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Ultrasonic Relaxation Dynamics of the Intramolecular Planar ⇌ Octahedral Equilibrium of a Nickel(II) Complex

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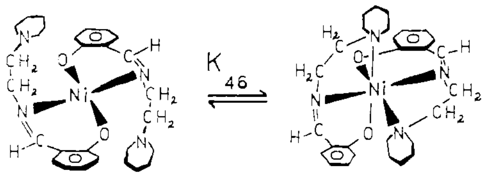
The ultrasonic resonator method was used to measure relaxation times for the intramolecular isomerization in cumene solutions between diamagnetic, four-coordinate, planar and paramagnetic, six-coordinate, octahedral forms of bis(*N*-(2-piperidinoethyl)salicylaldiminato)nickel(II), Ni(salpip)$_2$. The equilibrium constant K_{46} determined by the Evans ^{1}H NMR method is 0.74, and the relaxation time is $(71.6 \pm 0.8) \times 10^{-9}$ s. Rate constants k_{46} and k_{64} are calculated to be 5.9×10^6 s^{-1} and 8.0×10^6 s^{-1}, respectively, at 25 °C. From the temperature dependences of the equilibrium constant and the relaxation time, activation parameters are obtained of $\Delta H^{\ddagger}_{46} = 0.2$ kcal mol^{-1}, $\Delta H^{\ddagger}_{64} = 7.4$ kcal mol^{-1}, $\Delta S^{\ddagger}_{46} = -27.0$ cal deg^{-1} mol^{-1}, and $\Delta S^{\ddagger}_{64} = -2.1$ cal deg^{-1} mol^{-1}. From the relaxation amplitude the volume of the octahedral isomer is found to be 27 cm^3 mol^{-1} smaller than that of the planar form.

Introduction

Nickel(II) possesses a rich stereochemistry, with dynamic equilibria among a variety of four-, five-, and six-coordinate complexes.[1] Equilibria between diamagnetic planar and paramagnetic octahedral complexes can produce "anomalous" electronic and magnetic properties. Often such equilibria occur by addition of solvent or exogenous ligand molecules to a planar complex. In a few cases, however, intramolecular equilibria are effected by the coordination or dissociation of arms of multidentate ligands. The dynamics of such an equilibrium are reported here, between bis-bidentate and bis-tridentate isomers of bis(*N*-(2-piperidinoethyl)salicylaldiminato)nickel(II), Ni(salpip)$_2$, written as Ni(salpip$\sim$)$_2$ and Ni(salpip)$_2$, designated as IV and VI, respectively.



IV VI (1)

Sacconi et al. first studied this equilibrium, in *m*-xylene solutions, by magnetic moment measurements using the Gouy technique and by spectrophotometry.[2] Subsequently, the equilibrium constant was remeasured by using the Evans NMR method.[3] The trans-O planar and cis-meridional octahedral geometries were assumed to exist by analogy with closely related complexes, whose stereochemistry was inferred from dipole moment measurements.[4]

The dynamics of this equilibrium have now been investigated by using an ultrasonic relaxation technique previously applied to diamagnetic–paramagnetic equilibria of iron(II) complexes and low-spin–high-spin equilibria of iron(III) complexes.[5,6] In addition, the equilibrium constant was measured in cumene (isopropylbenzene), the solvent used for the ultrasonic measurements.

Experimental Section

Materials. The complex was prepared by the general method described in the literature.[2] A 20-cm^3 aqueous solution of sodium hydroxide (6.4 g, 0.16 mol; Merck AR) was added with stirring to an equal volume of ethanol (Merck AR) containing salicylaldehyde (17 g, 0.16 mol; Fluka purum). A saturated, filtered aqueous solution (200 cm^3) of nickel acetate (Merck AR) was added slowly and the resulting product collected by filtration. This material, bis(salicylaldehydato)nickel(II) dihydrate (12 g, 0.04 mol), was then refluxed with *N*-(2-aminoethyl)piperidine (10 g, 0.08 mol; Aldrich) in 50 cm^3 of ethanol for 2 h. The product was collected by filtration and recrystallized from CHCl$_3$ (Merck AR) and petroleum ether (mp 151–152 °C (lit.[2] mp 149–151 °C); 37% yield).

Cumene (Fluka purum) was used for the ultrasonic and ^{1}H NMR measurements. It was purified by washing with dilute sulfuric acid and then sodium carbonate solutions before distilling over calcium hydride.

