment of 0 μ_B and a paramagnetic triplet state with a moment of 3.3 μ_B (Figure 2). From these values, the equilibrium constants, free energies, enthalpy, and entropy of reaction 1 were calculated and are listed in Table I. The results are in satisfactory agreement with previous determinations made by using the Evans method,[3] the temperature dependence of the electronic absorption spectrum,[3] and the temperature dependence of the ^{1}H NMR contact shifts.[4] The first two measurements were made in solutions containing 0.2 M NaClO$_4$; our measurements and apparently the contact shift

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Table I. Collected Data and Results for Aqueous Solutions of Ni(Me₄cyclam)(ClO₄)₂[a]

	15 °C	25 °C	35 °C
$10^{17}A$, Np s² cm⁻¹	399.5 ± 1.3[b]	253.6 ± 0.7	125.6 ± 0.6
$10^{17}B$, Np s² cm⁻¹	40.3 ± 0.9[b]	22.2 ± 0.6	17.7 ± 0.5
τ, ns	23.8 ± 0.2[b]	16.8 ± 0.1	11.7 ± 0.1
μ_{eff}, μ_B	2.60	2.38	2.16
K_{46}	1.63	1.09	0.75
$\Delta G°$, kcal mol⁻¹		−0.05 ± 0.01	
$\Delta H°$, kcal mol⁻¹		−6.87 ± 0.16	
$\Delta S°$, cal deg⁻¹ mol⁻¹		−22.9 ± 0.4	
$10^3\Gamma$, M	16.5[c]	17.5[c]	17.2[c]
$\alpha_p/\rho C_p$, cm³ kcal⁻¹ [d]	0.15090	0.25825	0.34775
$\Delta V°$, cm³ mol⁻¹	−10.2	−10.3	−9.7
k_{46}, s⁻¹	2.60 × 10⁷	3.10 × 10⁷	3.66 × 10⁷
k_{64}, s⁻¹	1.60 × 10⁷	2.85 × 10⁷	4.91 × 10⁷
$\Delta G_{46}^{\ddagger}$, kcal mol⁻¹		7.23 ± 0.07	
$\Delta H_{46}^{\ddagger}$, kcal mol⁻¹		2.44 ± 0.02	
$\Delta S_{46}^{\ddagger}$, cal deg⁻¹ mol⁻¹		−16.06 ± 0.03	
$\Delta G_{64}^{\ddagger}$, kcal mol⁻¹		7.28 ± 0.02	
$\Delta H_{64}^{\ddagger}$, kcal mol⁻¹		9.31 ± 0.02	
$\Delta S_{64}^{\ddagger}$, kcal mol⁻¹		6.79 ± 0.01	

[a] The quoted errors are 1 standard deviation. [b] At 0.050 M, A = (264.3 ± 1.1) × 10⁻¹⁷ Np s² cm⁻¹, B = (29.5 ± 0.8) × 10⁻¹⁷ Np s² cm⁻¹, and τ = 24.5 ± 0.3 ns. [c] Total complex concentration was 0.070 M. [d] Pure solvent values were assumed for the constants.
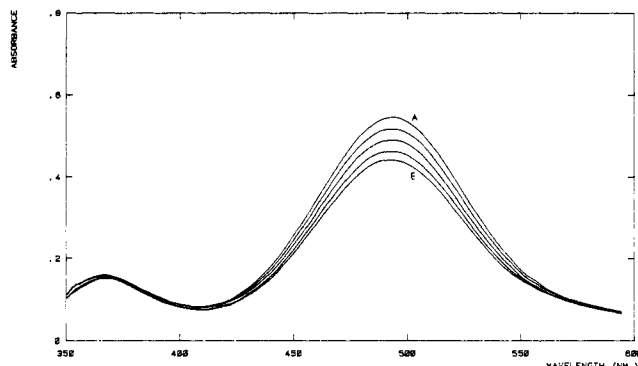
Figure 5. Electronic absorption spectra at pressures from A to E of 1, 340, 680, 1020, and 1312 bar.

measurements were made in solutions without added salt.

