state reaction mechanisms than has been possible for ground states (see ref 20), experiments with optically active chelates might further restrict the range of possibilities.

We have made no attempt in the preceding discussion to assess the spectroscopic description of our reactive excited states. This type of approach has been made, in some detail, by Zink[21] using conventional ligand field theory to predict σ- and π-bonding changes in various excited states. This approach should be very helpful in the case of cobalt(III) ammines where it does appear that the primary act is one of direct heterolytic bond cleavage at a labilized position. We retain a general concern that the thermally equilibrated excited (thexi[1]) states which presumably are the chemically reacting species may have a different geometry (and a different spin multiplicity) than the Franck-Condon states used by ligand field theory in treating absorption spectra. A further caution, mentioned in the Introduction, is that mechanistic interpretations of quantum yield variations may be specious; relative photoinertness could, for example, be due to an enchanced rate of radiationless deactivation and not to a mechanistic inability to react.

A final indication that much remains to be explained is illustrated in Figure 11. A near linearity exists in a plot of log k *vs.* log ϕ for the various dichloro complexes even though reactions of differing stereochemistry are being compared (and with *cis*-α-[Co(trien)Cl$_2$]$^+$ a clear exception). A similar correlation was noted for a series of chromium(III) amines,[22] also unexplained. The thought does emerge, however, that some correspondence may exist between thexi states and the transition states of thermal kinetics.

Acknowledgment. This investigation was supported in part by Grant 27984X2 from the National Science Foundation to the University of Southern California.

Registry No. *cis*-α-[Co(trien)Cl$_2$]Cl, 14883-58-0; *cis*-α-[Co(trien)(H$_2$O)Cl]$^{2+}$, 15490-27-4; *cis*-β-[Co(trien)Cl$_2$]Cl, 51965-59-4; *cis*-β-[Co(trien)(H$_2$O)Cl]$^{2+}$, 15155-11-0; *cis*-β'-[Co(trien)(H$_2$O)Cl]$^{2+}$, 52021-54-2; [Co(tren)Cl$_2$]Cl, 20023-19-2; β-[Co(tren)(H$_2$O)Cl]$^{2+}$, 33393-52-1; *trans*-[Co(trien)(H$_2$O)Cl]$^{2+}$, 52021-55-3.

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A Ligand Field Interpretation of the Quantum Yields of Photosolvation of d^6 Complexes

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Received January 22, 1974 AIC400480

A method of relating the solvation quantum yields of d^6 complexes having C_{4v} and D_{4h} site symmetries to their spectroscopic properties is developed. The fractional metal d-orbital compositions of photoactive excited states are derived using symmetry wave functions and configuration interactions. It is shown that the fractional metal d$_{z^2}$ orbital character, which may be calculated from the electronic absorption spectrum or approximated using the spectrochemical series, can be directly related to the sum of the quantum yields of solvation of ligands on the z axis. Deviations from the expected correlation lend support to the role of stereochemical hindrance in photosolvation. The derived relationships are discussed in terms of bond weakenings in the excited states and in terms of rates of excited-state deactivation processes including the rates of photochemical reactions and radiationless processes.

Introduction

The photochemistry of a wide variety of d^6 transition metal complexes,[1,2] particularly that of cobalt(III), has been extensively studied and is still receiving extensive current attention.[3] Recently, a ligand field model has been developed to interpret transition metal photoreactions.[4-7] According to the ligand field model the differences between the photoreactions in a series of complexes as the metal or the ligands are changed are a consequence of the differences in the photoactive excited state caused by the changes. The differences in the excited states and, hence, the different photoreactions can be understood in terms of spectroscopically derived ligand field parameters.

At its current stage of development, the model consists of three interrelated parts.[7] First, crystal field theory is used to determine the symmetry wave functions, the relative energies of the states, and hence the directionality of the photoreactions. Second, molecular orbital theory is included in the analysis to determine the distribution of the excitation energy along the labilized axis in order to understand which ligand on the axis will be preferentially labilized. Finally, a crystal field determination of the fractional d-orbital composition of the photoactive excited state is used (often in conjunction with the molecular orbital theory) to determine the relative quantum yields of the photoreactions. Of the three parts, the latter one is currently the most primitive. The purpose of this paper is to provide a careful treatment of the problem for the extensively studied group of monosubstituted and trans-disubstituted d^6 complexes.

Our fundamental approach to the problem is based on the idea that the more the excitation energy is concentrated along one molecular axis, the greater will be the quantum yield for loss of ligands on that axis. The distribution of the

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(6) J. I. Zink, *Inorg. Chem.*, 12, 1018 (1973).