Ultrasonic Measurements. Ultrasonic measurements were taken in the range 1–25 MHz with the use of a swept-frequency acoustic resonance cell based on a recent Eggers design.[7] This cell employs 25.4-mm-diameter, 5-MHz-overtone X-cut quartz crystals supplied by Valpey-Fisher, Hopkinton, MA, which were checked for flatness with a Fizeau interferometer.[8] The selected transducers were optically bonded onto 25-mm-o.d., 22-mm-i.d. Crown Corning Vycor cylinders, 15 mm long, of which one end had been optically polished.[9] The transducer rests against a Teflon washer and is held in place by the cylinder and a backing plate. This design ensures that the cell is solvent inert yet maintains the optical flatness required of the transducers for the measurements (Figure 1). Temperature control was as described previously.[5,6]

A Wandel and Goltermann PSM-5 level measuring set with a Dana 9000 microprocessing timer/counter interfaced to a Hewlett-Packard 9835A computer were used to measure the 3-dB bandwidths and frequencies of the resonance peaks. The computer was also used to analyze the data obtained.

Magnetic Measurements. The magnetic susceptibility of a 0.05 M solution of Ni(salpip)$_2$ in cumene containing Me$_4$Si ($\simeq$5% v/v) was measured by the Evans ^{1}H NMR technique[10] at 90 MHz on a Bruker HX-90 spectrometer. The sample temperatures were measured with internal capillaries of ethylene glycol (Merck AR)[11] or methanol (Merck AR).[12] Using a capillary of the solvent, the shift measurements were taken from the difference in chemical shifts between the two Me$_4$Si peaks.

The mass susceptibility of the solute, χ_g, is determined from the measured shift values, Δf (Hz), by using eq 2, where χ_o is the mass

$$\chi_g = \frac{3}{2\pi}\frac{\Delta f}{f m_o} + \chi_o + \chi_o\frac{d_o - d_s}{m_o} \qquad (2)$$

susceptibility of the solvent, m_o is the mass of the solute per cubic centimeter, d_s and d_o are the densities of the solution and solvent (g cm^{-3}), respectively, and f is the spectrometer frequency (Hz). The

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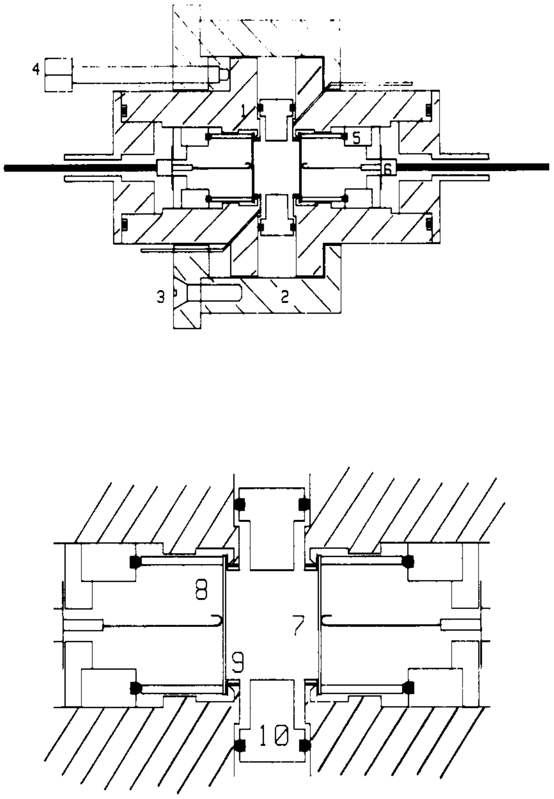

Figure 1. (a) Cross section of the resonance cell: 1, cell body; 2, cell holder; 3, screw (3 × 120°); 4, bolt for parallel adjustment (3 × 120°); 5, backing plate; 6, BNC—connector with gold coated contact wire. (b) Detail of the resonance cavity: 7, quartz transducer; 8, Vycor cylinder; 9, Teflon washer; 10, Teflon spacer with O-rings.

density difference $d_s - d_0$ depends on concentration and was measured at 25.0 °C with an Anton Paar DMA-02C precision density meter. The sample temperature was controlled by the same precision-temperature bath as was used for the ultrasonic measurements. These density measurements were obtained precise to $\pm 3 \times 10^{-5}$ g cm^{-3}. The m_0 data were corrected for changes in solvent density and hence sample concentration with temperature.[13] When these calculations are combined, it is found that the third term of eq 2 is temperature independent, the equation becoming

$$\chi_g = \frac{3}{2\pi}\frac{\Delta f}{f m_0} + \chi_0 + \chi_0 \frac{d_0^{25} - d_s^{25}}{m_0^{25}} \qquad (3)$$

where the superscripts indicate the temperature at which the density measurements were taken. The third term of eq 3 may be small and is often neglected. This simplification may lead to large errors, however, especially when the paramagnetic susceptibility is also small; thus, this term should always be calculated where possible. In these experiments the third term is 0.265×10^{-6} cgsu while χ_g ranges from 7×10^{-6} to 1×10^{-6} cgsu.