From the equilibrium constants and the relaxation times, rate constants k_{46} and k_{64} can be calculated ($\tau^{-1} = k_{46} + k_{64}$). From the Eyring equation activation parameters are obtained (Figure 3). These are given in Table I, and a thermodynamic profile of the reaction is presented in Figure 4.

The volume change of the reaction, $\Delta V°$, can be calculated from the amplitude of the ultrasonic absorption, A, with eq 3, where

$$A = \frac{2\pi^2 \rho v}{RT}\left(\Delta V° - \frac{\alpha_p}{\rho C_p}\Delta H°\right)^2 \Gamma\tau \qquad (3)$$

ρ is the solution density, v the sound velocity, α_p the coefficient of thermal expansion, C_p the specific heat, and Γ the concentration dependence ($\Gamma^{-1} = [IV]^{-1} + [VI]^{-1}$, where [IV] and [VI] denote the concentrations of the planar and octahedral complexes, respectively). From the data in Table I and values of the density and velocity of sound for pure water, $\Delta V°$ values were calculated. For the measurements at three different temperatures, the two roots from eq 3 gave a constant value of (−10.1 ± 0.2 cm³ mol⁻¹) or variable values of +5, +7, and +8 cm³ mol⁻¹. Hence, the negative value is more likely to be correct.

The volume change $\Delta V°$ can also be obtained from measurement of the pressure dependence of the electronic absorption spectrum, illustrated in Figure 5. From a molar absorptivity of 90.4 M⁻¹ cm⁻¹ at 494 nm determined from a solution of the perchorate salt in dry nitromethane, where it exists entirely in the diamagnetic form, the pressure dependence of the equilibrium constants K_{46} can be calculated. These are plotted as a function
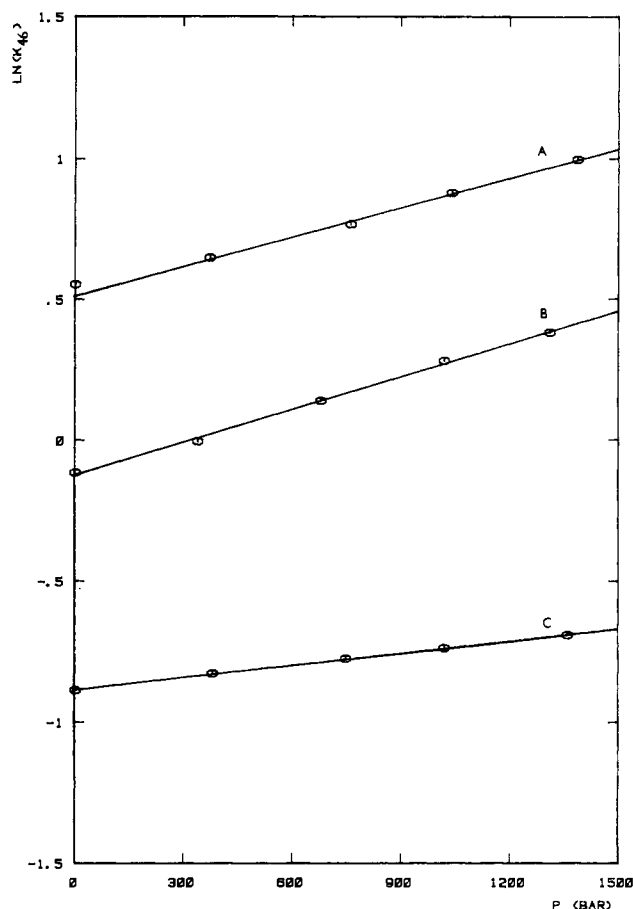
Figure 6. Pressure dependence of the equilibrium constants K_{46}: A, Ni(Me₄cyclam)²⁺ without electrolyte; B, Ni(Me₄cyclam)²⁺ in 0.3 M NaClO₄ solution; C, Ni(cyclam)²⁺ without electrolyte.

of pressure in Figure 6 for aqueous solutions of the complex containing no added electrolyte (A) and containing 0.3 M NaClO₄ (B). From the slopes, values of $\Delta V°$ are −8.6 ± 0.3 and −9.8 ± 0.3 cm³ mol⁻¹, respectively.

