The Effect of Coordinated Ligands on the Rate of Replacement of Bound Water by Ammonia in Nickel(II) Complexes

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Abstract: Temperature-jump relaxation techniques are used to study the reaction of ammonia with a series of nickel(II) complexes in aqueous solution. Multidentate ligands complexed to nickel are not displaced in the reaction; however, the exchange rates for coordinated water and ammonia are influenced by the nature of the multidentate ligand. The charge of the complex *per se* is not of much importance in the rate of replacement of bound water, and negative complexes are not necessarily more labile than positive complexes. Coordinated nitrogens tend to speed the water replacement as much or more than carboxylate groups. The electron-donating ability of the coordinated groups and to an even greater extent the structure of the complex are important. Diethylenetriamine is particularly effective in increasing the rate of water and ammonia exchange with nickel(II).

Rate constants for the substitution of water in the first coordination sphere of aquometal ions have been determined for many reactions.[1] It is possible to use these constants, which are characteristic for each metal ion, to predict reaction rates, for monodentate- (and in some cases[2] multidentate-) ligand substitution. However, many reactions of interest, such as those with enzyme metal substrate complexes, involve replacement of water not from the aquometal ion but rather from a metal complex which has several coordination sites occupied by other ligands. Information is sparse on this subject for the divalent metal ions. It had been proposed that the negatively charged carboxyl group in glycine complexes causes a loosening of the hydration shell and thus permits faster replacement of inner-sphere water molecules in Co(II) and Ni(II) complexes.[3] A test of the hypothesis that the rate of water substitution increases as the metal complex charge decreases was reported earlier[4] and, as a general rule, the hypothesis fails. On the other hand, there is evidence that the electron-donating properties of coordinated ligands do have a significant effect on the rate of water replacement.[5]

The present work is an extension of the earlier investigation[4] using a greater variety of nickel complexes and using computer calculations to permit more accurate determination of the rate and stability constants. The reaction studied to determine the effect of the coordinated ligand is given in eq 1, where L is a multidentate ligand and x is presumed to be six minus the number of coordination positions occupied by L. Temperature-jump relaxation methods were used. Reaction 1 was coupled with the much faster reactions in eq 2 and 3 to give an indicator color change for a sensitive method of detecting the relaxation. Multidentate ligands were used because their own rates of substitution are much slower than the rate of H_2O–NH_3 substitution. This eliminates interference or complications due to multiple relaxations. There are several advantages in studying the rate of the substitution reaction with ammonia rather than with other ligands. (1) The ammonia molecule is small and effects due to steric hindrance in entering the coordination sphere are minimal. (2) Because it is a neutral molecule with a dipole moment less than that of water, any outer-sphere association between ammonia and the nickel complexes is weak and depends on a solvent-cage effect rather than on the charge of the complex. This permits a direct comparison of the k_{12} rate constants for complexes of different charge without the necessity of correcting for different ion-pair association values.

$$[\mathrm{NiL(H_2O)}_x]^n + \mathrm{NH_3} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [\mathrm{NiL(H_2O)}_{x-1}(\mathrm{NH_3})]^n + \mathrm{H_2O} \quad (1)$$

$$\mathrm{NH_4^+} + \mathrm{OH^-} \rightleftharpoons \mathrm{NH_3} + \mathrm{H_2O} \quad (2)$$

$$\mathrm{In^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HIn} + \mathrm{OH^-} \quad (3)$$

This work shows that with aminocarboxylate and polyamine complexes of nickel the over-all charge of the complex has little effect, but the structure of the complex appears to play a significant role in determining the rate of water replacement from the metal.

