the spectrum of *trans*-$Cr(en)_2FBr^+$ is the appearance of a narrow, weak transition, superimposed on the second broad band, at 21,400 cm^{-1}. The position and intensity of this spectral band suggests that it is a transition to a doublet, ${}^2E$ or ${}^2B_2$, arising out of the ${}^2T_{2g}(t^3{}_{2g})$ manifold of the parent octahedral $Cr(en)_3{}^{3+}$ complex. Its appearance in the spectrum of *trans*-$Cr(en)_2FBr^+$ may be due to a combination of large spin-orbit coupling in this complex and near degeneracy of this transition with the ${}^4B_1 \rightarrow {}^4B_2$ transition.

The spectral data for *trans*-$Cr(NH_3)_4FCl^+$ is completely compatible with that of the corresponding ethylenediamine complex when the slightly smaller value of the splitting parameter 10*Dq* for NH_3 (compared to en) is taken into account. On this basis we believe the assignment of the trans structure to this molecule is valid. It is interesting to note that the extinction coefficients observed for *trans*-$Cr(NH_3)_4FX^{n+}$, where X = F^-, Cl^-, or H_2O, are all somewhat, but distinctly, lower than the values for the corresponding complexes of ethylenediamine. The data are in Table I. This phenomenon is also true of $Cr(NH_3)_6{}^{3+}$ compared to $Cr(en)_3{}^{3+}$, as well as a number of *cis*-CrN_4X_2 complexes[13] in which cases the effect is more dramatic. Whether this effect is simply a lowering of symmetry restrictions in the ethylenediamine complexes compared to ammonia complexes or arises from the nature of the vibronic combinations[14] is not clear to us.

Registry No. *trans*-$[Cr(en)_2FCl]ClO_4$, 26748-18-5; *trans*-$[Cr(en)_2FH_2O](ClO_4)_2$, 15688-01-4; *trans*-$[Cr(en)_2FBr]ClO_4$, 40029-15-0; *trans*-$[Cr(NH_3)_4F_2]ClO_4$, 40029-16-1; *trans*-$[Cr(NH_3)_4ClH_2O]Cl_2$, 18737-53-6; *trans*-$[Cr(NH_3)_4FCl]ClO_4$, 40029-18-3; *trans*-$[Cr(NH_3)_4FH_2O]^{2+}$, 40029-19-4.

Acknowledgment. This work was supported by a grant from the Academic Senate, University of California at San Diego. We are grateful for that support and wish also to thank George Malouf for help in analyzing some of the samples. C. B. acknowledges financial support from CONICIT, Caracas, Venezuela.

(12) J. R. Perumareddi, *Coord. Chem. Rev.*, 4, 73 (1969).

(13) See the data in C. S. Garner and D. A. House, *Transition Metal Chem.*, 6, 200 (1970).

(14) See, for instance, L. Dubicki and P. Day, *Inorg. Chem.*, **10**, 2043 (1971).

Contribution No. 3159 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Photochemical Implications of Configuration Interaction in d^3 Complexes

Jeffrey I. Zink

Received February 8, 1973

In recent publications, a model based on the antibonding properties of excited electronic states was presented which rationalized and predicted the types of photoreactions and relative quantum yields of chromium(III)[1] and cobalt(III) and rhodium(III)[2] complexes. The effects of the medium on the model's predictions have also been discussed.[3] In the case of the d^3 complexes, the model used quartet-state symmetry functions and doublet-state energy considerations when the photoeffects of the two types of states were considered.[1] In this note the photochemical consequences of configuration interaction, CI, are considered in detail. The primary importance of CI to the model is the result, derived herein, that the *fractional composition* of the lowest photoactive states vary in a regular manner. The relevance of fractional composition to the prediction of relative quantum yields in a series of chromium(III) complexes is discussed.