The volume change has also been measured from the pressure dependence of ¹H NMR contact shifts,[4] apparently in the absence of added salt, giving a value for $\Delta V°$ of −10.0 ± 0.1 cm³ mol⁻¹.

[1,4,8,11-Tetraazacyclotetradecane]nickel(II) Perchlorate. Aqueous solutions of this complex, Ni(cyclam)²⁺, also exhibit excess sound absorption, but the relaxation frequency appears to be ≤2 MHz, implying a relaxation time >10⁻⁷ s. Since the lower frequency limit of our ultrasonic apparatus is ∼0.5 MHz, we are not able to acquire a sufficiently complete relaxation curve to obtain reliable relaxation times. These observations are consistent, however, with recently reported ¹⁷O NMR experiments[9] on the rate of water exchange from Ni(cyclam)(H₂O)₂²⁺, as discussed below.

Variable-pressure electronic absorption spectra were also measured for aqueous solutions of Ni(cyclam)(ClO₄)₂ (0.017 M) with no added electrolyte. The change in K_{46} with pressure is included in Figure 6 and gives a value of $\Delta V°$ of −3.5 ± 0.1 cm³ mol⁻¹.

Discussion

Each of the physical measurements made on aqueous solutions of the *trans*-III isomer of Ni(Me₄cyclam)²⁺ indicates that a single equilibrium exists between planar and octahedral complexes, uncomplicated by the presence of other species. The amplitude of the ultrasonic relaxation absorption depends upon the presence of a significant concentration of the two species coupled by the perturbed equilibrium, as expressed in the Γ function. Hence, we can with confidence assign the observed ultrasonic relaxation to perturbation of the planar–octahedral equilibrium. This assignment is confirmed by the agreement between the values for the volume change of the reaction, $\Delta V°$, obtained from the ul-

trasonic measurements (-10.1 ± 0.2 cm^3 mol^{-1}) and from two static perturbations of the equilibrium (-8.6 ± 0.3 cm^3 mol^{-1} from electronic spectra and -10.0 ± 0.1 cm^3 mol^{-1} from NMR contact shifts[4]).

A thorough analysis of the reaction mechanism is not possible in the absence of solvent exchange rate data, potentially obtainable from NMR studies. It is unlikely, however, that the water-exchange rate will be significantly more rapid than the octahedral–planar transformation. The measured rate constant k_{64} of 2.8×10^7 s^{-1} ($\Delta H_{64}{}^* = 9.3$ kcal mol^{-1}) is the minimum rate of exchange of *two* water molecules from the octahedral isomer. This is surprisingly close to the rate of acetonitrile exchange on the same complex of 1.5×10^7 s^{-1} ($\Delta H^* = 9.9$ kcal mol^{-1}) calculated per one acetonitrile molecule. It is also similar to the rate of water exchange (per water molecule) of 2.1×10^7 s^{-1} ($\Delta H^* = 7.8$ kcal mol^{-1}) on octahedral Ni([12]aneN$_4$)(H$_2$O)$_2{}^{2+}$ assumed to be in a cis configuration[17] and to the rate of water exchange (per water molecule) of $(2.1 \pm 0.7) \times 10^7$ s^{-1} ($\Delta H^* = 9.6 \pm 1.6$ kcal mol^{-1}) on Ni(cyclam)(H$_2$O)$_2{}^{2+}$.[9]

We assume that the five-coordinate species intermediate between the planar and trans-octahedral species is paramagnetic. In other words, it is distinguished from the solvated planar complex by the change in electron and nuclear configurations that result in high-spin, lengthened nickel–nitrogen bonds. Hence, the transition from four- to five-coordinate nickel is accompanied by the exothermic formation of a new nickel–water bond and the endothermic lengthening of the nickel–nitrogen bonds. The transition from five- to six-coordinate nickel will be exothermic due to formation of the second nickel–water bond. The enthalpy profile of the reaction give in Figure 4 reflects this pattern. We conclude that the transition state closely resembles a paramagnetic five-coordinate intermediate.

