stable *RR,SS* configuration of *trans*-Co(3,2,3-tet)Cl$_2^+$. With these assumptions the *trans*-Co(3,2,3-tet)(OAc)$_2^+$ ion is of C_2 symmetry and *trans*-Co(2,3,2-tet)(OAc)$_2^+$ is of C_s symmetry. The amino acid complexes are prepared in acid solution, and the configuration of the secondary nitrogen atoms should be the same as that of the starting *trans*-dichlorotetramine complex. In both cases three components resulting from the splitting of the $^1T_{1g}$ state make it impossible to distinguish C_2 from C_s symmetry by the number of spectral components.

Optical Acitivity.—Whereas the visible spectra of the *trans*-Co(3,2,3-tet)(aaH)$_2^{3+}$ and *trans*-Co(2,3,2-tet)(aaH)$_2^{3+}$ ions are in accord with a D_4 crystal field model, the circular dichroism spectrum of *trans*-(*RR*)-Co(3,2,3-tet)(glyH)$_2^{3+}$ (Figure 2) distinctly shows the lower symmetry of the molecule. *trans*-Co(3,2,3-tet)(glyH)$_2^{3+}$ was not isolated but was prepared by warming (−)-*trans*-(*RR*)-[Co(3,2,3-tet)Cl$_2$]ClO$_4$ in a solution saturated with glycine and was detected in solution by comparing the electronic spectrum with that of *trans*-[Co(3,2,3-tet)(glyH$_2$)](ClO$_4$)$_3$ in a saturated glycine solution. There are three transitions apparent in the circular dichroism spectrum, as the degenerate $^1E_g(D_4)$ state has split into the two components expected in C_2 symmetry. The great similarity in shape between the CD curves of *trans*-(*RR*)-Co(3,2,3-tet)(glyH)$_2^{3+}$ and *trans*-(*RR*)-[Co(3,2,3-tet)Cl$_2$]ClO$_4$[15] is obvious on comparison, both showing the same order (+, −, +) and same magnitude for the $^1T_{1g}$ components. Those of the *trans*-bis-glycine complex occur at higher energy, reflecting the relative positions of the glycine and chloro ligands in the spectrochemical series.

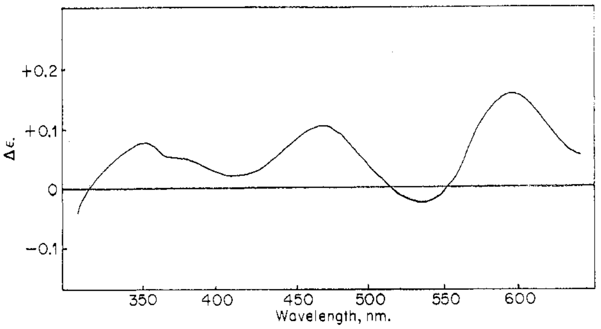

Figure 2.—Circular dichroism curve for (−)-*trans*-(*RR*)-Co(3,2,3-tet)(glyH)$_2^{3+}$.

In warm basic solutions, one of the amino acid residues is displaced by hydroxide. In a subsequent step, the remaining amino acid molecule undergoes intramolecular chelate ring closure with a concomitant topological shift. A detailed study of the steric course of these reactions is now in progress.

Acknowledgment.—We gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society under Grant No. 1155G3.

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A Nuclear Magnetic Resonance Study of Ligand-Exchange Kinetics of Cobalt(II)- and Nickel(II)-Dimethyl Sulfoxide Complexes in Mixed Solvents

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The ligand-exchange kinetics of ML$_6$ (M = Co or Ni, L = dimethyl sulfoxide (DMSO)) in DMSO and the mixed solvents DMSO–nitromethane and DMSO–methylene chloride are independent of the composition of the solvent. The following kinetic parameters have been obtained: NiL$_6^{2+}$, $k(25°) = 3.2 \times 10^3$ sec^{-1}, $\Delta H^* = 13.0$ kcal/mol, $\Delta S^* = 1.4$ eu; CoL$_6^{2+}$, $k(25°) = 3.1 \times 10^5$ sec^{-1}, $\Delta H^* = 12.2$ kcal/mol, $\Delta S^* = 9.8$ eu. The independence of the exchange parameters on the composition of the solution is consistent with a dissociative mechanism.

