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Ligand-Field Model of Photoinduced Isomerizations of Ruthenium(III) Complexes

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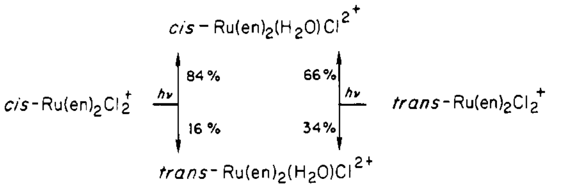
The substitution photostereochemistry of octahedral d^5 complexes is analyzed on the example of cis- and trans-disubstituted Ru(III) amines. On the basis of a dissociative mechanism, state correlation diagrams suggest important differences between d^5 and d^6 photochemistry. The absence of thermally equilibrated excited states in the five-coordinated fragment may be a specific d^5 feature.

Introduction

Ligand photosubstitutions in transition-metal complexes often induce substantial stereochemical changes.[1,2] Several detailed aspects of the observed photostereochemistry can be explained within the framework of ligand-field (LF) theory.[3] Although research on the photostereochemistry of six-coordinated compounds has been extensive,[4] all complexes studied to date contain either three or six d electrons. As could be anticipated, these two cases separate into two different rearrangement patterns, depending on the valence electron count.

Only recently, an effort was made to go beyond the description of the two paradigm systems. Rerek and Sheridan[5] reported the first detailed analysis of photolysis and photoisomerization results at a Ru(III) center, containing five d electrons. Their conclusions are summarized in eq 1, where en stands for ethylenediamine.[6]



$$\begin{tikzcd} & \textit{cis}\text{-Ru(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+} & \\ \textit{cis}\text{-Ru(en)}_2\text{Cl}_2^{+} \arrow[ur, "h\nu\ 84\%"] \arrow[dr, "16\%"'] & & \textit{trans}\text{-Ru(en)}_2\text{Cl}_2^{+} \arrow[ul, "h\nu\ 66\%"'] \arrow[dl, "34\%"] \\ & \textit{trans}\text{-Ru(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+} & \end{tikzcd} \qquad (1)$$

The most striking feature about this equation is that it is at variance with any established stereochemical pattern in analogous d^3 or d^6 compounds. Chloride loss in *trans*-Cr(en)$_2$Cl$_2^+$ is 100% stereomobile,[7] while both *cis*- and *trans*-Rh(en)$_2$Cl$_2^+$ yield *trans*-Rh(en)$_2$(H$_2$O)Cl^{2+} as the only photoproduct;[8] the Co(III) isomers photolyze to an identical mixture of *trans*- and *cis*-aquohalo products, with a 70/30 preference for the *trans* product.[9]

As a matter of fact, all these complexes are nonisoelectronic, and chemical similarities cannot really be expected. Nevertheless, it remains to be investigated if the LF model—which was used hitherto in explaining d^3 and d^6 photostereochemistry[10,11] —can be extended to incorporate d^5 systems as well.

LF Excited States of Strong-Field d^5 Complexes

Strong-field d^5 complexes with octahedral symmetry have a degenerate $^2T_{2g}(t_{2g}^5)$ ground state. The $t_{2g} \rightarrow e_g$ excitation gives rise to two low-lying quartet states ($^4T_{1g}$, $^4T_{2g}$) and several excited doublet states. It will be assumed that the lowest excited state ($^4T_{1g}$) of this manifold is the main precursor of the photosubstitutional activity. This assumption is certainly in line with excited-state mechanisms that are currently being proposed for d^3 and d^6 complexes (photochemical Kasha rule); moreover, there is no evidence for participation of the (low-lying) ligand-to-metal charge-transfer states in the ligand-exchange process.[5] It is true, however, that a direct experimental assessment of the photophysical mechanism is still lacking; no luminescence from a strong-field d^5 ligand-field state has been reported so far.[12]

Although in the three types of systems (d^3, d^6, d^5) the photoactive states originate from the same orbital excitation ($t_{2g} \rightarrow e_g$), differences arise as to the precise description of individual excited states. Adopting the symbols p, q, and r to denote all cyclic permutations of x, y and z, the photoactive state in $d^3(^4T_{2g})$ and $d^6(^3T_{1g})$-complexes corresponds to the orbital transitions[13] $pq \rightarrow p^2 - q^2$. Approximate wave functions can be written in a one-determinantal form, as given in eq 2a and 2b for $^4T_{2g}$ and $^3T_{1g}$, respectively.[14]