Symmetry Wave Functions

Symmetry functions for the doublet and quartet states of a d^3 configuration are tabulated or may be constructed from Table A24 in ref 4. Wave functions and energy matrices have also been published by Perumareddi.[5] The quartet states have been discussed elsewhere[1] and are reproduced here for convenience.

$$ {}^4B_{1g}({}^4A_{2g}) \qquad \phi_1 = |(xz)(yz)(xy)| \qquad (1)$$

$$ {}^4B_{2g}({}^4T_{2g}) \qquad \phi_2 = |(xz)(yz)(x^2-y^2)| \qquad (2)$$

$$ {}^4E_g({}^4T_{2g}) \quad \begin{cases} \phi_3 = -(1/2)|(yz)(xy)(x^2-y^2)| + & \\ \qquad (\sqrt{3}/2\ |(yz)(xy)(z^2)| & (3) \\ \phi_4 = -(1/2)|(xy)(xz)(x^2-y^2)| - & \\ \qquad (\sqrt{3}/2\ )|(xy)(xz)(z^2)| & (4) \end{cases}$$

$$ {}^4A_{2g}({}^4T_{1g}) \qquad \phi_5 = |(xz)(yz)(z^2)| \qquad (5)$$

$$ {}^4E_g({}^4T_{1g}) \quad \begin{cases} \phi_6 = -(1/2)|(yz)(xy)(z^2)| - & \\ \qquad (\sqrt{3}/2)|(yz)(xy)(x^2-y^2)| & (6) \\ \phi_7 = -(1/2)|(xy)(xz)(z^2)| + & \\ \qquad (\sqrt{3}/2)|(xy)(xz)(x^2-y^2)| & (7) \end{cases}$$

The members of the lowest manifold of doublet states with which we will be concerned are those which could lead to photochemical activity, *i.e.*, those which represent a substantial change in orbital population compared to the ground state $(d_{xz})^1(d_{yz})^1(d_{xy})^1$. As has been pointed out, the photoactive states can only involve the configurations $(d_{xz})^2(d_{yz})^1$, $(d_{xz})^1(d_{yz})^2$, $(d_{xy})^2(d_{xz})^1$, and $(d_{xy})^2(d_{yz})^1$. The former two represent an increase in electron population in the *z* direction; the latter two represent a decrease compared to the ground state. The symmetry functions involving the above four configurations are

$$ {}^2E({}^2T_1) \quad \begin{cases} \psi_1 = \dfrac{1}{\sqrt{2}}\left[(d_{xz})^2(d_{yz})^1 - (d_{xy})^2(d_{yz})^1\right] & (8) \\ \psi_2 = \dfrac{1}{\sqrt{2}}\left[(d_{xy})^2(d_{xz})^1 - (d_{yz})^2(d_{xz})^1\right] & (9) \end{cases}$$

$$ {}^2E({}^2T_2) \quad \begin{cases} \psi_3 = \dfrac{1}{\sqrt{2}}\left[(d_{xy})^2(d_{yz})^1 + (d_{xz})^2(d_{yz})^1\right] & (10) \\ \psi_4 = \dfrac{1}{\sqrt{2}}\left[(d_{xy})^2(d_{xz})^1 + (d_{yz})^2(d_{xz})^1\right] & (11) \end{cases}$$

The *symmetry functions* contain equal admixtures of increase and decrease of electronic population along the *z* direction and thus could not lead to photochemical consequences. The energies of the symmetry states are shown in Figure 1.

Configuration Interaction

For two wave functions, ψ_a and ψ_b, of the same irreducible

(1) J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972).

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

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

(4) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, U. K., 1964, pp 396–407.

(5) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967).

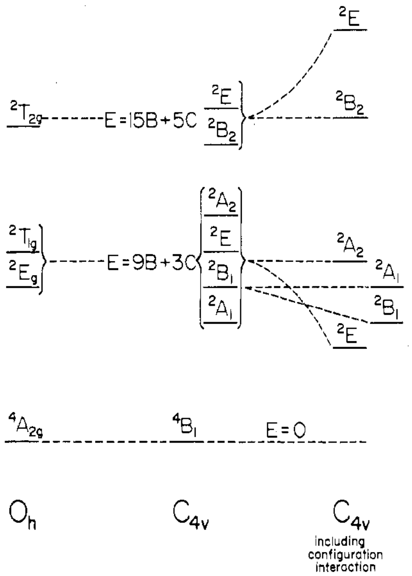

Figure 1. Correlation diagram for the lowest doublet states of a d^3 configuration. The states ^2E_g and $^2T_{1g}$ are accidentally degenerate neglecting CI and are not changed in energy under a tetragonal field.

