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### Molecular Orbital Approach to Photochemical Assignments of Excited States. Photoreactions of Coordinated Azide

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Recent molecular orbital calculations have shown that photosolvation reactions of first-row transition metal complexes can be understood in terms of the metal-ligand antibonding character acquired in the vertical ligand field photoexcited state.<sup>1</sup> One of the important implications of the excellent correlation between the calculated changes in antibonding character in the ligand field excited state and the observed photoinduced ligand losses is that the initial internuclear motions on the excited-state surface induced by the bond weakenings play an important role in the course of the photoreaction even if the surface is nondissociative. In order to determine the generality of the above method, a calculation of the photoreactions of a coordinated ligand initiated by transitions other than ligand field absorptions was carried out. The ligand chosen for study was the azide ion coordinated to cobalt(III), rhodium(III), and iridium(III) which has been systematically studied by Basolo and coworkers<sup>2-4</sup> and others.<sup>5</sup> In this note we show that the trends in the calculated bonding changes within the azide ion correlate with the trends in the

observed photoreactions as the metal is varied from cobalt to iridium. A new interpretation for the formation of the aquated metal is proposed which is consistent with all of the experimental data. Finally, it is shown how the calculations combined with the experimental data provide an approach to the chemical assignment of excited states.

### Methods of Calculations

The details of both the molecular orbital calculations of the complete acidiopentaammine complexes and the model problem are discussed elsewhere.<sup>1</sup> For  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ , the bond distances used were  $\text{M}-\text{N}(\text{NH}_3) = 1.968 \text{ \AA}$ ,  $\text{M}-\text{N}_1$  (azide) =  $1.943 \text{ \AA}$ ,  $\text{N}_1-\text{N}_2 = 1.208 \text{ \AA}$ , and  $\text{N}_2-\text{N}_3 = 1.145 \text{ \AA}$ .<sup>6</sup> The  $\text{M}-\text{N}_1\text{N}_2$  bond angle was  $125^\circ$ .<sup>6</sup> The numbering system is  $\text{M}-\text{N}_1-\text{N}_2-\text{N}_3$ .

In the model problem calculation of the  $\text{M}-\text{N}-\text{N}-\text{N}$  unit, the overlap integrals and VOIP's from the full EHMO-SCC calculation were used. The effect of varying the metal through the series  $\text{Co}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Ir}^{3+}$  was simulated by increasing the  $\text{M}-\text{N}_1$  overlap integral and decreasing the metal VOIP. The important states (*vide infra*) were more sensitive to the overlap integral than to the VOIP.

Only the calculated trends in bonding properties were used in this paper. Trends in the Mulliken overlap population<sup>7</sup> were used to interpret changes in the bonding.

The relative orderings of the levels in coordinated azide ion agree with those calculated for the free ion.<sup>8</sup> However, the metal has a profound effect on the energies of the orbitals and the N-N bonding characteristics. The importance of the perturbing effect of a coordinated group is illustrated by the unequal N-N bond lengths in coordinated azide (*vide supra*) and the large changes in N-N force constants (*e.g.*, in  $\text{HN}_3$ ,  $k_{\text{N}_1-\text{N}_2} = 1.01 \times 10^{-6} \text{ dyn/cm}^{-1}$  and  $k_{\text{N}_2-\text{N}_3} = 1.73 \times 10^{-6} \text{ dyn/cm}^{-1}$ ,<sup>9</sup> while in free azide  $k_{\text{N}_1-\text{N}_2} = k_{\text{N}_2-\text{N}_3} = 1.25 \times 10^{-6} \text{ dyn/cm}^{-1}$ ).<sup>10</sup> The changes in the N-N overlap populations upon coordination to a metal are discussed below.