Variable-Pressure Spectrophotometry. The pressure dependence of the electronic spectrum was observed with the use of apparatus at Melbourne University, including a Varian 635D spectrophotometer and a high-pressure spectrophotometer cell.

Results

Solutions of Ni(salpip)$_2$ display excess ultrasonic absorption, and an absorption curve is shown in Figure 2. The relaxation time, τ, is found to be concentration independent over a 2-fold concentration range. The absorption curves were fitted by nonlinear least-squares analysis to eq 4, which describes a

$$\alpha/f^2 = A(1 + \omega^2\tau^2)^{-1} + B \qquad (4)$$

single relaxation process.[14] Here α is the absorption coefficient (Np cm^{-1}), f is the frequency (Hz), ω is the angular frequency (rad^{-1}) = $2\pi f$, and A and B are constants for a particular relaxation curve. The results are summarized in Table I.

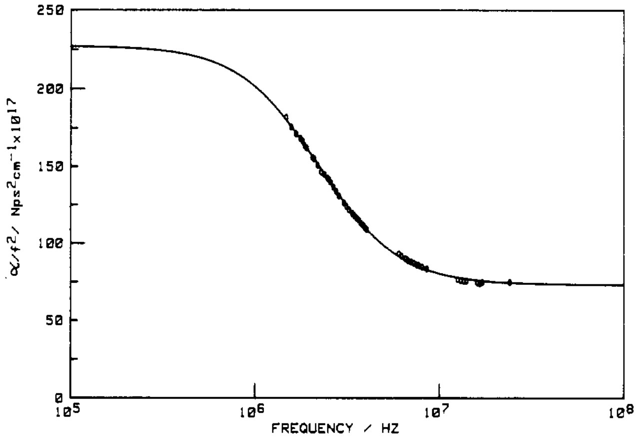

Figure 2. Typical ultrasonic absorption curve for a 0.04 M solution of Ni(salpip)$_2$ in cumene at 25 °C.

Table I. Ultrasonic and Thermodynamic Parameters for the Planar-Octahedral Isomerization of Ni(salpip)$_2$[a]

	25 °C	30 °C	40 °C
$10^{17}A$, Np s^2 cm^{-1}	154.2 ± 1.4[d]	152.2 ± 1.0	124.1 ± 0.8
$10^{17}B$, Np s^2 cm^{-1}	71.1 ± 0.6[d]	72.6 ± 0.6	70.9 ± 0.6
τ, ns	71.6 ± 0.8[d]	65.6 ± 0.8	46.7 ± 0.5
μ_{eff}, μ_{B}[b]	2.15	2.02	1.78
K_{46}	0.74	0.60	0.4
$\Delta H°$, kcal mol^{-1}	−7.2 ± 0.5		
$\Delta S°$, cal deg^{-1} mol^{-1}	−24.9 ± 1.8		
C_{total}, M	0.0393[d]	0.0400	0.0397
$10^3\Gamma$, M	9.590	9.375	8.179
ρ, g cm^{-3} [c]	0.857 51	0.853 23	0.844 67
v, cm s^{-1} [c]	130 500	128 880	125 150
$\alpha_p/\rho C_p$ cm^3 kcal^{-1} [c]	2.943	2.973	3.033
$\Delta V°$, cm^3 mol^{-1}	−26.4	−27.0	−28.5
$10^{-7}k_{46}$, s^{-1}	0.59	0.57	0.62
$10^{-7}k_{64}$, s^{-1}	0.80	0.95	1.52
$\Delta G^{\ddagger}_{46}$, kcal mol^{-1}	8.2 ± 1.8		
$\Delta G^{\ddagger}_{64}$, kcal mol^{-1}	8.0 ± 1.8		
$\Delta H^{\ddagger}_{46}$, kcal mol^{-1}	0.2 ± 0.1		
$\Delta H^{\ddagger}_{64}$, kcal mol^{-1}	7.4 ± 1.7		
$\Delta S^{\ddagger}_{46}$, cal deg^{-1} mol^{-1}	−27.0 ± 9.0		
$\Delta S^{\ddagger}_{64}$, cal deg^{-1} mol^{-1}	−2.1 ± 1.0		

[a] The quoted error bars are for one standard deviation. [b] The estimated error is ±0.05 μ_{B}. [c] Pure solvent values were assumed for the physical constants. [d] At 0.0189 M, $A = (67.6 \pm 2.3) \times 10^{-17}$ Np s^2 cm^{-1}, $B = (80.4 \pm 1.0) \times 10^{-17}$ Np s^2 cm^{-1}, and $\tau = 72.2 \pm 2.2$ ns.