$$d^3(^4T_{2g}):\quad |(pr)(qr)(p^2-q^2)| \qquad (2a)$$

$$d^6(^3T_{1g}):\quad |(pr)^2(qr)^2(pq)(p^2-q^2)| \qquad (2b)$$

In both cases the main t_{2g}-electron density is concentrated along the r axis. In a d^5 complex however a quartet excited state can only be formed if depopulation of the t_{2g}^5 shell leads to a triplet subsystem, e.g. $(pq)^2(pr)(qr)$. This t_{2g}^4 configuration will have its principal t_{2g}-electron density in the pq-coordinate plane. Hence the lowest excited d^5 state ($^4T_{1g}$)—which minimalizes $t_{2g} \leftrightarrow e_g$ interelectronic repulsion—is formed by assigning the fifth d electron to the r^2 orbital, i.e. at maximal distance from the pq plane. Assigning the fifth electron to the $p^2 - q^2$ orbital gives rise to the higher excited $^4T_{2g}$ state (see eq 3a and 3b).

$$d^5(^4T_{1g}):\quad |(pr)(qr)(pq)^2(r^2)| \qquad (3a)$$

$$d^5(^4T_{2g}):\quad |(pr)(qr)(pq)^2(p^2-q^2)| \qquad (3b)$$

In summary, population of $p^2 - q^2$ requires less energy than population of r^2 for d^3 and d^6 systems, whereas the opposite situation is realized for d^5 systems.

The configurational divergence between eq 2 and 3 has further consequences for the state splittings in complexes of lower symmetry. Both trans and cis disubstitution are char-

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(1) Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61.
(2) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.
(3) (a) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 164. (b) Zink, J. I. *Ibid.* **1973**, *5*, 151. (c) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.*, in press.
(4) Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 4.
(5) Rerek, M. E.; Sheridan, P. S. *Inorg. Chem.* **1980**, *19*, 2646.
(6) Apparently Table I in ref 5 is incorrect. For *cis*-Ru(en)$_2$Cl$_2^+$, ϕ_{isom} should read 0.0005 and ϕ_{ret} 0.0025.
(7) Rosebush, W. J.; Kirk, A. D. *Can. J. Chem.* **1976**, *54*, 2335.
(8) Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1979**, *18*, 1818.
(9) Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3027. Sheridan, P. S.; Adamson, A. W. *Ibid.* **1974**, *96*, 3032.
(10) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475.
(11) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.
(12) Porter, G. B. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 2.
(13) Here, we use the shorthand notation xy for d_{xy}, $x^2 - y^2$ for $d_{x^2-y^2}$, $y^2 - z^2$ for $d_{y^2-z^2}$, $p^2 - q^2$ for $d_{p^2-q^2}$, z^2 for d_{z^2}, r^2 for d_{r^2}, etc. For instance, the d^6 $^1A_{1g} \rightarrow {}^3T_{1g}$ transition corresponds to the three orbital excitations $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{yz} \rightarrow d_{y^2-z^2}$, and $d_{zx} \rightarrow d_{z^2-x^2}$, or $pq \rightarrow p^2 - q^2$ for short. Since there are only five linearly independent d functions, one has for instance $d_{x^2-z^2} = (-3^{1/2}/2)d_{z^2} + (1/2)d_{x^2-y^2}$ and $d_{y^2-z^2} = (-3^{1/2}/2)d_{z^2} - (1/2)d_{x^2-y^2}$; these relations are used in eq 4.
(14) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1979**, *18*, 897.

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acterized by an effective tetragonal symmetry. In D_{4h} the d^5 state of interest, $^4T_{1g}$, is split into two components, $^4A_{2g}$ and ^4E_g, which can be written[13] to zeroth order as in eq 4.

$$^4A_{2g}(^4T_{1g}):\quad |(xz)(yz)(xy)^2(z^2)|$$

$$^4E_{ga}(^4T_{1g}):\quad -\frac{3^{1/2}}{2}|(xz)^2(yz)(xy)(x^2-y^2)| - \frac{1}{2}|(xz)^2(yz)(xy)(z^2)| \quad (4)$$

$$^4E_{gb}(^4T_{1g}):\quad \frac{3^{1/2}}{2}|(xz)(yz)^2(xy)(x^2-y^2)| - \frac{1}{2}|(xz)(yz)^2(xy)(z^2)|$$

The first-order tetragonal splitting is proportional to the difference in average spectrochemical strength between the ligands on axial and equatorial sites, denoted $10\overline{Dq}_{ax}$ and $10\overline{Dq}_{eq}$, respectively:

$$E(^4E_g) - E(^4A_{2g}) = \tfrac{1}{2}(10\overline{Dq}_{eq} - 10\overline{Dq}_{ax}) \quad (5)$$

Hence, since $10Dq(\mathrm{Cl}) < 10Dq(\mathrm{en})$, the lowest excited quartet component in *trans*-$Ru(en)_2Cl_2^+$ is the nondegenerate $^4A_{2g}$ state, vs. ^4E_g in the cis complex.