Very accurate data under identical reaction conditions for both the planar–octahedral relaxation and the solvent-exchange process would be needed to determine whether the four–five or five–six coordinate step might be rate determining. Only if the solvent exchange rate were significantly more rapid than the establishment of the planar–octahedral equilibrium could it be concluded that the four–five coordinate transformation with the accompanying spin-state change were rate determining. For Ni(cyclam)(H$_2$O)$_2{}^{2+}$ the water-exchange rate of $(2.1 \pm 0.4) \times 10^7$ s^{-1} per water molecule corresponds to a minimum relaxation time of the planar–octahedral equilibrium of 80 ± 30 ns. This is within experimental error of the minimum of 10^{-7} s observed in the ultrasonic experiment. Hence, it is possible that for Ni(cyclam)(H$_2$O)$_2{}^{2+}$ the water-exchange process is effected by the planar–octahedral equilibrium with nearly concerted loss and addition of two water molecules.

There are small differences between Ni(Me$_4$cyclam)$^{2+}$ and Ni(cyclam)$^{2+}$, both in the trans configuration. Water addition to Ni(cyclam)$^{2+}$ is less exothermic (-5.0 kcal mol^{-1})[9] than to Ni(Me$_4$cyclam)$^{2+}$ (-6.9 kcal mol^{-1}). There is a slightly smaller decrease in entropy on water addition to Ni(cyclam)$^{2+}$ than to Ni(Me$_4$cyclam)$^{2+}$. In contrast, however, the rate of interconversion of the planar and octahedral species is slower for Ni(cyclam)$^{2+}$ than for Ni(Me$_4$cyclam)$^{2+}$. Finally, there is a 9–10 cm^3 mol^{-1} decrease in volume on adding two water molecules to Ni(Me$_4$cyclam)$^{2+}$ but only a 3–4 cm^3 mol^{-1} decrease in volume on the addition of two water molecules to Ni(cyclam)$^{2+}$. Since it is unlikely that there is a significant difference in the volume change due to expansion in the plane of the macrocycles, the differences probably arise from hydrogen-bonding effects associated with the amine protons. Further work is needed to elucidate these.

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Structures and Kinetics of Cr(CO)₅ and Cr(CO)₅·H₂O in Cyclohexane Solution. Flash Photolysis Study of Cr(CO)₆ with Infrared and Visible Detection[†]

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Flash photolysis of Cr(CO)₆ in cyclohexane solution generates Cr(CO)₅ coordinated by the solvent, i.e., Cr(CO)₅·C₆H₁₂. The transient infrared spectrum obtained after flash photolysis of the monolabeled chromium hexacarbonyl, Cr(CO)₅(^{13}CO), proves that the pentacarbonylchromium fragment adopts a square-pyramidal (C_{4v}) geometry at room temperature. The axial–equatorial bond angle, determined as 93°, indicates that the structures of Cr(CO)₅ in solution and in low-temperature matrices are similar. The presence of a water trace impurity in CO-saturated cyclohexane solutions has been kinetically and spectroscopically identified. Studies in H₂O/CO-saturated cyclohexane solutions show that Cr(CO)₅·C₆H₁₂ is 13 times more reactive with H₂O than with CO. Activation parameters for the decay of Cr(CO)₅·H₂O allow an estimate of 75 ± 15 kJ mol^{-1} for the dissociation of the H₂O ligand.

Introduction

Cr(CO)₅ is a 16-electron coordinatively unsaturated species that displays a remarkable interaction toward normally inert substances. In low-temperature matrices, Perutz and Turner[1] demonstrated that the position of the visible absorption band of Cr(CO)₅ was extraordinarily sensitive to the nature of the matrix. This was interpreted in terms of a specific interaction between the Cr(CO)₅ fragment and the matrix material, a shift to shorter wavelength indicating a stronger interaction. Evidence for such shifts has also been found in the gas phase,[2] and flash photolysis experiments

by Bonneau and Kelly[3] showed that similar interactions exist in room-temperature solution. The Cr(CO)₅ species generated in perfluoromethylcyclohexane reacts with CO and N₂ by nearly diffusion-controlled processes, whereas Cr(CO)₅ in cyclohexane (C₆H₁₂) is 3 orders of magnitude less reactive with these gases.[4,5] The Cr(CO)₅·C₆H₁₂ (λ_{max} 503 nm) interaction is similar to that

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