Cumene was used as the solvent in the ultrasonic experiments, and then in the magnetic measurements, rather than m-xylene as used previously[2,3] because cumene has a lower sound absorption, 61.2×10^{-17} Np cm^{-1} s^2, compared with 75.3×10^{-17} Np cm^{-1} s^2 for m-xylene, and because its absorption remains constant over the frequency range studied. Electronic absorption spectra taken on a Cary 17D spectrophotometer showed little difference between the complex in the two solvents, neither solution having peaks near 7700 cm^{-1}, reported to be diagnostic of five-coordinate species.[2] Thus, it was concluded that, as expected, cumene acts as a noncoordinating solvent. Hence, the excess sound absorption is ascribed to the perturbation of equilibrium 1.

Equilibrium constants and thermodynamic parameters for (1) used in interpreting the above results were obtained by measurement of the effective magnetic moments of solutions of the complex, employing the Evans ^{1}H NMR method be-

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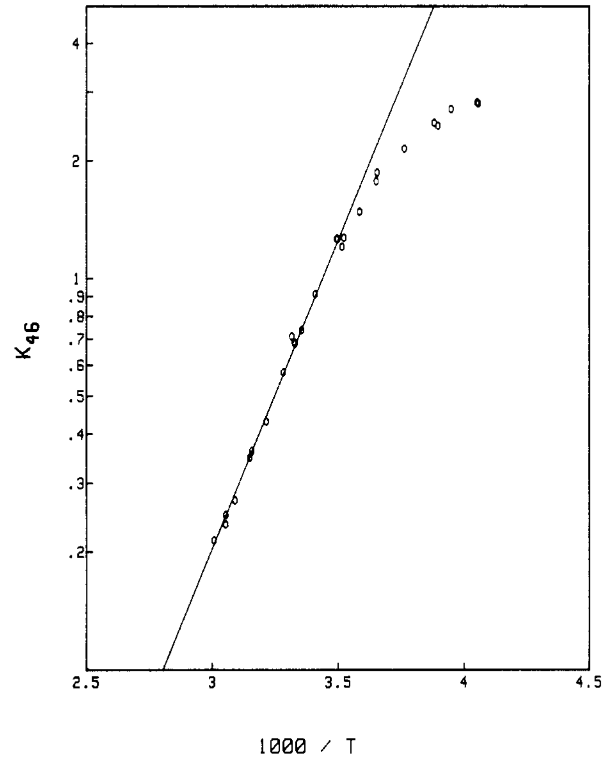

Figure 3. Temperature dependence of the equilibrium constant K_{46} for Ni(salpip)$_2$ in cumene.

tween −27 and +60 °C. To calculate the equilibrium constant, the magnetic moment of the high-spin form was taken to be 3.3 $\mu_B{}^2$ and that of the low-spin form to be 0 μ_B. The equilibrium constants were calculated from the expression

$$K_{46} = \frac{[\mathrm{VI}]}{[\mathrm{IV}]} = (\mu_{\mathrm{eff}}{}^2 - \mu_{\mathrm{LS}}{}^2)/(\mu_{\mathrm{HS}}{}^2 - \mu_{\mathrm{eff}}{}^2)$$

These were then plotted as ln K vs. T^{-1} and the data above 10 °C fitted by linear least-squares analysis as shown in Figure 3. In these NMR studies there is a significant deviation from linearity at lower temperatures. This is not due to precipitation of the compound, nor can the plot be linearized by the simple expedient of varying μ_{HS} and/or μ_{LS} in calculating K_{46}. Thus, there must be a new species in solution. Among the possibilities is a five-coordinate species that may become stable at lower temperatures. However, it is more likely, as observed in other salicylaldimine complexes,[2] that the square-planar complex aggregates to form pseudooctahedral complexes, thus altering the observed magnetic moment. The ultrasonic measurements have been taken at temperatures above the region of the deviation, and only two species are assumed.