Now the photochemical properties of these components can further be analyzed by means of the previously developed I^* methodology.[3,15] This method determines the LF contribution to the bond orders I^* in a particular state, as a function of the angular overlap model (AOM) parameters σ and π. Expressions appropriate for the zeroth-order functions of eq 4 are

$$\begin{aligned} ^4A_{2g}:\quad & I^*(M\text{–}L_{ax}) = \sigma_{ax} + 2\pi_{ax} \\ & I^*(M\text{–}L_{eq}) = \tfrac{7}{4}\sigma_{eq} + \pi_{eq} \\ ^4E_g:\quad & I^*(M\text{–}L_{ax}) = \tfrac{7}{4}\sigma_{ax} + \pi_{ax} \\ & I^*(M\text{–}L_{eq}) = \tfrac{11}{8}\sigma_{eq} + \tfrac{3}{2}\pi_{eq} \end{aligned} \quad (6)$$

Since the σ contributions are far more important than the π contributions, it can be concluded from eq 6 that the $^4A_{2g}$ state predominantly labilizes the axial ligands, whereas for the ^4E_g state bond weakening is mainly concentrated on the equatorial sites. These predicted site preferences are consistent with observed axial Cl^- loss in *trans*-$Ru(en)_2Cl_2^+$ and equatorial ligand loss in *cis*-$Ru(en)_2Cl_2^+$.

In a comparison of these results with those of the earlier published discussion[16] of d^3 and d^6 complexes, two points should be noted: (i) The tetragonal splitting in d^3 and d^6 photoactive states follows exactly the same parameter dependence as in the d^5 case (eq 5) but with opposite sign. (ii) The nondegenerate components in $d^3(^4B_{2g})$ and $d^6(^3A_{2g})$ labilize the equatorial ligands, while the doubly degenerate components ^4E in d^3 and ^3E in d^6 preferentially weaken the axial bonds. Again this behavior is exactly the opposite of the d^5 behavior described in eq 6.

In the perspective of a photochemical Kasha rule,[17] these two reversals neutralize each other. So, somewhat surprisingly, as a net consequence, the lowest (photochemically active) states in all three systems are expected to exhibit identical site preferences in an identical LF environment.

LF-State Correlation Diagrams

Ligand loss leads to the formation of a five-coordinated square-pyramidal (SPY) fragment in its lowest quartet state. This state is not particularly susceptible to nucleophilic attack since it has no vacant orbitals pointing to its empty coordination site. Only the low-spin SPY ground state provides the electron distribution that enables facile ligand addition. Since this process is stereorigid,[18] isomerization can only be induced if exchange of basal and apical ligands is accomplished *before* the electrophilic state is reached.

At first sight this situation is very similar to the stereochemical model that has been proposed for d^6 complexes.[11] Here too, photostereomobility is attributed to the nonrigidity of a five-coordinated fragment in a metastable (triplet) state. Nonetheless, factual evidence indicates that both systems behave quite differently. Therefore a more detailed comparison of the energy profiles for the rearrangement processes in the two cases must be pursued.

Figure 1A represents the state correlation diagram for the isomerization of a RuN_4Cl^{2+} fragment as compared to the previously determined[11] corresponding energy curves for the Rh(III) analogue (Figure 1B). The underlying orbital correlations have been published before.[11] The state energies were calculated from conventional LF theory by following standard procedures. The parameters used for Rh(III) are $B = 0.041$ μm^{-1}, $C = 5.66B$, $\sigma(\mathrm{en}) = 1.136\ \mu m^{-1}$, $\sigma(\mathrm{Cl}^-) = 0.862\ \mu m^{-1}$, and $\pi(\mathrm{Cl}^-) = 0.140\ \mu m^{-1}$. These parameters are identical with the ones used in our previous work,[11] except for C, which was set equal to $4B$ in ref 11. The modification of C does not affect our conclusions, but the factor 5.66 is more in line with the available spectral evidence.[20] Since a detailed spectroscopical analysis of the d → d transition in Ru(III) complexes is entirely lacking, no separate Ru(III) parameters could be obtained. However, one can reasonably expect that both cations will have extremely similar parameters. Hence the same parameter set was used in parts A and B of Figure 1.