representation of the molecular point groups, the complete energy matrix has the general form

$$\begin{array}{cc} \psi_a & \psi_b \\ \left(\begin{array}{c} E_a \\ v \end{array}\right. & \left.\begin{array}{c} v \\ E_b \end{array}\right) \end{array} \tag{12}$$

where $v = \langle\psi_a|H|\psi_b\rangle \neq 0$ and $E_i = \langle\psi_i|H|\psi_i\rangle$. The eigenfunctions are

$$\psi'_a = \frac{1}{\sqrt{1 + \lambda^2}}(\psi_a + \lambda\psi_b) \tag{13}$$

$$\psi'_b = \frac{1}{\sqrt{1 + \lambda^2}}(\lambda\psi_a - \psi_b) \tag{14}$$

Assuming that $|v/(E_a - E_b)| \ll 1$, the mixing coefficient λ has the value

$$\lambda = v/(E_a - E_b) \tag{15}$$

and the eigenvalues of the complete energy matrix have the forms

$$E'_a = E_a + \frac{v^2}{E_a - E_b} \qquad E'_b = E_b - \frac{v^2}{E_a - E_b} \tag{16}$$

The Hamiltonian matrix may also be diagonalized exactly to give

$$\psi'_a = \left[\frac{\epsilon - (E_a - E_b)}{2\epsilon}\right]^{1/2} \psi_a - \left[\frac{\epsilon + (E_a - E_b)}{2\epsilon}\right]^{1/2} \psi_b \tag{17}$$

where $\epsilon = [4v^2 + (E_a - E_b)^2]^{1/2}$

Doublet States. The appropriate matrix elements for the doublet states are[6]

$$\langle\psi_1|H|\psi_1\rangle = \langle\psi_2|H|\psi_2\rangle = 3A - 6B + 3C - (6/5)\Delta + 7Dt = E(^2E(^2T_1)) \tag{18}$$

$$\langle\psi_3|H|\psi_3\rangle = \langle\psi_4|H|\psi_4\rangle = 3A + 5C - (6/5)\Delta + 7Dt = E(^2E(^2T_2)) \tag{19}$$

$$\langle\psi_1|H|\psi_3\rangle = \langle\psi_2|H|\psi_4\rangle = -3Ds + 5Dt \tag{20}$$

$$\langle\psi_1|H|\psi_4\rangle = \langle\psi_2|H|\psi_3\rangle = 0 \tag{21}$$

The wave functions for the lowest of the doublet states, $^2E(^2T)$, including configuration interaction are

$$\psi'_1 = \frac{1}{\sqrt{1 + \lambda^2}}\left[\frac{1 + \lambda}{\sqrt{2}}(d_{xz})^2(d_{yz})^1 + \frac{\lambda - 1}{\sqrt{2}}(d_{xy})^2(d_{yz})^1\right] \tag{22}$$

$$\psi'_2 = \frac{1}{\sqrt{1 + \lambda^2}}\left[\frac{1 + \lambda}{\sqrt{2}}(d_{xy})^2(d_{xz})^1 + \frac{\lambda - 1}{\sqrt{2}}(d_{yz})^2(d_{xz})^1\right] \tag{23}$$

Quartet States. The appropriate matrix elements are[6]

$$\langle\phi_3|H|\phi_3\rangle = \langle\phi_4|H|\phi_4\rangle = 3A - 15B - (1/5)\Delta - (7/4)Dt \tag{24}$$

$$\langle\phi_6|H|\phi_6\rangle = \langle\phi_7|H|\phi_7\rangle = 3A - 3B - (1/5)\Delta + 2Ds + (3/4)Dt \tag{25}$$

$$\langle\phi_3|H|\phi_6\rangle = -\langle\phi_4|H|\phi_7\rangle = (\sqrt{3}/4)(Ds + 5Dt) \tag{26}$$

$$\langle\phi_3|H|\phi_7\rangle = \langle\phi_4|H|\phi_6\rangle = 0 \tag{27}$$

The wave functions for the lowest ^4E state including configuration interaction with $^4E(^4T_1)$ are

$$\phi'_3 = \frac{1}{\sqrt{1 + \lambda^2}}\left[\frac{\sqrt{3} - \lambda}{2}(d_{yz}d_{xy}d_{z^2}) + \frac{-\lambda\sqrt{3} - 1}{2}(d_{yz}d_{xy}d_{x^2-y^2})\right] \tag{28}$$

$$\phi'_4 = \frac{1}{\sqrt{1 + \lambda^2}}\left[\frac{-\sqrt{3} - \lambda}{2}(d_{xy}d_{xz}d_{z^2}) + \frac{\lambda\sqrt{3} - 1}{2}(d_{xy}d_{xz}d_{x^2-y^2})\right] \tag{29}$$

Interaction with $^4E(^4T_2(^4P))$ has not been included in the above analysis because its effect on λ will be less than half that of the $^4E(^4T_2(^4F))$ state.