From the temperature dependence of the equilibrium constant between 10 and 60 °C, $\Delta H°$ is calculated to be −7.2 kcal mol^{-1} and $\Delta S°$ to be −24.9 cal K^{-1} mol^{-1}. These may be compared with the values reported for *m*-xylene solution by Sacconi et al.[2] and by Crawford and Swanson[3] of −3.4 and −5.6 kcal mol^{-1} for $\Delta H°$ and −12 and −19.4 eu for $\Delta S°$, respectively. However, from the data published by Sacconi,[2] values for $\Delta H°$ and $\Delta S°$ may be recalculated as being −6.3 kcal mol^{-1} and −22.7 eu, which are different from those published by a factor of *R*. Crawford and Swanson's results have also been recalculated since they incorrectly used a positive value for χ_0 in eq 2 (they also failed to use any density correction). The values for $\Delta H°$ and $\Delta S°$ are thus −6 kcal mol^{-1} and −19 cal K^{-1} mol^{-1}, respectively. All these results are then in reasonable agreement.

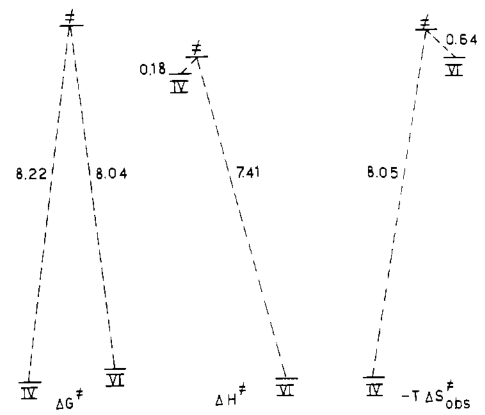

Figure 4. Activation parameters for Ni(salpip)$_2$ in cumene.

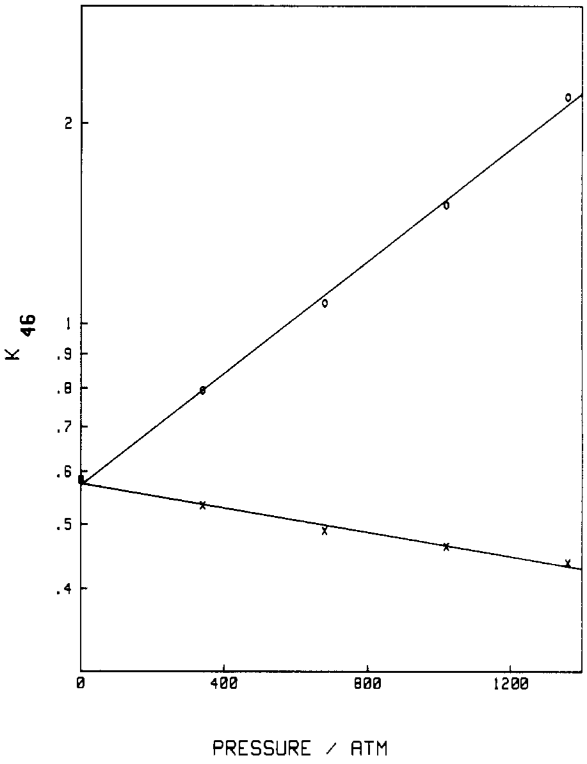

Figure 5. Pressure dependence of K_{46} for Ni(salpip)$_2$ in cumene at 25 °C with (O) and without (X) the compressibility correction.

The rate constants for the equilibrium between the isomers may now be calculated from the relaxation times and equilibrium constants for (1). For the unimolecular isomerization between the low-spin planar state and the high-spin octahedral state

$$\tau^{-1} = k_{46} + k_{64} = k_{64}(K_{46} + 1) \qquad (5)$$

Here k_{46} and k_{64} are the rate constants for the forward and reverse reactions, as written, respectively.

For Ni(salpip)$_2$ the rate constants $k_{46} = 5.9 \times 10^6$ s^{-1} and $k_{64} = 8.0 \times 10^6$ s^{-1} at 25 °C correspond to activation energies of $\Delta G^{\ddagger}{}_{46}$ = 8.2 kcal mol^{-1} and $\Delta G^{\ddagger}{}_{64}$ = 8.0 kcal mol^{-1}. Activation parameters have been obtained from the temperature dependences of the relaxation times and the equilibrium constant. The activation enthalpy $\Delta H^{\ddagger}{}_{64}$ is 7.4 kcal mol^{-1}. Since the endothermic enthalpy difference $\Delta H°_{46}$ is 7.2 kcal mol^{-1}, the enthalpy barrier of the planar–octahedral process, $\Delta H^{\ddagger}{}_{46}$, is only 0.2 kcal mol^{-1}. The values for the entropic barriers are found to be $-T\Delta S^{\ddagger}{}_{46}$ = 8.0 kcal mol^{-1} and $-T\Delta S^{\ddagger}{}_{64}$ = 0.6 kcal mol^{-1} at 25 °C. Thus, the rate constant k_{46} is determined by a small enthalpic barrier and a large entropic one, while the reverse rate constant k_{64} has a large enthalpic and a small entropic barrier (Figure 4).