A. Apical–Basal Ligand Exchange in the Intermediate-Spin State. Although different symmetry labels apply in parts A and B of Figure 1, there is a definite similarity in the behavior of the lowest intermediate-spin state (triplet for d^6, quartet for d^5).[19] In either case, the trigonal bipyramid (TBP), having the heteroligand in an equatorial position, acts as a transition state on the quartet or triplet route. Moreover, both curves reach a minimum for the SPY structure with the halo ligand in an apical position.

B. Selection Rules in the Intermediate-Spin State. Chloride release from a cis complex leads to a SPY structure, substituted in its basal plane. In the coordinate frame of Figure 1, the heteroligand is on the y axis. Now this structure can rearrange in two possible ways, depending on what bond axis will bend, z or y. The photoactive states are approximately characterized by the configurations

$$\begin{aligned} d^5:\quad & |^4A''\rangle \approx |(xz)(yz)^2(xy)(x^2)| \\ d^6:\quad & |^3A'\rangle \approx |(xz)^2(yz)^2(xy)(x^2)| \end{aligned} \quad (7)$$

The $^4A''$ corresponds to $^4E_{gb}(^4T_{1g})$, given in eq 4. Clearly the additional electron (from d^5 to d^6) has to be assigned to the xz orbital.[11] This is important: if xz is doubly occupied, the motion in the xz plane, leading to a TBP structure (Cl axial), is unfavorable. Hence for the d^6 fragment, there is a strong orbital selection rule that prevents the formation of this TBP isomer. In the Ru(III) case, on the other hand, this process is orbitally allowed, although it may require a small activation energy.

C. TBP Ground States. In Rh(III) the TBP ground state necessarily has intermediate-spin character,[21] whereas in the

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(15) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1981**, *20*, 110.

(16) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.

(17) Zink, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8039.

(18) Thermal substitutions of *cis*- and *trans*-$Ru(en)_2Cl_2^+$, which are thought to proceed via the low-spin SPY states, are stereoretentive.[5]

(19) High-spin, low-spin, and intermediate-spin states are quintet, singlet, and triplet for d^6 and sextet, doublet, and quartet for d^5.

(20) Thomas, T. R.; Crosby, G. A. *J. Mol. Spectrosc.* **1971**, *38*, 118.

(21) Vanquickenborne, L. G.; Pierloot, K. *Inorg. Chem.* **1981**, *20*, 3673.