(7) J. I. Zink, *Mol. Photochem.*, 5, 151 (1973).

excitation energy among the axes is determined by the crystal field parameters Ds, Dt, and B. The greater the tetragonal distortion, the greater the asymmetry in energy distribution. In order to avoid the complication of the distribution of energy between the two ligands along a given axis, treated extensively in a separate paper,[8] we will use the sum of the quantum yields of ligand loss along an axis in our treatment (*vide infra*). We first derive the distribution of energy in terms of the fractional d-orbital composition of the excited states using crystal field theory including configuration interaction. Several approximations of the exact expressions are discussed. The model's predictions are compared to experimental results and are shown to be in full accord with the quantum yields for cobalt(III), rhodium(III), and iridium(II) complexes.

Fractional d-Orbital Composition of Excited States

When symmetry wave functions are used to describe the electronic configurations of a complex, configuration interaction can take place between any two or more of the symmetry wave functions if they have the same overall symmetry and multiplicity. The spatial symmetry wave functions for the ground and lowest excited states of a d^6 configuration in the octahedral point group are[4,9]

$$\mathrm{A}_1 \qquad \Psi_1 = (\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^2{}_{yz}) \tag{1}$$

$$\mathrm{E(T_{1g})} \qquad \Psi_2 = \frac{\sqrt{3}}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{z^2}) + \frac{1}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{x^2-y^2}) \tag{2}$$

$$\Psi_3 = \frac{\sqrt{3}}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^1{}_{xz}\mathrm{d}^2{}_{yz}\mathrm{d}^1{}_{z^2}) + \frac{1}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^1{}_{xz}\mathrm{d}^2{}_{yz}\mathrm{d}^1{}_{x^2-y^2}) \tag{3}$$

$$\mathrm{A_2(T_{1g})} \qquad \Psi_4 = \mathrm{d}^1{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^2{}_{yz}\mathrm{d}^1{}_{x^2-y^2} \tag{4}$$

$$\mathrm{E(T_{2g})} \qquad \Psi_5 = -\frac{1}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{z^2}) + \frac{\sqrt{3}}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{x^2-y^2}) \tag{5}$$

$$\Psi_6 = -\frac{1}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^1{}_{xz}\mathrm{d}^2{}_{yz}\mathrm{d}^1{}_{z^2}) + \frac{\sqrt{3}}{2}(\mathrm{d}^2{}_{xy}\mathrm{d}^1{}_{xz}\mathrm{d}^2{}_{yz}d^1{}_{x^2-y^2}) \tag{6}$$

$$\mathrm{B_2(T_{2g})} \qquad \Psi_7 = \mathrm{d}^1{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^2{}_{yz}\mathrm{d}^1{}_{z^2} \tag{7}$$

The E(T$_{1g}$) and E(T$_{2g}$) wave functions can undergo configuration interaction as long as they are of the same multiplicity. The interaction matrix is

$$\begin{vmatrix} \langle\Psi_{\mathrm{E(T_{1g})}}|H|\Psi_{\mathrm{E(T_{1g})}}\rangle - W & \langle\Psi_{\mathrm{E(T_{1g})}}|H|\Psi_{\mathrm{E(T_{2g})}}\rangle \\ \langle\Psi_{\mathrm{E(T_{2g})}}|H|\Psi_{\mathrm{E(T_{1g})}}\rangle & \langle\Psi_{\mathrm{E(T_{2g})}}|H|\Psi_{\mathrm{E(T_{2g})}}\rangle - W \end{vmatrix} = 0 \tag{8}$$

The appropriate matrix elements are[10,11]

$$\langle\Psi_2|H|\Psi_2\rangle = \langle\Psi_3|H|\Psi_3\rangle = 15A - 30B + 14C - 14Dq + (21/4)Dt \tag{9}$$

$$\langle\Psi_5|H|\Psi_5\rangle = \langle\Psi_6|H|\Psi_6\rangle = 15A - 14B + 14C - 14Dq + 2Ds + (31/4)Dt \tag{10}$$

$$\langle\Psi_2|H|\Psi_6\rangle = \langle\Psi_3|H|\Psi_5\rangle = 0 \tag{11}$$

$$\langle\Psi_2|H|\Psi_5\rangle = \langle\Psi_3|H|\Psi_6\rangle = -\sqrt{3}(Ds - (5/4)Dt) \tag{12}$$