When $\omega << \tau$, the excess absorption due to the chemical relaxation is given by A, which may be written as

$$A = \frac{2\pi^2 \rho v}{RT}\left[\Delta V^\circ - \frac{\alpha_p \Delta H^\circ}{\rho C_p}\right]^2 \Gamma\tau \tag{6}$$

where 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 given by $\Gamma^{-1} = [\mathrm{IV}]^{-1} + [\mathrm{VI}]^{-1}$. Using the values for ΔH° and Γ from the NMR experiments and other values taken from the literature,[13,15] it is possible to calculate ΔV°. However, due to the squared term in eq 6, ΔV° is obtained as either −26.4 or −16.0 cm^3 mol^{-1} over the experimental temperature range 25–40 °C. To ascertain which value is correct, some variable-pressure electronic absorption spectra were obtained. Almost no absorbance change is experimentally observed however between atmospheric pressure and 1 kbar. This can be interpreted as due to the cancellation between the increase in absorbance due to the compression of the solvent and the decrease in absorbance from an increase in the concentration of the octahedral isomer.

From thermodynamic data[13,15] and our own sound velocity measurements, a value for the isothermal compressibility, κ, of cumene was found to be 8.81×10^{-10} Pa^{-1}, and this value was used to correct for the changes in concentration of the sample. The value for ΔV° was then calculated to be −23.7 ± 0.4 cm^3 mol^{-1}. This would indicate that the value of −26.4 cm^3 mol^{-1} rather than −16.0 cm^3 mol^{-1} obtained from the ultrasonics is the correct value. We note that values for ΔV° from the ultrasonic data at different temperatures are in close agreement (Table I). Because the relaxation time and the amplitude of the relaxation do vary, the constancy of the calculated ΔV° values indicates that there is only a single reaction observed, identified as reaction 1.

Discussion

The thermodynamic parameters indicate that the planar isomer is favored by entropy factors and the octahedral isomer by enthalpy terms. The conformational freedom of the uncoordinated piperidine chelates provides a ready interpretation of the additional entropy of the planar isomer, while the two additionl metal–ligand bonds in the octahedral form account for its lower enthalpy. At 25 °C these terms almost exactly cancel, giving both isomers the same free energy. At higher temperatures the planar isomer is the dominant species while at lower temperatures the fraction of the paramagnetic octahedral form increases.

Conversion from the diamagnetic planar isomer to the paramagnetic octahedral one causes the original four metal–ligand bonds to lengthen and weaken,[16,17] however, producing an endothermic contribution to the enthalpy change. Furthermore, a structural reorganization occurs. For the planar isomer a trans configuration is inferred from spectral and dipole moment measurements of analogous complexes.[4] The sp^2 hybridization of the coordinated imine nitrogen imposes a planar geometry on the ligand. When the tridentate ligand is fully coordinated, it is therefore required to occupy meridional sites.[18,19] A rearrangement of the coordination sphere must occur, producing a cis-O geometry. The path of this rearrangement is clearly illustrated in the crystal structure of the closely related bis(N-(2-(diethylamino)ethyl)-5-chlorosalicylaldiminato)nickel(II), which is five-coordinate.[18] One ligand occupies three sites in the plane. The oxygen donor of the other ligand occupies the fourth planar site with the imine nitrogen apical. This geometry is presumably intermediate in the transition between planar and octahedral isomers. It is significant that this five-coordinate species is paramagnetic.

There is no spectral evidence for a five-coordinate species of the piperidine complex in solutions in aromatic hydrocarbon solvents.[2] Furthermore, the ultrasonic absorption indicates a single unimolecular relaxation process between two species. Since the amplitude of the relaxation absorption depends on the concentration of the reacting species, these must be major and not minor components in the solution. Finally, there is reasonable agreement between the volume change calculated from the relaxation measurements and that estimated spectrally. All of this evidence indicates that the relaxation observed is between the planar and octahedral isomers and that any five-coordinate intermediate is not present in appreciable concentration.