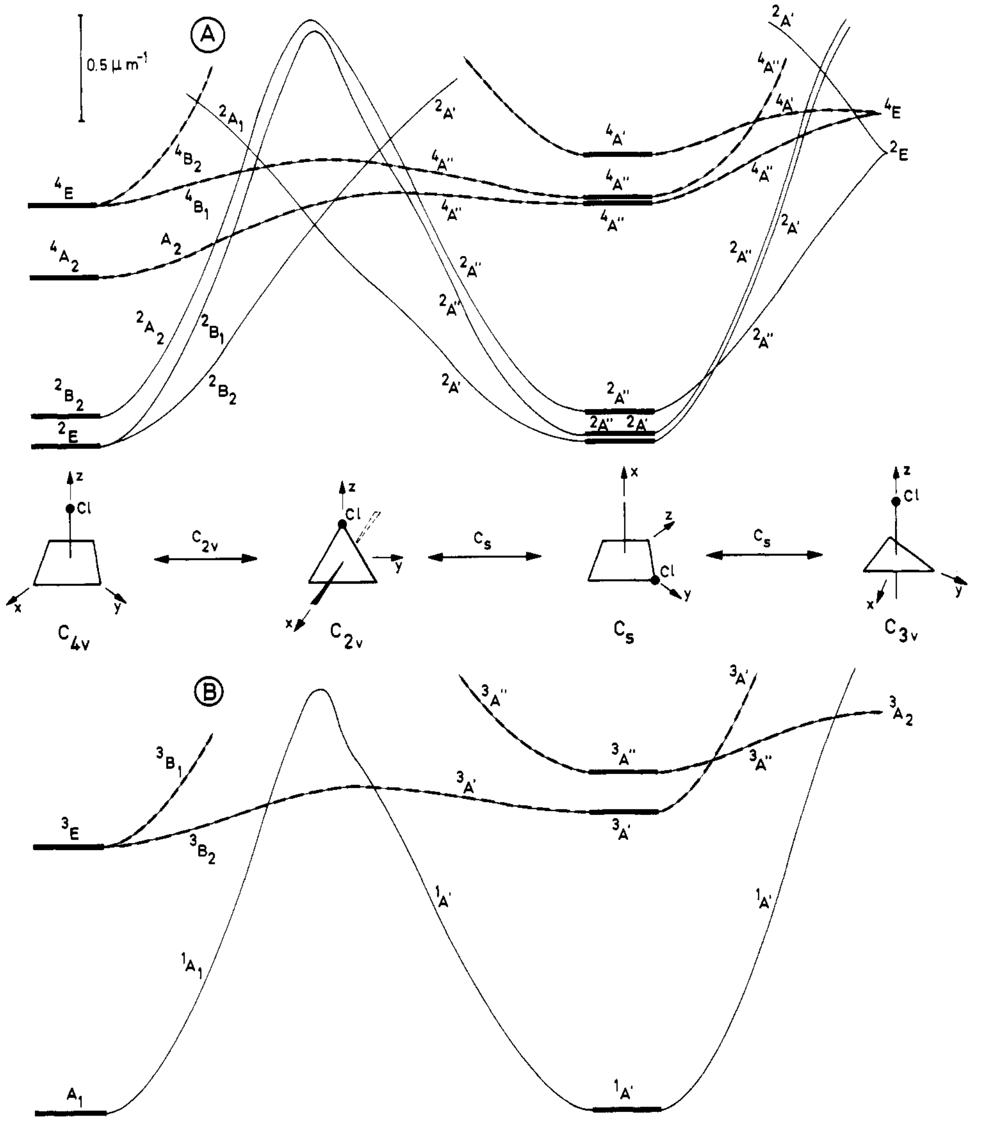

Figure 1. Schematic state correlation diagram for rearrangements of d^5 (A) and d^6 (B) five-coordinated fragments. Part B is a simplified version of the d^6 correlation diagram discussed in ref 11. In the square pyramids, the heteroligand is either in the apical or in a basal position; in the trigonal bipyramids, the heteroligand is either in an axial or in an equatorial position.

d^5 complexes a low-spin state is a valid alternative.

As always the spin pairing occurs at the expense of interelectronic repulsion energy but with a compensating gain in orbital energy.[22] This is schematically illustrated in Figure 2, for the simplified case of perfect trigonal symmetry. The actual calculations show (Figure 1A) that *both* TBP structures have doublet ground states, with $^4E''$ (or its components) close by in energy.

It should be stressed that the $^2E'$ ground state of the C_{3v} TBP structure (Cl axial), cannot be transformed into the C_{4v} SPY structure (Cl apical); the corresponding distortion gives rise to a high energy barrier,[10] and the resulting selection rule prevents the cycle in Figure 1A from being closed.

D. Low-Spin States and the Role of Spin–Orbit Coupling. At the SPY geometry, Figure 1A displays three low-lying doublet states vs. only one singlet state in Figure 1B. As a consequence, in the Ru(III) fragment, spin–orbit coupling (soc) interactions are much more pervasive and should be considered in detail.

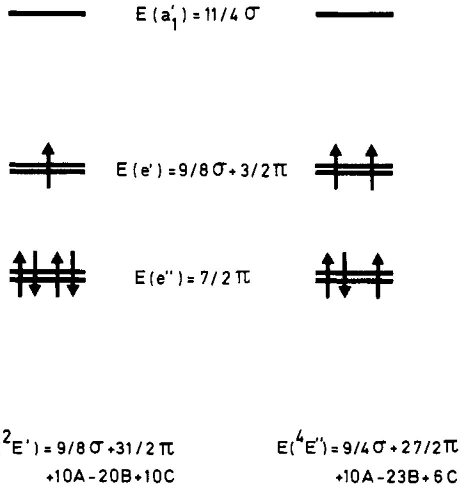

Figure 2. Two alternative ground states for a d^5 trigonal-bipyramidal fragment. Orbital energies of the five d orbitals are expressed in terms of the AOM σ and π parameters. The state energies include the repulsion contributions, expressed in terms of the Racah parameters *A*, *B*, and *C*.

Along the Cl apical–Cl basal exchange path, symmetry arguments alone do not lead to the prediction of zeros in the soc interaction matrix: all states involved in the doublet–quartet crossings give rise to equisymmetric Kramers doublets.

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(22) See, however: Vanquickenborne, L. G.; Haspeslagh, L. *Inorg. Chem.* **1982**, *21*, 2448.