### Results and Discussion

The four one-electron orbitals which will be considered here are in order of increasing energy  $\pi_{\text{non}}$ ,  $d_\pi$ ,  $d_\sigma^*$ , and  $\pi^*$  where  $\pi_{\text{non}}$  and  $\pi^*$  are ligand-centered nonbonding and antibonding  $\pi$  orbitals and  $d_\pi$  and  $d_\sigma^*$  are primarily metal-localized  $d$  orbitals. The  $\pi_{\text{non}}$  orbital is weakly  $\pi$  bonding with the metal when coordinated. The first two sets are filled. Thus, the four lowest energy transitions are  $d_\pi \rightarrow d_\sigma^*$  (ligand field, LF),  $d_\pi \rightarrow \pi^*$  (MTLCT),  $\pi_{\text{non}} \rightarrow d_\sigma^*$  (ligand to metal charge transfer, LTMCT), and  $\pi_{\text{non}} \rightarrow \pi^*$  (ligand localized, LL). The bonding changes caused by excitation into the LF bands have been extensively treated<sup>11-16</sup> and will not be discussed further here. Based on the known optical electronegativity<sup>17</sup> of the azide and cobalt(III) ions, the energies of the remaining three states in the cobalt complex probably follow the order  $\text{LTMCT} < \text{MTLCT} \sim \text{LL}$ . We will return to the question of the ordering. In the series of Co, Rh, and Ir complexes, the energy of the LTMCT state increases, and in the series Rh to Ir, the energy of the MTLCT state increases relative to the ground state.

The changes in bonding caused by populating the excited states are summarized in Table I. The calculated changes in the overlap populations from which the table is taken are graphically shown in Figure 1. Pertinent comparisons of the reactions expected on the basis of the calculated bond weakenings with those experimentally observed are enumerated below. (1) The predominant photoproducts observed from uv irradiation of azide-ammine complexes of cobalt(III) are  $\text{Co}(\text{II})$  and azide radicals.<sup>18,19</sup> The calculation shows that no N-N bond breaking of azide is expected in the LTMCT state. Thus, the  $\text{N}_3$  fragment is lost as a unit. (2) The observed photoproducts from 3500-Å irradiation of  $\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$  are

Table I

| Excited state <sup>a</sup> | Trend in bonding changes   |  |
|----------------------------|--|--|
|                            | Cobalt   | to Iridium   |
| LTMCT                      | No N-N labilization  | Weakly labilize N <sub>1</sub> -N <sub>2</sub> ; form IrN + N <sub>2</sub>                     |
| MTLCT                      | All N-N labilized; CoN <sub>2</sub> + N more probable <sup>b,c</sup> | Strongly labilize N <sub>2</sub> -N <sub>3</sub> ; form IrN <sub>2</sub> + N <sup>c</sup>      |
| LL                         | All N-N labilized; CoN <sub>2</sub> + N more probable <sup>b,c</sup> | Strongly labilize N <sub>1</sub> -N <sub>2</sub> ; form IrN + N <sub>2</sub> only <sup>c</sup> |

<sup>a</sup> LTMCT = ligand to metal charge transfer; MTLCT = metal to ligand charge transfer; LL = ligand localized. <sup>b</sup> N<sub>2</sub>-N<sub>3</sub> is labilized more than N<sub>1</sub>-N<sub>2</sub>. <sup>c</sup> There is only a very small change in the M-N<sub>1</sub> overlap population.

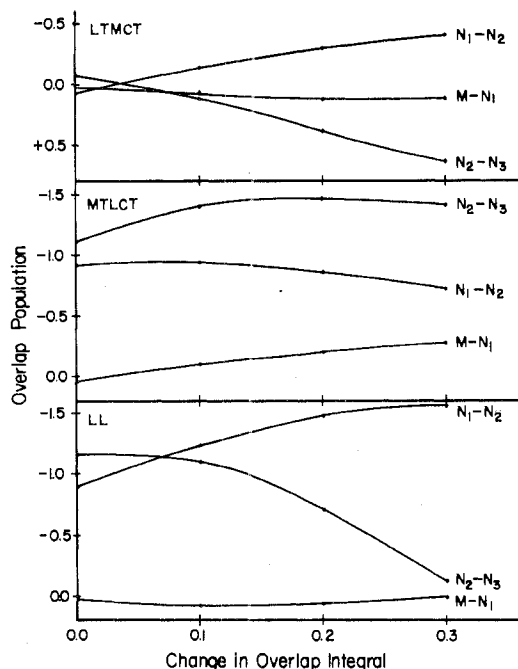


Figure 1. Calculated variations in the overlap populations of three excited states as a function of increasing metal-N<sub>1</sub> overlap integral. Positive numbers represent an increase in bonding; negative numbers, an increase in antibonding caused by the transition from the ground state to the indicated excited state.