Experimental Section

Reagents. Crystalline salts of mono(1,10-phenanthroline)nickel(II) and mono(5,6-dimethyl-1,10-phenanthroline)nickel(II) were prepared and fresh solutions were used to avoid bis and tris complexes. In all other cases, the mono(ligand)nickel complexes were prepared by stoichiometric addition of solutions of the ligand and nickel perchlorate. Ligand solutions were standardized by acid-base or complexometric titrations, or spectrophotometrically using a mole-ratio method. Nickel solutions were standardized with EDTA. EDTA and $\mathrm{Ni(ClO_4)_2 \cdot 6H_2O}$ were recrystallized from aqueous solution; dien and ammonia were purified by distillation. Sulfate salts of the acid forms of trien and of tetren, nitrilotriacetic acid, glycine, the disodium salt of iminodiacetic acid, and the trisodium salt of hydroxyethylethylenediaminetriacetic acid were recrystallized from water–ethanol solutions. Ethylenediamine (chromatographically pure) and α,β-diaminopropionic acid (Fluka Chemical Co.) were used without additional purification.

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Table I. Coordinated Ligands Studied, Experimental Conditions, and Results for Relaxation Data

	Conditions								
	Range of $[NiL]_T$ $\times 10^3$, M	Range of $[NH_3]_T$ $\times 10^3$, M	pH	μ	Temp, °C	n	$k_{12} \times 10^{-3}$, M^{-1} sec^{-1}	k_{21}, sec^{-1}	K, M^{-1}
Aquo ion	6.0–20	3.0	6.89 ± 0.03	0.25	25.0	+2	2.8	2.6	1050
Ethylenediamine (en)	4.9–27	11–51	7.79 ± 0.02	0.25	25.0	+2	12	66	174
Diethylenetriamine (dien)	12–36[a]	108–324	7.02 ± 0.02	0.45	25.0	+2	46	641	72
	12–36	11–32	8.17 ± 0.03	0.25	10.0	+2		154	138
	12–36	11–32	8.07 ± 0.04	0.25	15.7	+2	27	260	102
	12–36	11–32	8.03 ± 0.03	0.25	21.4	+2	34	399	86
	12–36	11–32	8.03 ± 0.03	0.25	25.0	+2	39	784	50
	12–36	11–32	7.98 ± 0.02	0.25	27.1	+2	43	651	65
	12–36	11–32	7.96 ± 0.03	0.25	35.0	+2	59	1630	36
Triethylenetetramine (trien)	7.9–36	1.4–6.4	8.03 ± 0.12	0.40	25.0	+2	2.1	86	25
Tetraethylenepentamine (tetren)	12–36	7.2–32	8.02 ± 0.04	0.40	25.0	+2	0.08	1.5	53
Glycine (gly)	3.7–25	11–51	7.86 ± 0.02	0.25	25.0	+1	14	61	225
α,β-Diaminopropionate (α,β-DPA)	7.9–36	2.8–13	7.98 ± 0.06	0.25	25.0	+1	2.7	36	75
Iminodiacetate (IDA)	7.9–36	7.2–32	7.99 ± 0.02	0.25	25.0	0	2.5	65	38
Nitrilotriacetate (NTA)	7.9–32	7.2–32	8.01 ± 0.07	0.25	25.0	−1	4.6	26	177
	7.9–36	7.2–36	8.03 ± 0.05	0.25	25.0	−1	4.7	29	164
	7.9–36	7.2–36	8.04 ± 0.04	0.25	15.7	−1	2.4	27	88
	7.9–36	7.2–36	8.04 ± 0.04	0.25	35.0	−1	9.7	63	155
N-Hydroxyethylethylenediaminetriacetate (HEEDTA)	7.9–36	7.2–36	8.02 ± 0.03	0.25	25.0	−1	0.29	8.3	35
Ethylenediaminetetraacetate (EDTA)	7.9–36	72–324	7.13 ± 0.03	0.40	25.0	−2	0.43	20	21
	7.9–36	7.2–32	8.03 ± 0.02	0.40	25.0	−2	0.48	19	25
	7.9–36[b]	0.74–3.3	8.84 ± 0.03	0.40	25.0	−2	0.45	20	22
	7.9–3.6	7.2–32	8.12 ± 0.05	0.25	10.0	−2	0.28	2.9	96
	7.9–3.6	7.2–32	8.08 ± 0.06	0.25	15.7	−2	0.41	5.8	71
	7.9–36	7.2–32	7.90 ± 0.02	0.25	25.0	−2	0.71	12	59
	7.9–3.6	7.2–32	7.94 ± 0.06	0.25	35.0	−2	1.5	31	50
1,10-Phenanthroline (phen)	1.5–7.9	18–60	7.00 ± 0.03	0.25	25.0	+2	1.5	3.8	398
5,6-Dimethyl-1,10-phenanthroline (5,6-diMephen)	1.1–6.2	11–60	6.98 ± 0.03	0.25	25.0	+2	2.2	3.9	555

[a] Only four points. [b] Phenolphthalein indicator.