In this respect, d^5 complexes are again noticeably different from d^6 complexes. Indeed, in the latter case, the singlet–triplet crossing is invariably allowed, since the singlet is totally symmetric, while the triplet has always at least one component that is not totally symmetric. In d^5 systems, on the other hand, because of the equisymmetric nature of the relevant Kramers doublets, spin–orbit coupling might affect the allowed character of one or more reaction paths. More specifically, if the intersections of the lowest quartet with $^2A_2$ or $^2B_1$ (along the C_{2v} path) or with the two $^2A''$ states (along the C_s path) were strongly disallowed, barrier crossing might become forbidden. As a consequence, the qualitative behavior of the five-coordinated fragment would be radically changed. In what follows, we will show that this hypothesis—however attractive—will not lead to answers that are compatible with the experimental observations.

The problem was worked out by diagonalizing the complete set of ligand field eigenstates with respect to soc interactions. Surprisingly, along the first half of the C_{2v} distortion path, the relevant eigenvectors still closely resemble the pure octahedral parent states. Except for the immediate vicinity of the crossing point, one has, following Griffith's notation[23]

$$|^4A_2\rangle \approx |t_{2g}^4e_g;\ ^4T_{1g}\ z\rangle \qquad |^2A_2\rangle \approx |t_{2g}^5;\ ^2T_{2g}\ \zeta\rangle$$
$$|^2B_1\rangle \approx |t_{2g}^5;\ ^2T_{2g}\ \eta\rangle \tag{8}$$

With use of these approximate wave functions a discussion of the role of spin–orbit coupling is much simplified. Indeed, inspection of the wave functions[23] shows that there is no first-order coupling between $^4A_2$ and $^2A_2$ since both states differ in two spin orbitals. The coupling of $^2B_1$ and $^4A_2$ is less trivial. In the C_{2v} double group the four $^4A_2$ components give rise to two Kramers doublets that are degenerate to first order. The nonzero interaction elements between both states are given in eq 9.

$$\left\langle ^4A_2 \pm \frac{3}{2}\middle|\mathcal{H}_{\text{soc}}\middle|^2B_1 \pm \frac{1}{2}\right\rangle = -\frac{i3^{1/2}}{2}\zeta$$
$$\left\langle ^4A_2 \pm \frac{1}{2}\middle|\mathcal{H}_{\text{soc}}\middle|^2B_1 \mp \frac{1}{2}\right\rangle = -\frac{i}{2}\zeta \tag{9}$$

$\mathcal{H}_{\text{soc}}$ stands for the spin–orbit coupling operator and ζ represents the usual one-electron coupling constant. From eq 9, it is possible to construct two wave functions describing an alternative Kramers doublet that has zero interaction elements with the $^2B_1$ state. The appropriate linear combinations of the noninteracting $^4A_2$ Kramers doublet are given by eq 10.

$$\psi_\pm = \frac{1}{2}|^4A_2 \pm \frac{3}{2}\rangle - \frac{3^{1/2}}{2}|^4A_2 \mp \frac{1}{2}\rangle \tag{10}$$

Therefore, along the C_{2v} reaction coordinate, there is an *adiabatic* quartet path, where the molecular fragment does not change its spin multiplicity when it traverses the coupling region.

In C_s symmetry, the spin–orbit interaction is more pronounced, resulting in more complicated wave functions. Although the description is definitely less transparent than in the C_{2v} symmetry, the two situations are sufficiently similar for the same conclusions to apply: for some quartet components at least, the crossing probability will be very close—if not quite equal—to unity.

In summation, spin–orbit coupling does not appear to be at the basis of the observed difference in behavior between d^5 and d^6 systems. It does not generate an additional barrier, preventing the molecule from reaching the TBP intermediate, either from the cis fragment, or from the trans fragment.

Discussion

The existing stereochemical model of d^6 photochemistry is based[11] on the requirement that the intermediate-spin state exists long enough to allow internal rearrangement: it is supposed to be a thermally equilibrated excited state (thexi state). Clearly, under this assumption, the asymmetric triplet barrier at the central TBP in Figure 1B explains a preferential basal → apical shift of the halo ligands and hence selective trans-product formation. This hypothesis has been further tested and confirmed in a variety of new experiments.[1,3c] More direct evidence for the finite lifetime of the excited state has been presented recently by Clark and Petersen.[24] They showed that thermal activation could affect the stereochemical course of a d^6 photosubstitution reaction.

Commenting on the Rerek–Sheridan results on d^5 systems, Petersen[25] has proposed that excited Ru(III) fragments might also follow essentially the same mechanism as the Rh(III) fragments. In order to reproduce the experimental product ratio, he had to introduce certain assumptions on the relative rate constants of the different processes. For instance, he had to assume that the radiationless quartet → doublet deactivation was 34 times faster in SPY (Cl basal) than in SPY (Cl apical). In principle, this picture might be correct, but it cannot be denied that it has a good deal of ad hoc character. It is always possible to fit the rate constants so as to mimic the experimental values of eq 1, but the similarity between the curves in parts A and B of Figure 1 is certainly not suggestive of a radically different kinetic control. Moreover, Petersen's scheme does not account for the absence of a selection rule in d^5 systems, turning the SPY (Cl basal) → TBP (Cl axial) transition into an allowed process. Figure 1A shows that the Ru(III) photostereochemistry requires the explicit consideration of the *two* TBP isomers.