The values shown are for the triplet states; for singlets add $2C$. The eigenvalues of this matrix are

$$W_\pm = \frac{E_1 + E_2}{2} \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4H^2} \tag{13}$$

where E_1 and E_2 are the respective energies for the E(T$_{1g}$) and E(T$_{2g}$) levels and H represents the off-diagonal element $\langle\Psi_{\mathrm{E(T_{1g})}}|H|\Psi_{\mathrm{E(T_{2g})}}\rangle$ or $\langle\Psi_{\mathrm{E(T_{2g})}}|H|\Psi_{\mathrm{E(T_{1g})}}\rangle$. Solving (13) for the case where $(E_1 - E_2)^2 \gg 4H^2$, we have

$$W_\pm = \frac{E_1 + E_2}{2} \pm \frac{E_1 - E_2}{2}\sqrt{1 + \frac{4H^2}{(E_1 - E_2)^2}} \tag{14}$$

or

$$W_\pm = \frac{E_1 + E_2}{2} \pm \frac{1}{2}(E_1 - E_2)\left(1 + \frac{2H^2}{(E_1 - E_2)^2}\right) \tag{15}$$

$$W_+ = E_1 - \frac{H^2}{E_2 - E_1} \tag{16}$$

$$W_- = E_2 + \frac{H^2}{E_2 - E_1} \tag{17}$$

The new normalized wave functions $\Phi_{\mathrm{E(T_{1g})}}$ and $\Phi_{\mathrm{E(T_{2g})}}$ corresponding to W_+ and W_-, respectively, are

$$\Phi_{\mathrm{E(T_{1g})}} = \frac{1}{\sqrt{1 + \lambda^2}}[\Psi_{\mathrm{E(T_{1g})}} - \lambda\Psi_{\mathrm{E(T_{2g})}}] \tag{18}$$

and

$$\Phi_{\mathrm{E(T_{2g})}} = \frac{1}{\sqrt{1 + \lambda^2}}[\Psi_{\mathrm{E(T_{2g})}} + \lambda\Psi_{\mathrm{E(T_{1g})}}] \tag{19}$$

where the mixing coefficient λ is

$$\lambda = H/(E_2 - E_1) \tag{20}$$

The wave function of the lowest energy state of E symmetry can be explicitly written as

$$\Phi_{\mathrm{E(T_{1g})}} = \frac{1}{\sqrt{1 + \lambda^2}}\left[\left(\frac{\sqrt{3} + \lambda}{2}\right)(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{z^2}) + \left(\frac{1 - \sqrt{3}\lambda}{2}\right)(\mathrm{d}^2{}_{xy}\mathrm{d}^2{}_{xz}\mathrm{d}^1{}_{yz}\mathrm{d}^1{}_{x^2-y^2})\right] \tag{21}$$

Photochemical Implications

Using the fundamental postulate of our model that the

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[8] J. I. Zink, *J. Amer. Chem. Soc.*, 96, 4464 (1974).

[9] For D_{4h} symmetry, add the subscript g. The spatial orbitals occurring in the wave functions representing singlet and triplet states are the same.

[10] J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, 4981 (1956).

[11] J. S. Griffith, "Theory of Transition Metal Ions," Cambridge University Press, Cambridge, England, and New York, N. Y., 1957, Chapter 9.

lowest excited state of a given multiplicity will be the dominant photoactive level of that multiplicity,[4] the photochemistry of d^6 complexes then hinges on the properties of the lowest excited state wave function Φ (eq 21). The changes occuring in the metal-ligand σ and π bonds caused by populating the excited state will be used to explain the photoreactions of d^6 complexes. Compared to the ground state, Φ represents loss of electron density in the d_{yz} orbital. The amount of loss is independent of the value of λ because the amount of $(d^2_{xy}d^2_{xz}d^1_{yz})$ character in Φ is independent of the value of λ (eq 21). Therefore, Φ represents strengthening of the π bonds for π-donor ligands on the y and z axes compared to the ground state. In contrast, however, the amount of d_{z^2} and $d_{x^2-y^2}$ character in Φ is not independent of λ. The amount of σ antibonding along a given axis will depend on the mixing parameter (*vide infra*). The explicit dependence of the per cent d_{z^2} character in the Φ wave function on the value of λ is illustrated in Figure 1. The larger the per cent d_{z^2} character in the Φ wave function, the more antibonding the metal-ligand bonds on the z axis become, thereby increasing the probability of photolabilization of the z-axis ligands.[12] Thus, the relative quantum yields of z-axis photoaquation in a homologous series of complexes should be directly related to the per cent of d_{z^2} character.

Determination of the Mixing Parameter

Because the per cent d_{z^2} character in the total $E(T_{1g})$ wave function (eq 21) is prescribed by the mixing parameter, λ, the photochemical reactivity of the $E(T_{1g})$ state is dictated by λ. The value of λ can, in principle, be calculated from spectroscopically determined data.