Ionic strength was controlled with recrystallized sodium perchlorate except for the phenanthroline complexes where sodium nitrate was used.

Kinetic Measurements. The temperature-jump relaxation spectrometer used was designed by L. DeMaeyer and obtained from Messanlagen Studien Gesellschaft, Göttingen, Germany. A Bausch and Lomb high-intensity grating monochromator and a tungsten source were used. The instrumental response was displayed on a Tektronix 564 storage oscilloscope and photographed on Polaroid film. The temperature-jump cell was thermostated to ±0.1°. The magnitude of the temperature jump was calibrated by comparing absorbance values at 550 mμ on a Cary 14 spectrophotometer against the temperature jump apparatus as a function of temperature. A glycine solution (0.02 *M*) at pH 9 containing phenolphthalein (5.0×10^{-5} *M*) was used. Initial temperatures were varied from 4.8 to 20.7°, and the ionic strength was tested at 0.10 and 0.25 *M*. All conditions gave the same temperature rise, an average value of 5.7° for a 40-kv discharge with a standard deviation of 0.3°.

Phenol red (at 560 mμ) was used as the indicator in reaction 3 except for the EDTA complex at pH 8.8 where phenolphthalein (550 mμ) was used. Reactions 2 and 3 are very fast[1,6] compared to reaction 1, and usually there were no relaxations observed in the absence of the nickel complex. When conditions were such to give an observable relaxation from reactions 2 and 3, the τ values were smaller by factors of 10 to 1000 than that due to reaction 1.

Relaxations which might arise from the formation and dissociation of L with Ni(II) were not significant because of the sluggishness of this reaction relative to the addition and loss of ammonia and because the concentrations of uncomplexed L or Ni(II) were very small. A second relaxation was observed for glycine with a τ value of 40 times that of the ammonia reaction and for ethylenediamine with a τ value of 20 times that of the ammonia reaction.

A mixed complex of NiL and ammonia formed with each ligand. Large ratios of $[NiL]/[NH_3]$, $[NiL]/[NiLNH_3]$, and $[NH_4^+]/[NH_3]$ were used in order to give only the monoammine complex, to simplify the relaxation expression, and to avoid hydrolysis of nickel The relaxation expression was

$$1/\tau = k_{21} + k_{12}(\overline{[NiL]} + \overline{[NH_3]}) \qquad (4)$$

where τ is the observed relaxation time, k_{21} and k_{12} are defined in eq 1, and the mean concentrations of the reactants are after the temperature jump. Each τ value was obtained from an average of four relaxation measurements. Six to eight different concentrations of NiL and NH_3 were used (the range of initial conditions is given in Table I). Appropriate protonation constants for ammonia[7] were used for each temperature, but with the exception of Ni^{2+} and $NiEDTA^{2-}$ most of the mixed ammonia complex constants were unknown. Therefore, the values of k_{12}, k_{21}, and $K = k_{12}/k_{21}$ were calculated from each set of relaxation data. A computer program (for an IBM 7094) was used which first assumed that ($\overline{[NiL]}$ + $\overline{[NH_3]}$) equaled the total NiL (which was the approximate experimental condition) and gave a least-squares fit of k_{21} and k_{12} for eq 4. It then solved for *K* and for the corrected concentrations of NiL and NH_3. The complete equation was used for a new least-squares fit and the process reiterated until the *K* value was constant to ±2%. The reliability of this method was confirmed by the agreement of the *K* values with equilibrium studies. Figure 1 shows the best and the poorest fit of eq 4 for all the experiments.