In fact, one of the most striking features of Figure 1A is the existence of the intersection region near the TBP (Cl equatorial) ground state, where three states come quite close together and where the intersystem-crossing rate should be very important. It seems therefore quite probable that the intersystem crossing should take place in the TBP, and not in the SPY, as in the d^6 case.

When these features are taken together, a new picture emerges for the photostereochemistry of Ru(III) complexes. The photoactive quartet of d^5 systems behaves qualitatively differently from the photoactive triplet in d^6 systems. Along the quartet potential surface, the SPY structures will be able to rearrange so as to reach one of the $^2A'$ crossing points. Indeed, these crossing points will generally be lower than the top of the barrier, and—under the influence of spin–orbit coupling[26]—they will be even lower in energy than shown in Figure 1A. But at the crossing point, the molecular fragment will be diverted to one of the available doublet states and, from there, to one of the SPY's and to six-coordination. Crossing of the top of the barrier and basal–apical ligand exchange becomes a very improbable process. In this view, the d^5 photoactive quartet would not be a thexi state at all.

As a consequence, the SPY is transformed into an unstable TBP-like structure, regenerating a SPY along the different geometrical paths available. On purely statistical grounds, any TBP has three equally probable distortion modes resulting in a SPY. Therefore the predicted cis:trans product ratios can be expected[27] to be 2:1 for photolysis of *trans*-$Ru(en)_2Cl_2^+$ and

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(23) Griffith, J. S. "The Theory of Transition-Metal Ions"; Cambridge University Press: New York, 1964.

(24) Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1981**, *20*, 280.

(25) Petersen, J. D. *Inorg. Chem.* **1981**, *20*, 3123.

(26) The spin–orbit interaction between the lowest quartet and the two $^2A'$ states of $^2E'$ parentage is comparatively important; there are no zero matrix elements as discussed in part D of the section on LF-state correlation diagrams.

5:1 for photolysis of *cis*-$\mathrm{Ru(en)_2Cl_2^+}$. These predictions are very well confirmed by the experimental results, summarized in eq 1.

It should be noted that our predictions are largely independent of the specific parameter values, the only critical factor being the ratio of LF strength vs. interelectronic repulsion. If the LF strength decreases, a quartet ground state would tend to be favored in the TBP structure, inducing increased stereoretention in the photosubstitution process.

In conclusion, the present LF model points to important differences in the electronic structure of excited states in d^5 and d^6 systems; application of one and the same photostereochemical model appears inappropriate. A different role of the electronic selection rules and the nonexistence of a thexi state in the $\mathrm{RuN_4Cl^{2+}}$ fragment are suggested as new characteristic features of Ru(III) photochemistry. A critical evaluation of these proposals in future experimental work is most desirable.

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Registry No. *cis*-$\mathrm{Ru(en)_2Cl_2^+}$, 38687-00-2; *trans*-$\mathrm{Ru(en)_2Cl_2^+}$, 45839-20-1; Ru, 7440-18-8.

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(27) The three TBP distortions resulting in a SPY can be characterized by the one equatorial ligand that becomes apical. See also: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 250.

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The pK_a of Pyraziniumpentacyanoruthenate(II), $\mathrm{(CN)_5Ru(pzH)^{2-}}$

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The synthesis and characterization of $\mathrm{(CN)_5Ru(pz)^{3-}}$ (pz = pyrazine) and its N-methylated derivative, $\mathrm{(CN)_5Ru(pzCH_3)^{2-}}$, are described. The proton NMR spectra of pz or $\mathrm{pzCH_3^+}$ coordinated to $\mathrm{(NH_3)_5Ru^{2+}}$, $\mathrm{(CN)_5Ru^{3-}}$, $\mathrm{(CN)_5Fe^{3-}}$, and $\mathrm{(CN)_5Co^{2-}}$ are discussed. The effective pK_a's of $\mathrm{(CN)_5Ru(pzH)^{2-}}$ and $\mathrm{(CN)_5Fe(pzH)^{2-}}$ have been measured by spectrophotometric titration as 0.4 ± 0.1 and 0.065 ± 0.06 in contrast with 2.85 ± 0.1 for $\mathrm{(NH_3)_5Ru(pzH)^{3+}}$. The influence of $\mathrm{CN^-}$ on π back-bonding as compared to that of $\mathrm{NH_3}$ is discussed for complexes of the Fe(II), Ru(II), and Os(II) triad.