Substituting (12) into (20), the mixing parameter λ can be expressed in terms of the crystal field parameters Ds and Dt[13,14]

$$\lambda = \frac{\sqrt{3}\left(\frac{5}{4}Dt - Ds\right)}{E_2 - E_1} \tag{22}$$

The energy difference in eq 22 can either be measured or calculated.[13] Using the calculated expression for the energy separation from Figure 2, eq 22 becomes

$$^3\lambda = \sqrt{3}\left(\frac{5Dt - 4Ds}{32B + 8Ds + 10Dt}\right) \tag{23}$$

$$^1\lambda = \sqrt{3}\left(\frac{5Dt - 4Ds}{64B + 8Ds + 10Dt}\right) \tag{24}$$

where the superscript on λ indicates the spin multiplicity. Values of λ can be calculated from eq 23 and 24 for those compounds where B, Ds, and Dt can all be measured. For most d^6 complexes, splitting of the high-energy T_{2g} state is rarely observed making experimental determinations of Ds impossible.[13]

In order to determine the relative importance of changes in the parameters B, Ds, and Dt on the changes in λ, the total differential of the mixing parameter, which explicitly represents how changes in B, Ds, and Dt affect λ, is derived for the triplet state (eq 23) and the singlet state (eq 24)

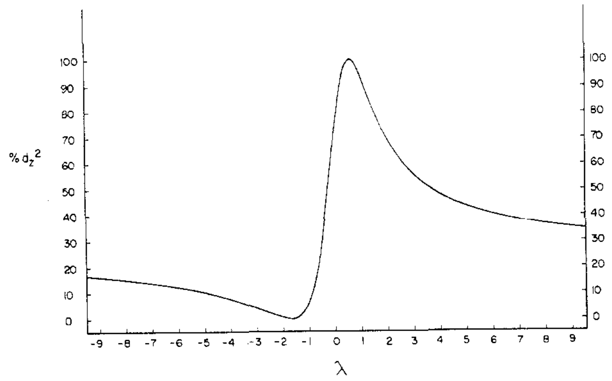

Figure 1. Plot of % d_{z^2} of $\Phi_{E(T_{1g})}$ (eq 21) as a function of the mixing parameter λ. % $d_{z^2} = (\sqrt{3} + \lambda)^2/4(1 + \lambda^2)$.

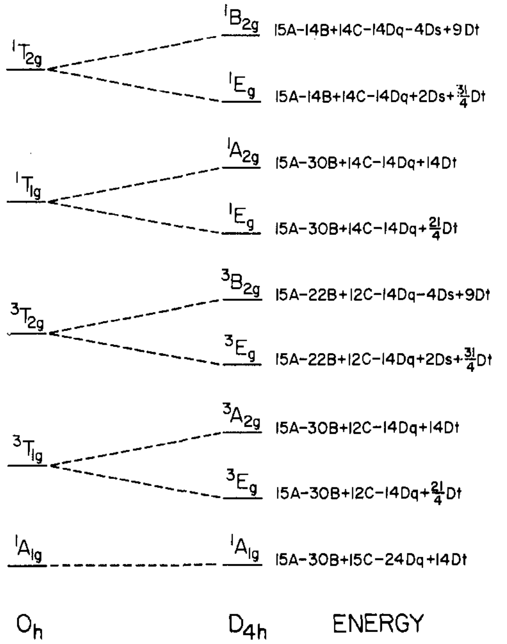

Figure 2. Correlation diagram for the singlet and triplet states of a d^6 configuration. The energies of the levels are shown on the right.

$$d(^3\lambda) = \frac{(-160Dt + 128Ds)\,dB + (160B + 80Ds)\,dDt - (128B + 80Dt)\,dDs}{(32B + 8Ds + 10Dt)^2} \tag{25}$$

$$d(^1\lambda) = \frac{2(-160Dt + 128Ds)\,dB + (320B + 80Ds)\,dDt - (256B + 80Dt)\,dDs}{(64B + 8Ds + 10Dt)^2} \tag{26}$$

In order to determine the importance of dB, dDs or dDt, their respective coefficients in eq 25 and 26 must be determined. Representative values for B, Ds, and Dt were determined for cobalt(III) complexes as follows. Upper limits of Ds were calculated following Wentworth and Piper[13] by taking the splitting of the low-energy manifold as an upper limit to the splitting of the high-energy manifold. The splitting of the $^1T_1$ band is $(35/4)Dt$. Using the smallest reported value[13] of Dt, 80 cm^{-1}, the splitting of $^1T_1$ will be 700 cm^{-1}. Taking this value as the maximum splitting of the $^1T_2$ manifold, a range of Ds values from -150 to $+185$ cm^{-1} is ob-

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(12) J. I. Zink, *Inorg. Chem.*, 12, 1957 (1973).
(13) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965).
(14) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 5.