Many nmr studies have been reported on the ligand-exchange kinetics of octahedral paramagnetic transition metal complexes in a neat solution of the ligand.(2) Under these conditions, pseudo-first-order kinetics, the role of the ligand as a stoichiometric component of the reaction cannot be definitively studied. Mixed solvents can be utilized to elucidate the dependence of the ligand-exchange rate on the ligand concentration. Experiments of this type should aid in elucidating a reaction mechanism. We report data on the ligand-exchange kinetics of M(DMSO)$_6^{2+}$, M = Co(II) or Ni(II), in dimethyl sulfoxide (DMSO) and in admixtures with with nitromethane and methylene chloride.(3) The latter two solvents are inert in the sense that they are noncoordinating.

Experimental Section

The metal complexes of DMSO were prepared as described previously except dehydration with triethyl orthoformate of M-

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(1) Rohm and Haas Co., Philadelphia, Pa. 19137.

(2) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967).

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$(H_2O)_6(ClO_4)_2$ was performed prior to the addition of DMSO.[4] DMSO was purified as described previously.[5] Nitromethane-d_3 (99%) was obtained from Brinkmann Instruments Inc. No solvent impurites could be detected at an amplitude setting at which the 1% CHD_2NO_2 signal is clearly displayed. Use of deuterated nitromethane was necessary because the high-field ^{13}CH resonance partially overlaps the DMSO peak in the presence of the metal complexes. All data were obtained on a Varian A-60 spectrometer.

Nmr Theory

The temperature dependence of the observed transverse relaxation time $(1/T_{2p})$, corrected for the ligand relaxation time in the absence of the metal complex, can be analyzed using the results of Swift and Connick.[6] When $\Delta\omega_M{}^2 \gg 1/T_{2M}{}^2$, $1/\tau_M{}^2$ or $1/T_{2M}{}^2 \gg \Delta\omega_M{}^2$, $1/\tau_M{}^2$.

$$1/T_{2p} = P_M/\tau_M \qquad (1)$$

P_M is the probability that a DMSO molecule is in the primary coordination sphere of the metal ion, $\Delta\omega_M$ is the contact shift in radians per second, $1/T_{2M}$ is the rate of proton relaxation in the coordination sphere of the metal ion, and $1/\tau_M$ is the ligand-exchange rate. The limiting conditions $1/\tau_M{}^2 \gg \Delta\omega_M{}^2 \gg 1/T_{2M}\tau_M$ give

$$1/T_{2p} = P_M\tau_M\Delta\omega_M{}^2 \qquad (2)$$

while $1/T_{2M}\tau_M \gg 1/T_{2M}$, $\Delta\omega_M{}^2$ leads to

$$1/T_{2p} = P_M/T_{2M} \qquad (3)$$

The temperature dependence of $1/\tau_M$ is according to transition-state theory given by

$$1/\tau_M = (kT/h)\exp(-\Delta H^*/RT + \Delta S^*/R)$$

where ΔH^* and ΔS^* are the activation enthalpy and entropy and the other symbols have their usual meaning. The observed transverse relaxation time is obtained from the line width at half-height $(\pi\Delta\nu = 1/T_{2p})$.

Results

The solvation numbers, n, were obtained by dissolving a known amount of solute ([Co] = 0.20 M, [Ni] = 0.23 M) into CH_3NO_2 and subsequent integration of the bound DMSO peak *vs.* CH_3NO_2. At 38 and −30° $n = 5.9 \pm 0.2$ for Ni(II) while Co(II) gave $n = 6.0 \pm 0.2$. These data conclusively show that nitromethane coordination does not occur to any significant degree. A comparison of the proton relaxation times $(1/T_{2M})$ of the bound DMSO peak at 38 and −30° gave the following activation energies E_A = 2.0 kcal for Co(II) and E_A = 1.4 kcal for Ni(II). These small activation energies appear typical for both tetrahedral[7,8] and octahedral[9-12] Ni(II) and Co(II) complexes and have been assigned to the temperature dependence of a correlation time which is controlled by an electron relaxation process.