Photochemical Consequences

In a recent paper we showed that changes in quantum yields of ligand labilization in a series of complexes can be explained in terms of changes in the π-bonding and antibonding effects of doublet states.[1] The predictions based on the simple one-electron picture required the assumption that changes in relative population of several doublets are caused by changing the ligands. In terms of the more exact representation of the doublet states including configuration interaction, we show here that the changes in quantum yields are determined by the relative proportion of the photoactive configuration in a populated excited doublet state.

The low-energy, potentially photoactive doublet configurations are $(d_{xz})^2(d_{yz})^1$, $(d_{yz})^2(d_{xz})^1$, $(d_{xy})^2(d_{xz})^1$, and $(d_{xy})^2(d_{yz})^1$. The first pair (labeled α in ref 1) labilizes π bonding in the z direction and strengthens π bonding in the xy direction between π-donor ligands and the metal. The second pair (γ in ref 1) causes the opposite changes. When configuration interaction is neglected, the lowest energy doublet state containing the above configurations, $^2E(^2T_1)$, contains equal contributions of each (eq 8, 9) and thus would be photochemically inactive. When CI is included, the lowest energy ^2E state contains as its major component the pair of configurations which are lowest in energy (*vide infra*). For example, if the energies of the one-electron d orbitals are d_{xz}, $d_{yz} > d_{xy}$ (class I of ref 1), the pair of configurations $(d_{xy})^2(d_{xz})^1$ and $(d_{xy})^2(d_{yz})^1$ are lower in energy than

---

[6] Reference 4, Chapter 9.

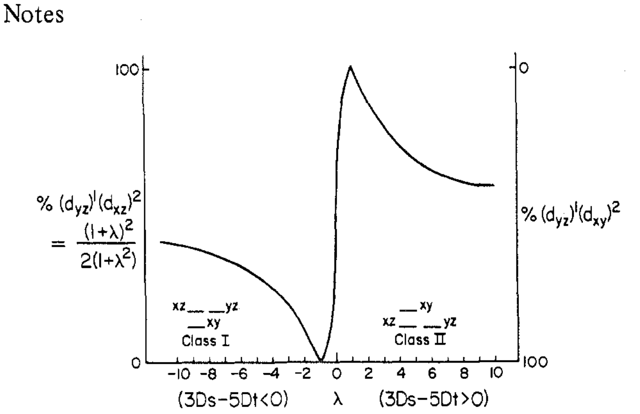

Figure 2. Plot of the per cent composition of the $^2E(^2T_{1g})$ state as a function of the mixing parameter λ. The 50% composition occurs at the crossover point between class I and class II when $\lambda = 0$.

$(d_{xz})^2(d_{yz})^1$ and $(d_{yz})^2(d_{xz})^1$ and the lowest doublet will be mainly $(d_{xy})^2(d_{xz})^1$ and $(d_{xy})^2(d_{yz})^1$ in character. The results of an explicit calculation of the per cent $(d_{xy})^2(d_{xz})^1$ or $(d_{xy})^2(d_{yz})^1$ character in the lowest ^2E state are shown in Figure 2. In the figure, the square of the coefficient of the above-named configurations in the ^2E wave function of eq 22 and 23 (representing the per cent contribution of them to the wave function) is plotted *vs.* the mixing coefficient λ. The 50% composition occurs exactly at the crossover between class I and class II, *i.e.*, where $3Ds - 5Dt = 0$.

The variation in quantum yield of ligand aquation which occurs as the axial ligand is continuously changed from a π donor (class I) to a π acceptor (class II) may be explained in terms of the continuous change of composition of the lowest ^2E state. The previous assumption that the changing relative populations of several doublet states caused the variation in quantum yield is not necessary.