Results

The rate constants k_{12} and k_{21} resulting from the fit of the τ values to eq 4 are summarized in Table I. In each case the concentration variation gave a good fit and the fact that k_{21} was appreciable compared to $k_{12}(\overline{[NiL]} + \overline{[NH_3]})$ allowed reliable values to be calculated for the stability constants of the mixed complexes.

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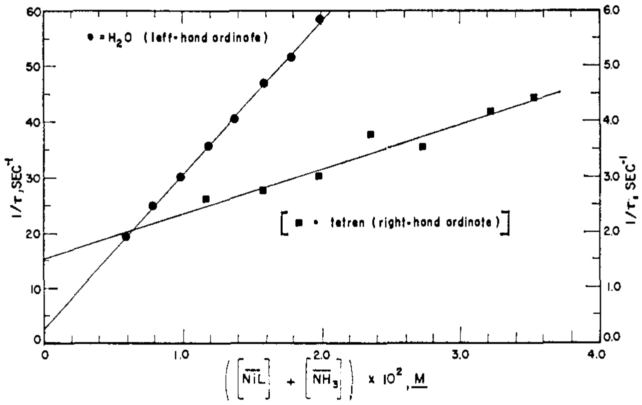

Figure 1. Reciprocal of the relaxation times for mean concentrations of reactants. The mean values are obtained by iterative computation of k_{12} and k_{21}. Shown are the best fit of data (aquonickel system) and poorest fit of all data (nickel-tetren system).

Thus, for nickel-NH_3, the relaxation data gave $K = 1050\ M^{-1}$ (0.25 M $NaClO_4$, 25°), and a literature value at slightly different ionic strength is 630 M^{-1} (0.1 M NH_4NO_3, 25°).[8] Similarly, relaxation data gave $K_{av} = 23\ M^{-1}$ for nickel-EDTA-NH_3 (0.40 M $NaClO_4$, 25°) and $K = 177\ M^{-1}$ for nickel-NTA-NH_3 (0.25 M $NaClO_4$, 25°) while independent spectrophotometric determination of these constants gave values of 25 M^{-1} (0.5 M $NaClO_4$, 25°) and 310 M^{-1} (0.5 M $NaClO_4$, 25°),[9] respectively. Considering the differences in ionic strength the agreement is good.

Variation of pH proved to have no effect on the values calculated for k_{12} and k_{21} in the nickel-EDTA and NH_3 or the nickel-dien and NH_3 systems. The pH was kept well below that needed for appreciable nickel hydrolysis[10] or for the formation of mixed hydroxide complexes (*e.g.*, $K_{\text{NiYOH}} \simeq 2.5$, $K_{\text{NiNTAOH}} \simeq 100$).[11]

Variation of the NH_4^+ concentration at constant NH_3 concentration also showed no effect on the k_{12} value with the EDTA system. This eliminates any possibility that NH_4^+ might be a reactant with the negatively charged complex as is the case with HCN.[12] The kinetic behavior of nickel-EDTA indicates the complex has one free carboxylate group and one bound H_2O.

The reaction of aquonickel ion with ammonia provided additional checks for the validity of the reported rate constants. Thus, flow techniques permitted a value of $k_{NH_3}{}^{Ni} = 2.5 \times 10^3$ (25°, $\mu \simeq 0.6$ M) to be calculated from the dissociation rate constant and the stability constant.[13] In addition, other temperature-jump experiments by Rorabacher[14] gave $k_{NH_3}{}^{Ni} = 2.9 \times 10^3$ (20°, 0.1 M NH_4NO_3). The data of Hammes and Steinfeld[3] for the reaction of aquonickel ion with the neutral imidazole molecule gave a rate constant equal to $5.0 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ (25°, 0.15 M KNO_3). All these constants are in reasonable agreement with our value: $k_{12} = 2.8 \times 10^3\ \text{sec}^{-1}$ for the NH_3 reaction in 0.25 M $NaClO_4$. The rate constant for gly⁻ reacting with Ni(gly)⁺ was $6.0 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ (25°, 0.15 M KNO_3) compared to $k_{12} = 1.4 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ for NH_3 and Ni(gly)⁺ (25°, 0.25 M $NaClO_4$). A larger value is to be expected for k_{12} when there is electrostatic attraction between the reactants.