A plot of $(P_MT_{2p})^{-1}$ *vs.* reciprocal temperature for $Ni(DMSO)_6{}^{2+}$ in DMSO, DMSO–CD_3NO_2, and DMSO–CH_2Cl_2 mixed solvents is given in Figure 1. The compositions of the solutions used are given in Figure 1. The values of $(P_MT_{2p})^{-1}$ are independent of the concentration of DMSO in the bulk solution, the concentration of $Ni(DMSO)_6{}^{2+}$, and the solvent medium. The low-temperature data, $4.05 \times 10^{-3} > T^{-1} > 3.50 \times 10^{-3}$, correspond to a large positive activation energy, E_A = 13.6 kcal. This temperature region can only be assigned to a relaxation time controlled by the solvent-exchange rate. A least-squares treatment of the solid linear portion of Figure 1 gives the following ligand-exchange parameters: ΔH^* = 13.0 kcal/mol, ΔS^* = 1.4 eu, and $k(25°) = 3.2 \times 10^3$ sec^{-1}. In the temperature range $4.05 \times 10^{-3} > T^{-1} > 3.85 \times 10^{-3}$ the error in the data is relatively large since the excess line widths are small at the metal concentrations utilized. For this reason these data were not employed in the calculation of the ligand-exchange parameters. Considering the points used to calculate the ligand-exchange parameters, the correction for second-sphere relaxation time effects should be comparatively small. The temperature range $3.30 \times 10^{-3} > T^{-1} > 3.1 \times 10^{-3}$ corresponds to the advent of a region which has a large negative activation energy. This temperature region can only be ascribed to eq 2. Earlier work to be described employed this kinetic region.

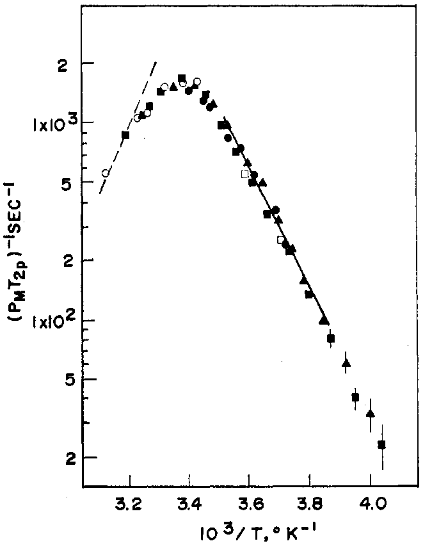

Figure 1.—Temperature dependence of $(P_MT_{2p})^{-1}$ for the protons in DMSO in solutions of $Ni(DMSO)_6{}^{2+}$. Composition of solutions: [Ni] = 7.48×10^{-2} M in DMSO (○); [Ni] = 1.12×10^{-2} M, [DMSO] = 2.26 M (●); [Ni] = 1.03×10^{-2} M, [DMSO] = 1.04 M (■); [Ni] = 1.07×10^{-2} M, [DMSO] = 0.621 M (▲) in CD_3NO_2; [Ni] = 0.96×10^{-2} M, [DMSO] = 1.08 M (□) in CH_2Cl_2.

The solution used to obtain the solvation number gave a contact shift, extrapolated to 25° ($\Delta\omega_M \propto 1/T$), of 475 cps. Contact shifts of 395,[13] 485,[14] and 460 cps[15] at 25° in neat DMSO have been extrapolated from previous results. Using the kinetic data obtained from

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region 1 and the temperature dependence of the contact shift, the high-temperature contribution has been calculated and is indicated by the dashed line in Figure 1.

Kinetic data have recently been reported for $Ni(DMSO)_6^{2+}$ in pure DMSO: $\Delta H^* = 12.1$ kcal/mol, $\Delta S^* = 1.2$ eu, $k(25°) = 4.2 \times 10^3$ sec^{-1} (Angerman and Jordan[13]); $\Delta H^* = 11.7$ kcal/mol, $\Delta S^* = -1$ eu (Matwiyoff[11]). Earlier results[14,15] are not in good agreement with these more recent data.

The data for $Co(DMSO)_6^{2+}$ are summarized in Figure 2. The compositions of the solutions used are given in Figure 2. The values of $(P_M T_{2p})^{-1}$ are independent of the concentration of DMSO in the bulk solution, the concentration of $Co(DMSO)_6^{2+}$, and the solvent medium. The data in Figure 2 are in agreement with the previously reported observation that $(P_M T_{2p})^{-1}$ for $Co(DMSO)_6^{2+}$ in pure DMSO shows a relatively small temperature dependence as required by eq 3.[13,14] In the temperature region $3.80 \times 10^{-3} > T^{-1} > 3.50 \times 10^{-3}$ $(P_M T_{2p})^{-1}$ shows a large negative activation energy, $E_A = 10.2$ kcal, in accordance with eq 2. The contact shift was referenced from the proton peak of nitromethane (CHD_2NO_2) to eliminate paramagnetic susceptibility effects. The contact shift at 25° is 570 cps and shows the anticipated temperature dependence as has been previously reported. Contact shifts of 605[14] and 215 cps[13] at 25° in neat DMSO have been extrapolated from previous results. The data in the temperature region $3.90 \times 10^{-3} > T^{-1} > 3.20 \times 10^{-3}$ were analyzed by the equation