tained using the relationship that the splitting of the $^1T_2$ band is $(5/4)Dt - 6Ds$. Using the value of B for the hexaamminecobalt(III) ion, Wentworth and Piper's values of Dt,[13] and the maximum and minimum value of Ds calculated by the above procedure, the respective coefficients for the differentials can be calculated for a large variety of monoacidopentaammine and diacidotetraamminecobalt(III) complexes. In each case the coefficients of dDt and dDs are an order of magnitude larger than the coefficients of dB, and the coefficient of dDt was always at least 150% larger than that of dDs. On the basis of the above analysis, it is reasonable to approximate the trends in λ by the trends in Dt. Even when the values of Ds are deliberately overestimated as in the above analysis, Dt remains the parameter dominating λ. Of the tetragonal crystal field parameters Dt is the easiest to interpret physically. It is defined as the difference between the Dq values of the in-plane and axial ligands[13]

$$Dt = Dq^{xy} - Dq^z \qquad (27)$$

Armed with only a spectrochemical series, the relative values of Dt, λ, and thus the relative quantum yields for photoaquation can easily be estimated for a homologous series of complexes.

The correlation of λ with Dt could break down when the Dq values for in plane and axial ligands are comparable but their Ds values are dissimilar. In such a case changes in Ds could become more important than changes in Dt in eq 25 and 26. The correlation could also break down for highly covalent complexes. In such cases crystal field theory is less applicable than it is for the ionic complexes treated in this paper.

The parameter B, the interelectronic repulsion parameter (eq 23 and 24), is a measurement of the electronic repulsions in the outer shell of an ion or atom.[15] The larger the e^-–e^- interaction, the larger the value of B. Without a complete spectroscopic analysis, a quantitative determination of the importance of B cannot be established. The effect of trends in B on trends in λ could be important whenever the metal is changed in a series of $ML_{6-n}X_n$ complexes or when the covalent properties of the ligands are drastically changed (*e.g.*, ammonia to cyanide, *vide infra*).

Discussion

1. General Predictions. Using the formalism developed above, the general predictions for three different classes of complexes can be derived and then compared to experimental results.

Class A1. The leaving group is the same in a series of complexes and the ligand trans to it is varied. Consider the photoaquation in the homologous series of complexes ML_5A, ML_5B, and ML_5C, where M is a d^6 metal ion, the ligand L trans to ligand A is the leaving group, and the Dq values for the ligands are $Dq^A > Dq^B > Dq^C$. The contribution of ligand L to the trans M–L bond is essentially constant in the series. The variable which dominates the changes in the photoreactivity when the molecule is photoexcited is λ (which is approximated by Dt). Assuming that $Dq^{xy} > Dq^A > Dq^B > Dq^C$, the order of the Dt values (from eq 27) is $Dt_{ML_5C} > Dt_{ML_5B} > Dt_{ML_5A}$. Thus the trend for the mixing parameter is $\lambda_{ML_5C} > \lambda_{ML_5B} > \lambda_{ML_5A}$. In order to correlate the trends in the mixing parameter with the trends in quantum yield of aquation, a reference point on the curve in Figure 1 must be known. When the values of the parameters used in the differential analysis are substituted into eq 23, λ never exceeds ± 1. Thus the quantum yields for photoaquation will be expected to follow the order $\Phi_{ML_5C} > \Phi_{ML_5B} > \Phi_{ML_5A}$.

Class A2. The leaving group is different in a series of monosubstituted complexes, *i.e.*, the series above when A, B, or C is the leaving group.

Class B. The leaving group is different in a series of trans disubstituted complexes such as the series *trans*-ML_4X_2, where X = A, B, or C and is also the leaving group. In classes A2 and B, the contribution of the leaving group to the metal–ligand bond can vary quite markedly in the series. The major complication to the interpretation in these classes arises from π interactions because the π-bonding changes in the excited state vary in the series even though the per cent metal d_{xz} and d_{yz} composition of the excited state is constant. In other words, the total bond between the metal and the leaving ligand (both σ and π) has a component which can vary independently from the per cent d_{z^2} composition. Deviations from the predicted quantum yield ordering would be expected to occur for the most strongly π-interacting ligands. Molecular orbital calculations show that for halide ligands, changes in the π interactions are less than one-third as important as those for σ interactions.[8] The minor importance of π bonding is exhibited by the good correlation between the per cent d_{z^2} character and the experimental quantum yields for class A2 and B complexes (*vide infra*). The orderings of the quantum yields predicted by the per cent d_{z^2} character deduced from Dt are $\Phi_{ML_5C} > \Phi_{ML_5B} > \Phi_{ML_5A}$ and $\Phi_{ML_4C_2} > \Phi_{ML_4B_2} > \Phi_{ML_4A_2}$.