primarily Rh(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>Cl<sup>3+</sup> and N<sub>2</sub>.<sup>2,3</sup> The quantum yield for formation of each of the products equals that for loss of the starting material. The calculated bonding change in both the LTMCT and the LL states is the weakening of the N<sub>1</sub>-N<sub>2</sub> bond leading to formation of Rh(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>2+</sup> + N<sub>2</sub>. The calculated quantum yields of formation of N<sub>2</sub> and Rh(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>Cl<sup>3+</sup> and loss of Rh(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>2+</sup> are also equal (following Basolo's argument that the coordinated nitrene intermediate quantitatively yields the Rh(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>Cl<sup>3+</sup> product).<sup>3</sup> (3) At shorter wavelengths (2540–2750 Å), the products of irradiating Rh(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>2+</sup> are Rh(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>Cl<sup>3+</sup>, Rh(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup>, and N<sub>2</sub>. The calculated effect of the MTLCT state on the bonding is a weakening of the N<sub>2</sub>-N<sub>3</sub> bond resulting in the formation of Rh(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>2+</sup> + N. The metal complex rapidly aquates to form Rh(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup> + N<sub>2</sub> as is observed. (4) The only products of photolysis of Ir(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>2+</sup> at 250–400 nm are Ir(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>Cl<sup>3+</sup> and N<sub>2</sub>. The calculated effect of populating the LL state is formation of Ir(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>2+</sup> + N<sub>2</sub>.

The experimental results and calculated predictions are totally consistent with the following assignments of the excited states. For cobalt, the photoredox reactions which have been observed with irradiation down to 2537 Å emanate from the LTMCT state. The other states are much higher in energy

in the cobalt complex and do not participate to any great extent. For rhodium, the long-wavelength (3500 Å) reactions originate from the LTMCT and LL states. The former is more efficiently populated but the latter is more reactive. As the wavelength of irradiation decreases, the LL state is more effectively populated and the quantum yield of nitrene formation increases. Simultaneously, the MTLCT state also becomes increasingly important and the aquopentaammine product is formed with increasing quantum yield. Thus, the disappearance quantum yield of the starting material and the nitrene formation quantum yield increase but the ratio of nitrene formation to disappearance quantum yields decreases. For iridium, the photoreactions originate from the LL state. The MTLCT state, which produces IrN<sub>2</sub> + N according to the calculations, is higher in energy (on the basis of the VOIP of the 5d orbitals and the raising of the π\* orbital because of metal-ligand π interactions) and does not participate. The above assignments differ from the previous interpretations<sup>2-4</sup> in two ways. First, the formation of coordinated nitrene is here ascribed to a combination of the LTMCT and LL states rather than to the LL state alone. However, as shown in Figure 1, the bonding changes in the LTMCT state are less than 50% as great as those in the LL state because the LTMCT transition depopulates an orbital (π<sub>non</sub>) which is primarily nonbonding. These small LTMCT bonding changes are very sensitive to changes in the metal VOIP because the π<sub>non</sub> orbital is the one which primarily mixes with the metal d<sub>π</sub> orbitals. The only reason for considering it here is to emphasize that it can reinforce the highly reactive LL state. The calculated reactivity of the LL state supports the assignment of Basolo, *et al.*<sup>2-4</sup> Second and most significantly, the formation of Rh(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>2+</sup> is here ascribed to formation of Rh(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>3+</sup> followed by rapid aquation rather than to formation of Rh(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> + N<sub>3</sub> followed by "additional reactions"<sup>3</sup> including reoxidation of the Rh(II) complex.

Additional support for the MO assignments is provided by the observed quantum yields of nitrogen formation. In the MO interpretation, 1 mol of N<sub>2</sub> should always arise from 1 mol of azide regardless of whether the azide is photolyzed *via* the M-N + N<sub>2</sub> or MN<sub>2</sub> + N pathway.<sup>20</sup> This prediction is in total accord with experiment. If the previously proposed mechanism<sup>4</sup> of Rh(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> + N<sub>3</sub> formation were true, all of the N<sub>2</sub> would arise from N<sub>3</sub> → <sup>3</sup>/2N<sub>2</sub>.<sup>4</sup> The observed discrepancy (1 N<sub>2</sub> was found from each N<sub>3</sub><sup>-</sup>) was previously attributed to alternative reaction paths.<sup>4</sup> In the MO interpretation, the observed amount of N<sub>2</sub> production is a natural consequence of the photolysis.