$$1/P_M T_{2p} = 1/T_{2M} + \tau_M \Delta\omega_M^2$$

taking into account the temperature dependence of $\Delta\omega_M$. The contribution from $1/T_{2M}$, indicated by the low activation energy, dashed line in Figure 2, was obtained from the solvation number experiment. The high activation energy dashed line corresponds to the contribution from $\tau_M \Delta\omega_M^2$. A least-squares analysis gives the following ligand-exchange parameters: $\Delta H^* = 12.2$ kcal/mol, $\Delta S^* = 9.8$ eu, and $k(25°) = 3.1 \times 10^5$ sec^{-1}. The solid line in Figure 2 was obtained by adding the contributing terms. At low temperature, $T^{-1} > 4.00 \times 10^{-3}$, the advent of a large positive activation energy is observed and assigned to eq 1. The dashed line in this temperature region was calculated from the ligand-exchange parameters.

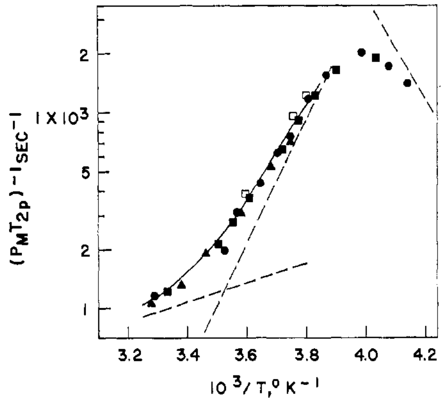

Figure 2.—Temperature dependence of $(P_M T_{2p})^{-1}$ for the protons in DMSO in solutions of $Co(DMSO)_6^{2+}$. Composition of solutions: [Co] = 1.33×10^{-2} *M*, [DMSO] = 2.23 *M* (●); [Co] = 1.12×10^{-2} *M*, [DMSO] = 1.06 *M* (■); [Co] = 0.98×10^{-2} *M*, [DMSO] = 0.574 *M* (▲) in CD_3NO_2; [Co] = 1.02×10^{-2} *M*, [DMSO] = 1.09 *M* (□) in CH_2Cl_2.

Discussion

The relative values of the ligand-exchange parameters for Ni(II) and Co(II) are consistent with the generally accepted dissociative mechanism of exchange for divalent metal ions.[2,6,16,17] The structure of the transition state is generally accepted to approach a five-coordinate complex with some interaction with the solvating entering group in the second coordination sphere of the metal complex. Bond breaking is therefore considered more advanced than bond formation to the entering ligand. A true five-coordinate intermediate may exist with a sufficient lifetime to react with a DMSO molecule in the second coordination sphere even if the site of activation had a solvent molecule other than DMSO at the instant of formation of the activated complex (D mechanism). A second possibility retains the entering ligand as a stoichometric component of the transition state. This arises if the five-coordinate intermediate does not have a sufficient lifetime relative to the lifetime of the second coordination sphere to react selectively but rather must react with the molecule in the second coordination sphere at the instant of formation of the transition state or not react at all. The latter mechanism has been called dissociative interchange (I_d mechanism).[17]

The fact that our results are virtually independent of bulk medium effects is certainly surprising. A detailed kinetic picture depends on the change in the second coordination sphere and not directly on bulk composition. The molar ratio of free DMSO to metal is not less than 50:1 in this study. Assuming any reasonable second coordination sphere number leads to the conclusion that there is sufficient DMSO present to solvate the complex. A large excess of DMSO is necessary to apply the results of Swift and Connick[6] in the usual manner. The large solubility (solvation number data) would certainly suggest that nitromethane is capable of solvating the complex, especially when the molar ratio of nitromethane to DMSO is relatively large as in our case (up to 30:1). Leffier[18] has recently interpreted his results with $M(H_2O)_6^{2+}$ in water–methylene chloride mixed solvents to indicate that methylene chloride can compete surprisingly well with water for the second coordination sphere. In view of these results it is probable that the second coordination sphere has undergone a change in composition over the range of bulk compositions studied. Since the exchange rates are independent of the concentration of DMSO, the D mechanism appears to give a more accurate description