The parallels between the spectral properties and chemical reactivities of $\mathrm{(CN)_5FeL^{3-}}$ and $\mathrm{(NH_3)_5RuL^{2+}}$ complexes (L = aromatic nitrogen heterocycle) have been well documented.[1-3] It has become clear that π back-bonding from the metal to the ligand (L) is important for these low-spin d^6 complexes. The determination of the pK_a of the coordinated pyrazinium ion ($\mathrm{pzH^+}$) has been used to evaluate the back-bonding capability of the metal centers in such complexes. The complexes of pyrazine with $\mathrm{(CN)_5Fe^{3-}}$,[1] $\mathrm{(NH_3)_5Ru^{2+}}$,[4] and $\mathrm{(NH_3)_5Os^{2+}}$[5] have been examined in this regard. Direct comparison of results within the group is hindered by the requirement for a very strong-field ligand ($\mathrm{CN^-}$) to maintain low-spin Fe(II). In order to explore more fully the effect of $\mathrm{CN^-}$ on the back-bonding capability of the metal toward the sixth ligand (L), we have prepared a series of $\mathrm{(CN)_5RuL^{3-}}$ complexes (L = pyridine, pyrazine (pz), imidazole, pyrazole, and their derivatives).[6] The results of a study of $\mathrm{(CN)_5Ru(pz)^{3-}}$ are reported here.

The pyrazine ligand has been important in the development of the chemistry of the $\mathrm{(NH_3)_5RuL^{2+}}$ series. The classic experiment of Ford, Rudd, Gaunder, and Taube[4] in determining the pK_a of $\mathrm{(NH_3)_5Ru(pzH)^{3+}}$ and the subsequent syntheses of the Creutz–Taube ions,[7] $\mathrm{[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+,5+,6+}}$, are illustrative of this point. In this paper we report the pK_a's for $\mathrm{(CN)_5Ru(pzH)^{2-}}$ and $\mathrm{(CN)_5Fe(pzH)^{2-}}$. The results reveal a dramatic influence of $\mathrm{CN^-}$ vs. $\mathrm{NH_3}$ in competition with pyrazine for back-donation from Ru(II). A rich chemistry analogous to that found for the $\mathrm{(NH_3)_5RuL^{2+}}$ series is suggested for the $\mathrm{(CN)_5RuL^{3-}}$ complexes.

Experimental Section

Materials. Aldrich Gold Label pyrazine was used in the syntheses of the complexes. Potassium hexacyanoruthenate(II) trihydrate was used as received from Alfa. *N*-methylpyrazinium iodide was prepared by a literature method.[8] Other chemicals were reagent grade.

Preparation of the Pyrazine Complexes. The preparations of $\mathrm{Na_3[(CN)_5Fepz]\cdot 4H_2O}$,[1] $\mathrm{Na_2[(CN)_5Fepz]\cdot}x\mathrm{H_2O}$,[9] $\mathrm{K_2[(CN)_5Co(pz)]}$,[8] and $\mathrm{[(NH_3)_5Ru(pz)](ClO_4)_2}$[10] were carried out according to literature procedures with only minor modifications. All complexes were dried and stored under vacuum.

$\mathrm{K_3(CN)_5Ru(pz)}\cdot x\mathrm{H_2O}$. In a typical preparation, 0.0468 g (0.1 mmol) of $\mathrm{K_4[Ru(CN)_6]\cdot 3H_2O}$ was dissolved in 10 mL of water. Pyrazine, 0.08 g (1 mmol), was added. While the mixture was stirred, 10 mL of $\mathrm{Br_2}$ water (0.01 M $\mathrm{Br_2}$, 0.1 M KBr) was added slowly. The reaction of $\mathrm{Br_2}$ with $\mathrm{Ru(CN)_6^{4-}}$ is rapid and produces the pale yellow color of $\mathrm{(CN)_5RuOH_2^{3-}}$ (λ_{max} = 310 nm). One hour was allowed for the reaction with pyrazine to become complete. As $\mathrm{(CN)_5Ru(pz)^{3-}}$ is produced, the yellow color of the solution intensifies. The reaction was checked for completion spectrophotometrically. Upon completion, the solution was chilled in an ice/water bath and the product was precipitated by the addition of cold acetone or a 50/50/ (v/v) mixture

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