Temperature variation for the dien, NTA, and EDTA reaction systems gave linear Arrhenius plots for k_{12}. The activation parameters are summarized in Table II, including data from Rorabacher.[14]

Table II. Activation Parameters for k

L	E_a, kcal mole⁻¹	Log A
H_2O[14]	11.3	11.8
dien	7.1	9.8
NTA	11.5	12.1
EDTA	11.6	11.4

Discussion

A comparison of the k_{12} values in Table I shows that in contradiction to the conclusion of Hammes and Steinfeld, negatively charged carboxylate groups do not necessarily lead to a loosening of the hydration shell and a more rapid replacement of coordinated water. The complexes with $n = -2, -1, 0$, and $+1$ resulting from EDTA, HEEDTA, IDA, and α,β-DPA have k_{12} values equal to or less than the +2 complexes of the aquo ion, dien, and trien. It would be unfortunate to apply their suggested criteria for bonding[3] because this would force the untenable conclusion that the carboxylate groups are not coordinated in any of the complexes. Our data for the effect of glycine on the rate of replacement of water agree very well with those of Hammes and Steinfeld, but ethylenediamine has the same effect. The mono- and bisglycine complexes increase the lability of the coordinated water, but the specific assignment of a four- to tenfold increase due to each carboxylate group is not valid. *There is no evidence that negative groups per se contribute to a faster replacement of water in nickel complexes.*

Coordinated groups do have important effects on the speed of water replacement. Comparing complexes of 2+ charge shows nickel-dien reacts 14 times faster than aquonickel and 500 times faster than nickel-tetren. Even more striking is the fact that the activation energy for substitution of the dien complex is 4.2 kcal mole⁻¹ less than that of the aquo complex. Comparing complexes with the same number of coordinated water molecules shows k_{12} ratios of 0.86 for en/gly, 16 for dien/NTA, 0.44 for trien/NTA, and 0.3 for HEEDTA/tetren.

What are the most significant factors affecting the ease of replacement of water in metal complexes? Electron-donating properties of the coordinated ligands undoubtedly have some effect. Glycine, en, dien, and NTA increase the rate of water substitution. The amine nitrogens, which are more strongly coordinated than the carboxylate groups, may supply the greater electron density to nickel. This is consistent with their spectral effect in ligand-field theory. On the other hand, imidazole and 1,10-phenanthroline complexes

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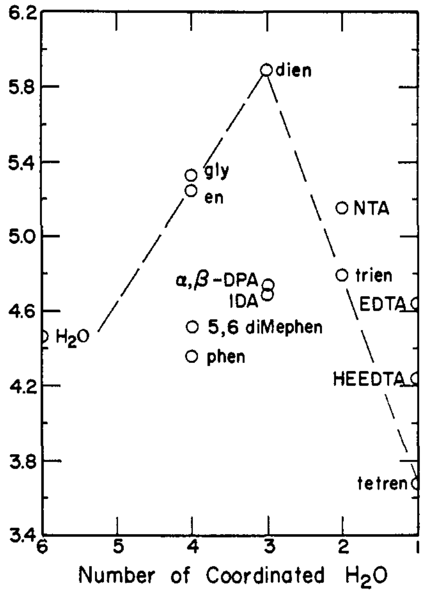

Figure 2. First-order water replacement rate constants for nickel complexes at 25°. The k_{12} values are corrected for outer-sphere association and statistical effects in order to compare all k^{-H_2O} values to that of aquonickel. The dashed line illustrates the effect for the nickel–polyamine complexes.