Since the coordination of the two dangling piperidine donors with the required stereochemical rearrangement is unlikely to occur simultaneously, the question arises as to which is the rate-determining step:

$$\mathrm{Ni(salpip{\sim})_2} \underset{k_{54}}{\overset{k_{45}}{\rightleftharpoons}} \mathrm{Ni(salpip)(salpip{\sim})} \tag{7}$$

$$\mathrm{Ni(salpip)(salpip{\sim})} \underset{k_{65}}{\overset{k_{56}}{\rightleftharpoons}} \mathrm{Ni(salpip)_2} \tag{8}$$

The enthalpy of the transition state is close to that of the planar isomer and its entropy close to that of the octahedral isomer. Since the five-coordinate species is paramagnetic, its formation from the planar isomer requires the endothermic process of lengthening the metal–ligand bonds, compensated by formation of a fifth metal–ligand bond. Further reaction to the six-coordinate isomer would be strongly exothermic due to formation of the sixth metal–ligand bond. In contrast, most of the configurational entropy is lost in forming the five-coordinate species. Examination of a molecular model indicates that even the uncoordinated piperidine is sterically constrained in the five-coordinate species. We conclude that the transition state resembles a paramagnetic five-coordinate intermediate. This is probably a high-energy intermediate, not stabilized by any solvent interaction in the noncoordinating solvent cumene. In other words, k_{54} and k_{56} are much greater than k_{45} and k_{65}. The data do not allow a strong inference about the relative magnitudes of k_{45} and k_{65}, i.e. which step is rate determining.

The occurrence of the spin-state change in the transition between the four- and five-coordinate species is not sufficient reason to assign it as the rate-determining step. Our investigations of the more strongly spin-forbidden $\Delta S = 2$ transitions in iron(II)[5] and iron(III)[6,20] complexes indicate that these are nonadiabatic with transmission coefficients no smaller than 10^{-2}–10^{-3}. In nickel(II) the singlet and triplet states are directly mixed by spin–orbit coupling. We infer that these $\Delta S = 1$ transitions will be nearly or completely adiabatic. In other words, there is little or no quantum restriction on the electronic transition between singlet and triplet states. There are, of course, the Franck–Condon restrictions imposed by the changes in metal–ligand bond lengths accompanying the spin-state change. It is these, rather than the electronic factor, that impose the barrier to $\Delta S = 1$ spin-state changes.

The present results are related to those reported for the addition and elimination of pyridine to a planar nickel(II) complex,[21,22] although the latter reaction occurs rather more

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slowly. The exchange of pyridine occurs with the same rate as the interconversion between planar and octahedral complexes. This implies that any five-coordinate intermediate is a high-energy unstable species. In contrast, water exchange on $Ni([12]aneN_4)(H_2O)_2^{2+}$ occurs much more rapidly than conversion to the planar complex.[23] This is clear evidence that the conversion of the planar species to a five-coordinate intermediate is the rate-determining step in this case, which probably involves a cis-trans rearrangement of the macrocyclic ligand. In the present study it would be necessary to determine independently the rate of the piperidine ligand dissociation from the octahedral complex to establish the rate-determining step in the planar-octahedral equilibrium.

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Electron Transfer. 65. Cerium Catalysis of the Disproportionation of Carboxylato-Bound Chromium(V)[1]

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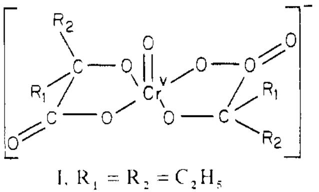
Among the tripositive metal ions, Ce(III) is uniquely effective in catalyzing the disproportionation of chelated 2-hydroxy carboxylato complexes of chromium(V): $3Cr^V \xrightarrow{Ce(III)} 2Cr^{VI} + Cr^{III}$. When these reactions are carried out in acetate buffers in the presence of the parent hydroxy carboxylic acid, the Cr(III) product is the nonchelated monocarboxylato derivative of $(H_2O)_5Cr^{III}$. Reaction rates are inversely proportional to the concentration of added parent carboxylate, directly proportional to $[OAc^-]^2$, and inversely proportional to the binomial expression $(1 + a[H^+])$. Kinetic results are consistent with a mechanism initiated by rapid and reversible loss of one carboxylato group from the Cr(V) complex, followed by formation of a Cr^V–$Ce^{III}(OAc)_2$ precursor complex and attendant deprotonation, then an internal electron transfer to form Cr(IV) and Ce(IV), and, finally, parallel oxidations of Cr(V) by the two tetrapositive centers. It appears further that breakage of the second chelate ring occurs at the Cr(IV) level, implying that Cr(IV) is more substitution labile than either Cr(III) or Cr(V) but less so than Cr(VI).