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[18] A. J. Leffler, *J. Phys. Chem.*, **74**, 2810 (1970).

of the exchange process.[19] The other possibility, I_d mechanism, requires very strong preferential solvation by DMSO and seems less likely.[20]

Because the solvent mixtures possess lower dielectric constants, there should be an increase in the concentration of second-sphere perchlorate ion pairs relative to pure DMSO. Apparently this effect does not significantly alter the ligand-exchange parameters.[21]

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The Far-Infrared and Electronic Spectra of Some Bis-Ethylenediamine and Related Complexes of Copper(II) and the Relevance of These Data to Tetragonal Distortion and Bond Strengths

By A. B. P. Lever* and E. Mantovani

Received August 24, 1970

The far-infrared spectra (500–200 cm^{-1}) of the complexes Cu(N-N)$_2$X$_2$ are assigned [(N-N) = ethylenediamine, 1,3-propylenediamine, and symmetric and asymmetric *N,N*-dimethyl- and *N,N*-diethylethylenediamines and X = Cl, Br, I, NCS, ClO$_4$, BF$_4$, and NO$_3$]. A straight-line correlation is observed between the square of the highest metal–nitrogen stretching vibration and the energy of the main electronic d–d band. The position of a complex on the line is a measure of its tetragonal distortion and of the in-plane bond strength.

While the far-infrared spectra of complexes of the more simple ligands such as the halogens, ammonia, carbon monoxide, nitric oxide, and oxygen have been studied and the metal–ligand vibrational modes have been identified unequivocally,[1] *systematic* studies with more complex ligands are generally unavailable, and the identification of metal–ligand modes is less secure. The purpose of this work is to identify the metal–nitrogen stretching modes in ethylenediamine complexes of the first-row transition metals and to see whether relationships may be derived between these data and other properties, such as electronic transition energies and thermodynamic parameters. It is realized that metal–ligand stretching frequencies are rarely "pure," coupling with other normal modes of vibration of the same symmetry, in the molecule, generally being expected. The question of whether such coupling is so important as to invalidate any bonding or structural conclusions is explored. Certainly if the complex has high symmetry the possibility of other modes of vibration occurring with the same symmetry and with similar energies, such that coupling is important, is minimized.

Copper complexes of the general formula Cu(N-N)$_2$X$_2$ where N-N = ethylenediamine, 1,3-propylenediamine, and the symmetric and asymmetric N-substituted dimethyl- and diethylethylenediamines and X = Cl, Br, I, NCS, BF$_4$, NO$_3$, and ClO$_4$ are discussed. A number of corresponding cobalt(II) and nickel(II) complexes are included for comparison purposes, but detailed discussion of these latter derivatives will be presented elsewhere.[2]

Some of the complexes were deuterated, the amine hydrogen atoms being replaced, to facilitate identification of the various normal modes of vibration.

Experimental Section

Preparation of the Complexes.—Most of the complexes have been prepared previously; references thereto are indicated in Table I.

Previously unknown complexes were prepared by the general method of mixing stoichiometric amounts of the copper salt and the appropriate ligand in ethanol followed, where possible, by recrystallization from the same solvent. A purple isomer of the previously reported Cu(*asym*-Et$_2$en)$_2$(NO$_3$)$_2$ complex was obtained by heating this complex to 160°. It cannot be recrystallized.

Deuteration.—This was achieved by dissolving or wetting the complex with deuterium oxide and pumping to dryness, the procedure being repeated until an infrared spectrum indicated absence of –NH stretching modes near 3200 cm^{-1}. In some cases a few drops of the free ligand were added to suppress decomposition. The integrity of the complex was assured by comparison of the electronic spectra thereof with that of the hydrogen analog starting material. However many of the complexes decomposed when treated in this manner.

Spectroscopic Techniques.—Far-infrared spectra were recorded as Nujol mulls on polythene plates with a Beckman IR-12 spectrophotometer. Electronic spectra were also recorded *via* transmittance through Nujol mulls using an Applied Physics Cary 14 spectrophotometer.

Results and Discussion

X-Ray structural data are available for many of the

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