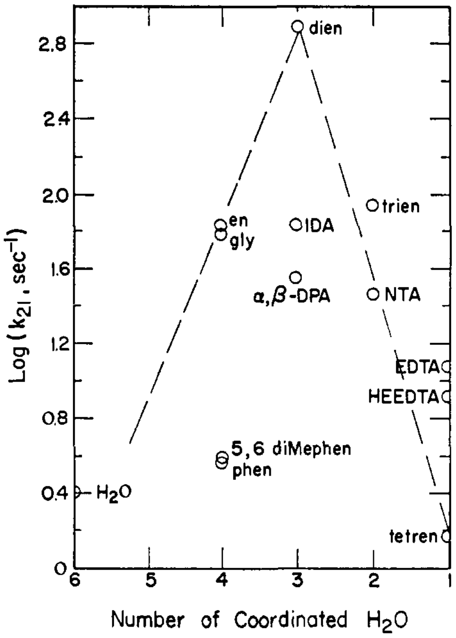

Figure 3. First-order dissociation rate constants (k_{21}) for the loss of ammonia from nickel complexes at 25°. The dashed line indicates the effect for the nickel–polyamine complexes.

can have π backbonding from the metals. Accordingly the fact that the k_{12} values for phen are much less than those for en could be because the electron density at the nickel is less. Furthermore, substituents of 1,10-phenanthroline in the 5 positions have been shown[5] to alter the rate of reaction of the nickel complex with $Hdien^+$, with NTA^{3-}, and in the present work with NH_3. The effects are not large but are real and are most easily understood in terms of change of the electron density at the metal. A secondary observation arising from the different Hammett ρ values for $Hdien^+$ and NTA^{3-} was the suggestion that equatorially coordinated water molecules (in the plane of Niphen) were influenced by phen substituents to a greater extent than axial waters. The reaction with NH_3 provides another test of this observation because unlike $Hdien^+$, NH_3 would be expected to substitute equatorially and should follow the behavior of NTA^{3-}. Indeed the ratios of rate constants for 5,6-diMephen to 5-H are 1.18 for $Hdien^+$, 1.47 for NTA^{3-}, and 1.47 for NH_3.

The k_{12} values in Table I are second-order constants and can be written as the product of an outer-sphere association constant, K_{os}, and the rate constant for the inner-sphere exchange of H_2O, k^{-H_2O}. It has been well

$$k_{12} = K_{os}k^{-H_2O} \tag{5}$$

established that ions of opposite charge first diffuse together and form outer-sphere ion pairs before water is replaced from the metal.[15,16] There are several ways to estimate K_{os} but a direct experimental calculation is possible if we assume that k^{-H_2O} for the NH_3 exchange has the same value which has been measured for the exchange of H_2O for H_2O[17] and of SO_4^{2-} for H_2O.[15] The activation energies are similar for the H_2O–H_2O exchange and the NH_3–H_2O exchange. When k^{-H_2O} for the SO_4^{2-}–H_2O exchange (1.6×10^4 at 20°) is corrected at 25°, it agrees with the value of 2.7×10^4 for the H_2O–H_2O exchange. Therefore, $K_{os} = (2.8 \times 10^3)/(2.7 \times 10^4) = 0.1$ for the outer-sphere complex of aquonickel ion and ammonia. This is in good agreement with calculated values of K_{os} suggested by Rorabacher.[14] These values are based on the diffusion of two species to their nearest neighbors and their redissociation or based on an outer-sphere association in which one species is uncharged.[14,18] As a result, except for a statistical correction, the K_{os} value should be the same for all the nickel complexes. The statistical factor arises from the number of water molecules available for exchange and the possibility that an ammonia molecule in the outer sphere is in position to react. Figure 2 graphs values of k^{-H_2O} (a log scale is used for convenience only; it has no physical significance) calculated from (k_{12}/K_{os})(6/number of H_2O) against the number of water molecules coordinated to nickel. The values of k^{-H_2O} will be the same as the H_2O–H_2O exchange values if the mechanism proceeds by rupture of the nickel–H_2O bond. However, the first-order constant should be valid even if NH_3 participates in the nickel–H_2O bond rupture. The scatter of the values in Figure 2 emphasizes the point that there is not a simple relationship between the nature of the coordinated ligand and the k^{-H_2O} value. Only the polyamines appear to follow a regular trend with a sharp maximum for dien, but neither this maximum nor the variations for the other ligands are explained by electron density at the metal. It is noteworthy that terpyridine, another tridentate ligand, also gives much faster substitution rates than bipyridine or 1,10-phenanthroline complexes.[19]