Class C. The leaving group is the same in a series of complexes but the ligands cis to it are varied. For example, consider the series ML_4X_2, ML'_4X_2, and ML''_4X_2 where $Dq_L > Dq_{L'} > Dq_{L''} > Dq_X$. The Dt values for the complexes are in the order $Dt_{ML_4X_2} > Dt_{ML'_4X_2} > Dt_{ML''_4X_2}$. Thus, the trends in the mixing parameters for the complexes will be $\lambda_{ML_4X_2} > \lambda_{ML'_4X_2} > \lambda_{ML''_4X_2}$. Therefore, the order of quantum yields for photoaquation of X in the series is predicted to be $\Phi_{ML_4X_2} > \Phi_{ML'_4X_2} > \Phi_{ML''_4X_2}$.

2. Comparison with Experiment. Table I contains a compilation of the quantum yields of photoaquation Dt values and classification for (ionic) d^6 complexes of C_{4v} or D_{4h} site symmetry. Each section of the table lists complexes in order of decreasing Dt in which one or more ligands are changed to form a homologous series.

In the table only data for the quantum yields for the formation of photoaquated products are used. Disappearance quantum yields are not included because they do not necessarily reflect the true quantum yield for photoaquation.

In section I of the table, the correlation of Dt with the quantum yields is perfect. Likewise, in section II, the correlation appears to hold. However, the data reported for the compounds in this section contain three ambiguities. First, the actinometry for the halo-substituted compounds was reported to be in error[16-18] and the quantum yields are apparently too large by a factor of approximately 0.21.[16,17] The data reported in the table are corrected for this error. Second, for the aquo and hydroxo complexes, only quantum yields for loss of cyanide were determined.[19] The aquo

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(15) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, England, 1962, Chapter 8.

(16) A. W. Adamson, *J. Inorg. Nucl. Chem.*, 13, 275 (1960).

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(18) A. W. Adamson, A. Chiang, and E. Zinato, *J. Amer. Chem. Soc.*, 91, 5467 (1969).

(19) M. Wrighton and D. Bredesen, *Inorg. Chem.*, 12, 1707 (1973).

Table I. *Dt* Values and Solvation Quantum Yields for d^6 Complexes

Compd	Solvation quantum yield	*Dt*, cm^{-1}	Class
	Section I		
$Co(NH_3)_5N_3^{2+}$	0.3[a]	404[b]	A1
$Co(NH_3)_5Br^{2+}$	0.07[c]	321[b]	A1, A2
$Co(NH_3)_5Cl^{2+}$	0.0068[d]	226[b]	A1, A2
$Co(NH_3)_5F^{2+}$	0.0025[d]	183[b]	A1, A2
$Co(NH_3)_5NCS^{2+}$	0.00054[c]	80[b]	A2
	Section II		
$Co(CN)_5I^{3-}$	0.18[e]	1410[f]	A2
$Co(CN)_5Br^{3-}$	0.15[g]	800[f]	A2
$Co(CN)_5Cl^{3-}$	0.05[g]	685[f]	A2
$Co(CN)_5(OH)^{3-}$	0.05[h]	650[f]	A1
$Co(CN)_5(OH_2)^{2-}$	0.002[h]	630–685[f]	A1
	Section III		
$Rh(NH_3)_5I^{2+}$	0.83[i,j]	789[f]	A2
$Rh(NH_3)_5Br^{2+}$	0.20[j]	560[f]	A2
$Rh(NH_3)_5Cl^{2+}$	0.16[j] 0.13[k] 0.14[l]	457[f]	A2
	Section IV		
trans-$Rh(en)_2I_2^+$	0.280[m]	1320[f]	B
trans-$Rh(en)_2Br_2^+$	0.100[m]	1111[f]	B
trans-$Rh(en)_2Cl_2^+$	0.086[m] 0.057[k]	983[f]	B
	Section V		
trans-$Rh(NH_3)_4I_2^+$	0.48[i]	1300[f]	B
trans-$Rh(NH_3)_4Cl_2^+$	0.17[k] 0.42[m]	960[f]	B
	Section VI		
trans-$Ir(en)_2Cl_2^+$	0.089[n]		C
trans-$Ir(py)_4Cl_2^+$	0.037[n]		C
	Section VII		
trans-$Rh(cyclam)Cl_2^+$	0.011[k]		C
trans-$Rh(en)_2Cl_2^+$	0.057[k] 0.086[m]	983[f]	C
trans-$Rh(NH_3)_4Cl_2^+$	0.13–0.17[k] 0.042[m]	960[f]	C
trans-$Rh(py)_4Cl_2^+$	0.024[m]		C