Consider next the quartet states which are primarily responsible for the photoactivity of six-coordinate chromium(III) complexes.[7] The per cent composition of the lowest quartet state of all three classes, $^4E(^4T_2)$, is 75% d_{z^2} not including configuration interaction. As λ increases from -1.73 to $+0.59$, the per cent d_{z^2} character increases from 0 to 100%. Using eq 15, 26, 28, and 29 and previously calculated tetragonal crystal field parameters,[8,9] we calculate that for *trans*-$Cr(en)_2X_2^+$, when $X^- = F^-$, % $d_{z^2} = 66\%$; when $X^- = Cl^-$, % $d_{z^2} = 87\%$; and when $X^- = Br^-$, % $d_{z^2} = 88\%$. It is thus expected that populating the $^4E(^4T_2)$ state will result in increasing amounts of *x*- and *y*-axis labilization relative to *z*-axis labilization in the series $Br^- \cong Cl^- < F^-$. The *trans*-difluoro complex is unique in the series of *trans*-dihalo complexes because it is the only one with the majority of its labilizing character in the *xy* plane when the antibonding character of a pure d_{z^2} orbital in the *xy* plane is taken into account. This result, in addition to π stabilization discussed in a previous publication,[1] explains the aquation of ethylenediamine in *trans*-difluorobis(ethylenediamine)chromium(III) ion.

The above calculations of configuration interaction between the excited doublet states and between the excited quartet states of tetragonal chromium(III) complexes reveal that the concept of per cent composition of a configuration in a state is important when applying our ligand field model to predict photoreactions and relative quantum yields. The results are particularly satisfying for the doublet-state considerations because they remove the necessity of assuming that varying *populations* of the doublet states result in varying quantum yields.[1] The populations probably do vary in the manner suggested in the previous work when the energy differences between the doublets are small. When the energy differences become large because of a rapid decrease in ^2E energy, the quantum yields are governed by the per cent composition of the lowest state.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

---

[7] N. Sabbatini and V. Balzani, *J. Amer. Chem. Soc.*, 94, 7587 (1972), and references therein.

[8] D. A. Rowley, *Inorg. Chem.*, **10**, 397 (1971).

[9] R. L. Klein, Jr., N. C. Miller, and J. R. Perumareddi, paper presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., 1972; submitted for publication.

Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Controlled Mechanisms of Electron-Transfer Reduction of Coordinated Nitrosyls[1]

J. Armor

Received January 15, 1973

Although the reduction of metal-ligand systems has been the subject of recent attention,[2-4] generally,[5] the ligands have not been among those recognized as being reducible in multiple steps. We wish to report the results of some recent investigations into the area of the reduction of coordinated nitrosyls which demonstrate the importance of considering both the type of metal nitrosyl undergoing reduction and the dramatic variations in reactivity which can occur.

Nitrosyl,[6] as a ligand, can be reduced successively through several stable intermediate oxidation states (NO^0, NO^-, N_2, NH_3OH^+, N_2H_4, NH_3). Although the physical properties[7,8] of metal nitrosyls are under intensive investigation, their chemical properties have received little attention. Several years ago, Griffith[9] described some initial experiments on the reduction of ruthenium nitrosyls with Sn(II) in Cl^- media. These studies indicated that ruthenium ammines *may* be produced; however, Griffith concluded that none of his "formulations were convincing, and, clearly, this is a field which should be more fully investigated."[9]

At the outset, the extent of the reduction of the nitrosyl might be expected to be controlled by the metal centers and/or the ligand environment. Three nitrosyls, $Ru(NH_3)_5NO^{3+}$, $Co(NH_3)_5NO^{2+}$, and $CrNO^{2+}$, will be discussed. We have chosen as our common reductant Cr^{2+}. This ion has several

---

[1] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, and at the American Chemical Society Symposium on the "Activation of Small Molecules by Transition Metals," Buffalo, N. Y., June 1972.

[2] J. Armor and H. Taube, *J. Amer. Chem. Soc.*, 93, 6476 (1971).

[3] C. Norris and F. Nordmeyer, *J. Amer. Chem. Soc.*, 93, 4044 (1971).

[4] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **10**, 198 (1970); *J. Amer. Chem. Soc.*, 93, 625 (1971).

[5] E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966).

[6] The term nitrosyl refers to NO, NO^-, or NO^+ bound to a metal center.

[7] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

[8] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 93, 1789 (1971).

[9] W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, p 199.