It is the structure of the complex which appears to play an important role in the reactivity of the coordinated water. Figure 3 shows that the lability of the

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coordinated NH_3 follows the same general pattern. The k_{21} values are more subject to error because they are determined as intercepts, while the k_{12} values are obtained from slopes. If the substitution reaction proceeds by loss of water (or ammonia) to form a five-coordinate transition state, then dien must stabilize the lower coordination state. More highly coordinated ligands such as EDTA or tetren would require greater rearrangement of the bound groups. Rigid chelate rings in the phenanthroline complexes or strained rings in the α,β-DPA complex might account for their effects. The problem of predicting behavior is difficult because of the lack of detailed knowledge of the effect of structure on the reactant, much less the transition state. Structural effects could include the relative positions of different donor groups, chelate ring size, and steric strain in the complexes. Preliminary work with other metal ions indicates that the same ligands have much different effects on different metals. This is to be expected since different coordination positions are preferred by different metals. Much more data are needed before the relationship between ligand structure and the reactivity of the complex can be well characterized.

In summary, the electron-donating ability of the coordinated groups is more important than the over-all charge of the complex, but the structural arrangement of the coordinated ligand appears to be of still greater importance in determining the rate of replacement of bound water.

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Infrared Spectra of and Bonding in Some X–SO_2–Y Gaseous Molecules[1,2]

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Abstract: The infrared spectra in the range 400 to 4000 cm^{-1} of gaseous and condensed dimethyl sulfone, methyl sulfonyl chloride, and methyl sulfonyl fluoride have been obtained and assigned. The spectra are correlated with those of other X–SO_2–Y molecules (X and/or Y being F, OH, Cl, or CH_3, and including sulfuryl halides, sulfonic acids, and sulfuric acid). Linear relations are observed between the average electronegativity of X and Y and (a) the -SO_2 asymmetric, (b) the -SO_2 symmetric, (c) the S–X stretching, (d) the -SO_2 bending, and (e) the -SO_2 rocking frequencies. They are compared in part to similar correlations for chromyl and molybdenyl compounds and are explained in terms of participation of the d orbitals in the bonding. The three vibrations of sulfur dioxide also fit into these correlations. Previously made correlations are modified and used to predict bond distances for, *e.g.*, gaseous H_2SO_4.

Bonding in molecules of the type X–SO_2–Y[2] has been the subject of some interest,[3,4] in particular because of the participation of the 3d orbitals of sulfur in the bonding. The theoretical aspects have been developed and summarized by Jaffé and Orchin.[4] The species to be considered here[2] have X and Y whose main effect should be inductive and hence well suited for a test of the theory. Direct investigation of the electronic spectra of these molecules has proved difficult because no spectra have been observed in the glass or quartz ultraviolet regions.[4]

The -SO_2 stretching frequencies are accessible to observation and have been characterized by Bellamy and Williams[5] as being essentially free from mass and coupling effects. As such, they should provide a useful probe into the bonding of these compounds. Robinson[6] and Gillespie and Robinson[7] have made extensive studies of these compounds, mostly in the condensed phases. They have also made quantitative correlations of the -SO_2 bond angle and of the S–O bond length with the -SO vibration frequencies.

For purposes of investigating the nature of the bonding, elimination of such perturbations as hydrogen bonding, dipole–dipole effects, and other condensed-phase interactions is desirable; gas-phase spectra are indicated. The gas-phase spectra are of added interest because many high-temperature gaseous molecules of the type X–MO_2–Y (M = Cr, Mo, W, U)

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[2] For the purposes of this paper, X and/or Y include F, OH, Cl, and CH_3. The compounds included, therefore, are the sulfuryl halides, sulfonic acids, sulfuric acid, sulfonyl halides, and dimethyl sulfone.

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[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 17.

[5] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 863 (1957).

[6] E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

[7] R. J. Gillespie and E. A. Robinson, *ibid.*, **41**, 2074 (1963).