2-Hydroxy carboxylato complexes of chromium in its unusual pentapositive (Cr^V) state were characterized by Krumpolc and Roček[2] in 1979 and were reported by these workers to undergo slow disproportionation

$$3Cr^V \rightarrow 2Cr^{VI} + Cr^{III} \qquad (1)$$

in aqueous solution. This mode of decomposition appears to be minimal at pH 3.3–4.7 and may be further retarded by addition of the parent hydroxy acid.[2,3] We find, on the other hand, that this reaction is promoted by several polyvalent metal ions, by far the most effective of which is Ce^{3+}. Since this center differs from the others (Al^{3+}, La^{3+}, Pr^{3+}, and Gd^{3+}) in the accessibility, in solution, of an oxidation state 1 unit higher, we suspect that electron transfer plays a part in this acceleration, although no net oxidation of the lanthanide is detectable. The present paper deals with the Ce(III) catalysis of the disproportionation of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) and its 2-methyl analogue (II).



I, $R_1 = R_2 = C_2H_5$
II, $R_1 = CH_3$, $R_2 = C_2H_5$

Experimental Section

Materials. Lithium perchlorate was prepared as described[4] and was recrystallized three times before use in kinetic runs. The remaining perchlorates (G. F. Smith products) were used as received; $Ce(ClO_4)_3$ contained 0.28% $Pr(ClO_4)_3$ and 0.65% $Nd(ClO_4)_3$ as impurities.[5] Other lanthanide perchlorates had been derived from the corresponding oxides to which purities of 99.9% were assigned. Sodium salts of the complexes bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) and its 2-methyl analogue (II) were prepared as monohydrates as described by Krumpolc[2,6] and were stored at 0 °C. Cation-exchange resin (Bio-Rad 50W-X2, 200–400 mesh) used in separations was pretreated as described.[7]

Stoichiometric Studies. The quantity of Cr(VI) formed from a known amount of Cr(V) was estimated, after allowing the Ce(III)-catalyzed reaction to proceed for 4–5 h in a $HOAc$–OAc^- buffer, by measuring the absorbance at 350 nm ($\epsilon_{Cr(VI)} = 1750$ M^{-1} cm^{-1} in this buffer). To estimate Cr(III) in such reaction mixtures, a slight excess of $Ba(ClO_4)_2$ was added, the mixture allowed to stand for 10 h, the precipitated $BaCrO_4$ filtered off, the filtrate adjusted to pH 0 with $HClO_4$, the mixture kept at 90 °C for 10 h to convert all Cr(III) to $Cr(H_2O)_6^{3+}$, the slight turbidity removed by centrifugation, and the concentration of $Cr(H_2O)_6^{3+}$ estimated at 574 nm ($\epsilon = 13.4$ M^{-1} cm^{-1}).[8] Results are summarized in Table I. The absence of measurable quantities of Ce(IV) in the reaction mixtures was confirmed by examination in the range 390–320 nm.

Examination of the Chromium(III) Product. A reaction mixture (5 mL) that was 0.0130 M in the 2-ethyl-2-hydroxybutyrato complex of Cr(V) (I), 0.035 M in the parent carboxylic acid, 0.20 M in acetic

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[2] Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

[3] Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

[4] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[5] Determinations of Pr^{3+} and Nd^{3+} were carried out spectrophotometrically, the former at 482 nm ($\epsilon = 4.0$ M^{-1} cm^{-1}), the latter at 575 nm ($\epsilon = 7.1$ M^{-1} cm^{-1}). See, for example: Holleck, L.; Hartinger, L. *Angew. Chem.* **1955**, *67*, 648.

[6] In our hands, Krumpolc's procedure[2] for preparing the 2-methyl-2-hydroxybutyrato complex, which calls for a 6:1 mole ratio of hydroxy acid to $Na_2Cr_2O_7$, yielded product significantly contaminated with Cr(VI) unless this ratio was increased to 7:1. Preparation of the 2-ethyl-2-hydroxybutyrato complex proceeded free of difficulty with the specified 6:1 ratio of reactants.

[7] Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

[8] Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3465. The second $Cr(H_2O)^{3+}$ peak at 408 nm, ($\epsilon = 15.6$) is not suited for determination of Cr(III) in these systems since there is some distortion of this peak from the "tail" of the absorbance resulting from the small quantity of Cr(VI) remaining after precipitation.