[a] J. F. Endicott, private communication. [b] Reference 13. [c] A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 162 (1960). [d] A. W. Adamson, private communication. [e] A. W. Adamson, A. Chiang, and E. Zinato, *J. Amer. Chem. Soc.*, **91**, 5467 (1969). [f] This work. [g] A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958). [h] M. Wrighton and D. Bredesen, *Inorg. Chem.*, **12**, 1707 (1973). [i] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 1797 (1972). [j] T. L. Kelly and J. F. Endicott, *ibid.*, **94**, 278 (1972). [k] C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1453 (1973). [l] L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967). [m] M. M. Muir and W. Huang, *Inorg. Chem.*, **12**, 1831 (1973). [n] M. M. Muir and W. Huang, *ibid.*, **12**, 1930 (1973).

complex is known to undergo photoexchange.[18] Thus, the total quantum yield for the *z* axis could be larger if the quantum yield for photoexchange were included. Finally, only a range of *Dt* values could be calculated for the aquo complex because of the poor resolution of the splitting of the low-energy band.[19] Using the best available data as shown in the table, the correlation between *Dt* and the quantum yields holds very well for these strongly π covalent complexes. However, because of the ambiguities in the data, we cannot be as certain that the correlation is as good as that exhibited in the other sections of the table. In sections III–V, the correlation of *Dt* with quantum yields for photoaquation again holds without exception.

In sections VI and VII, several *Dt* values cannot be calculated for lack of spectroscopic data for the parent octahedral complexes. In these cases, the spectrochemical series can be used to estimate the trends in *Dt* values by comparing the trends in the *Dq* values for the variable ligands in the series. For example, *Dq* for en is larger than that for py, and thus *Dt* for *trans*-$Ir(en)_2Cl_2^+$ is larger than that of *trans*-$Ir(py)_4Cl_2^+$. For the iridium complexes in section VI, the correlation of quantum yields with the approximated trend in *Dt* holds.

Similarly, section VII represents class B complexes for which trends in *Dt* must be estimated. The spectrochemical series for the in-plane ligands is cyclam > en > NH_3 ~ py. Thus, the quantum yields for photoaquation of chloride in *trans*-$RhL_4Cl_2^+$ (L_4 = cyclam, 2 en, 4 py, 4 NH_3) complexes would be expected to follow the series cyclam > en > py ~ NH_3. The deviation from our predicted trend, shown in the table, lends more quantitative support to Adamson's interpretation that some type of stereochemical hindrance plays an important role in the photochemistry.[20] Comparing *trans*-$Rh(en)_2I_2^+$ in section IV to *trans*-$Rh(NH_3)_4I_2^+$ in section V, the same type of reversal is also found. The quantum yield data reported by Muir do correlate with the estimated values of *Dt*. However, the two groups do not agree about the photoaquation quantum yield of *trans*-$Rh(NH_3)_4Cl_2^+$ (see Table I, section VII).

The ligand field model can also offer an explanation for the variation in quantum yields in a series where five ligands are changed. For example, the larger quantum yields observed for the $Co(CN)_5X^{2+}$ series (section I) compared to the $Co(NH_3)_5X^{2+}$ series (section II) ($X^- = Cl^-, Br^-, I^-$) could be a consequence of the larger *Dt* values and also the smaller *B* (*vide infra*) values for the cyano complexes compared to the ammine complexes. For $Co(CN)_6^{3-}$, $B = 418\ cm^{-1}$ compared to 528 cm^{-1} for $Co(NH_3)_6^{3+}$.[13] Because λ varies as $1/B$ (eq 23 and 24) the increased quantum yield is reinforced by *B*. In addition, the ligand field theory can also offer an explanation to quantum yield differences for different metals. The larger value of aquation quantum yields for $Rh(NH_3)_5X^{2+}$ complexes compared to the analogous $Co(NH_3)_5X^{2+}$ complexes could also be explained in terms of the larger *Dt* values for the rhodium complex and perhaps the smaller *B* values.

3. Alternative Interpretations of the Ligand Field Concept. The major criticism which might be made concerning our interpretation of the correlation between the mixing parameter λ and the solvation quantum yields derived in this paper is that excited-state deactivation processes other than the photoreactions have apparently been neglected. The traditional approach to reaction quantum yields has been to express them as ratios of the rates of deactivating processes

$$\Phi = \frac{k_r}{k_r + k_n + k_l} \tag{28}$$

where k_r is the rate of photochemical reaction, k_l is the rate of luminescence, and k_n is the rate of nonradiative processes. Attempted interpretations of solvation quantum yields in terms of the rate approach represented by eq 28 are not useful when the parameters are impossible to measure.

The rate approach to quantum yields suggests alternative interpretations of our ligand field model in terms of the parameters in eq 28. One extreme, representing the simplest connection between the rate approach and our bonding approach, would be to assume that the antibonding character between a metal and a ligand in the excited state is directly related to the rate of photosolvation of that ligand.

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According to this assumption, as the antibonding character increases in a series of complexes, the rate of photochemical reaction increases, thus increasing the quantum yields or *vice versa, i.e.*, $d\Phi/dk_r > 0$.

The conditions under which the above assumption is valid can be derived using a differential analysis of eq 28. The total differential is

$$d\Phi = \frac{(k_n + k_l)dk_r - k_r(dk_n + dk_l)}{(k_r + k_n + k_l)^2} \tag{29}$$

From eq 29, the change in quantum yield with respect to k_r will always be positive when

$$dk_r > \frac{k_r}{k_n + k_l}(dk_n + dk_l) \tag{30}$$

Numerical values for $k_r/(k_n + k_l)$ can be calculated from eq 28. For example for cobalt(III)-ammine complexes, $\Phi = 0.05$ and $k_r/(k_n + k_l) = 0.053$; for rhodium(III)-ammine complexes, $\Phi = 0.5$ and $k_r/(k_n + k_l) = 1$. Thus, assuming the simplest connection between the rate and bonding models, it can be seen that the assumed neglect of other deactivation processes (k_n and k_l) does not put severe constraints on the applicability of our bonding model. It can also be seen that the bonding model will be most likely to fail when (1) the reaction quantum yields approach unity and (2) the changes in the sum of the rates of radiative and nonradiative processes are of the same order of magnitude and of the same sign as the change in the rate of reaction.

As another extreme, the correlation between the mixing parameter λ and the quantum yields of solvation could be interpreted totally in terms of changes in the per cent $d_{x^2-y^2}$ character causing changes in the rate of radiationless deactivation *via* vibrational deactivation in the *xy* plane. In our bonding model, the per cent $d_{x^2-y^2}$ character decreases as the per cent d_{z^2} character increases. A decreasing rate of radiationless deactivation can be associated with decreasing $d_{x^2-y^2}$ character if it is assumed that the σ-antibonding character in the *xy* plane is not great enough to cause photochemical reactions but instead is dissipated *via* ligand vibrations. This interpretation is consistent with the "strong coupling" scheme in the Englman-Jortner theory.[21,22] Because of the inverse relationship between the rate of nonradiative deactivation and the quantum yield in eq 28, decreasing $d_{x^2-y^2}$ character would result in an increase in the quantum yield.

Our preferred interpretation of our correlation between fractional excited-state composition and the quantum yield of solvation lies between the two extremes. Both the rates of reaction and the rates of radiationless deactivation are implicitly contained in the bonding model. Experimental determination of which of the rates is most important in affecting the quantum yields will probably be limited to those few systems where luminescence and photochemical reactions are observed under the same conditions. We wish to stress, however, that the ligand field bonding model is self-contained and, in principle, is capable of explaining all of the experimental observables. The rate model starts from a completely different point of view and uses completely different language. Any discussion of the bonding model in terms of rates, or *vice versa*, must rest on connective assumptions and must be considered an interpretation of one model in terms of the other. Because both models explain the same observables, explicit points of connection between them can be found.

Registry No. Cobalt, 7440-48-4; rhodium, 7440-16-6; iridium, 7439-88-5.

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Metal Ion Controlled Syntheses of Novel Five-Coordinate Zinc and Cadmium Complexes Containing a Helical Coordination Geometry and Their Template Reaction to Form Complexes of a Pentadentate Macrocyclic Ligand

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Received March 18, 1974 AIC40186P

Zinc and cadmium ions induce rearrangement of 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine under basic conditions producing complexes of the deprotonated tautomeric Schiff base. The complexes are five-coordinate and the coordinated Schiff base is present in a novel helical configuration. Zinc and cadmium complexes of this ligand, 2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine, readily react with methyl iodide to yield complexes of the corresponding S,S′-dimethylated ligand, which contain two coordinated iodide ions and appear to be seven-coordinate. The corresponding reactions with a bifunctional alkyl halide, α,α′-dibromo-*o*-xylene or 1,4-diiodobutane, result in a number of ring-closing S-alkylation reactions. Shorter chain difunctional alkylating agents fail to span the sulfur-sulfur distances and ring closure does not occur.

Introduction

Condensation of an aldehyde or a ketone with 2-aminobenzenethiol does not normally lead to the isolation of the corresponding Schiff base but rather the main product is usually a benzothiazoline.[2,3] Nevertheless, in solution, the benzothiazoline may exist in equilibrium with its tautomeric Schiff base. Such is the case for 2-(2′-pyridyl)benzothiazoline (I) which is obtained by condensation, in alcohol, of 2-

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