The excellent agreement between the calculated and observed photoreactivity suggests that the combination of photochemistry and simple molecular orbital theory may offer a generally useful method of assigning the excited states of transition metal complexes. This application is under further investigation in our laboratories. The agreement and self-consistency between the calculations, spectroscopy, and photochemistry of coordinated azide show that molecular orbital considerations are as useful for understanding the photoreactions of a coordinated ligand as they are for interpreting metal-ligand bond labilization.

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Registry No. Azide, 14343-69-2.

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## Correspondence

### A Model to Account for Differences in Excited-State Reactivity and Cage Recombination Processes in the Photoredox Chemistry of Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup> and Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup> 1

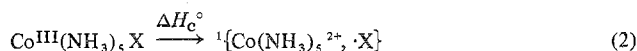
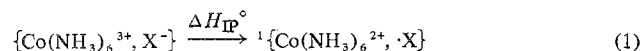
AIC403760

Sir:

The photoredox behavior of coordination complexes has long been of interest and several models, usually involving radical-pair species, have been proposed to account for both the charge-transfer spectra and photochemistry.<sup>2-6</sup> We have recently been systematically examining the energetics of charge transfer to metal (CTTM) spectra of Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> complexes and attempting to use this information together with the variations in product yield with composition of the solvent medium to provide insight into the mechanistic details of photoredox decompositions of these complexes.<sup>7,8</sup> In the progress of these studies it has become evident that Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup> is unique among the simple acidopentaammine complexes (*i.e.*, for X = Br, Cl, N<sub>3</sub>, and NCS, as well as NO<sub>2</sub>). Among the contrasts in photochemical behavior are the following. (1) A limiting value of the redox quantum yield,  $\phi_{\text{lim}}^{\text{Co}^{2+}}$ , has been found for ultraviolet charge-transfer excitation of each complex except Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup>.<sup>6-9</sup> (2) The photoredox yield has been found to be a far more complicated function of solvent (*e.g.*, in alcohols, acetonitrile, phosphoric acid, etc.) for Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> (X = Br, Cl, N<sub>3</sub>, NCS)<sup>8</sup> than for Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup>.<sup>9</sup> (3) The photoredox, Co<sup>2+</sup> + NO<sub>2</sub>, and the photoisomerization, Co(NH<sub>3</sub>)<sub>5</sub>ONO<sub>2</sub><sup>2+</sup>, products have been found to be competitively formed from a common precursor<sup>9b</sup>—this precursor has been postulated to be a radical-pair species which dissociates to form redox products or recombines to form the linkage isomer; however, *recombination does not appear to produce the more stable Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup> isomer.*<sup>9b,10</sup> (4) For the Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> (X = Br, Cl, NCS, N<sub>3</sub>) complexes we have found that the extrapolated threshold excitation energy for appreciable photoredox decomposition,  $E_{\text{th}}$ , is within 2 kK of the threshold energy for CTTM absorbance,  $E'_{\text{th}}$ ,<sup>7,8</sup> for Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup>,  $E'_{\text{th}} - E_{\text{th}} \approx 6$  kK.<sup>6,9,11</sup>

Consideration of the above points suggests that some dynamic components should be introduced into models for the chemistry of CTTM excited states and this can lead to an interpretation of the photoredox behavior of Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup>. Few features of the approach employed in the present report appear to have been anticipated in previous mechanistic discussions,<sup>2-9</sup> but the general approach does seem to have some mechanistic generality.

**A. General Considerations. 1. Energetics.** We have recently shown that  $\Delta H_{\text{IP}}^\circ$ , for reaction 1, and  $\Delta H_c^\circ$ , for reaction 2,



may be estimated from thermodynamic and kinetic parameters<sup>12</sup> and that comparison of these parameters with CTTM spectra of the cobalt(III) complexes implies an appreciable Franck-Condon contribution to the spectra of the ion-pair complexes.<sup>7,8b</sup> For several Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> complexes (*i.e.*, with X = Cl, Br, N<sub>3</sub>, NCS) our estimates of thermodynamic and spectroscopic parameters are such that  $\Delta H_c^\circ - E_{\text{th}} = 2 \pm 1$  kK/mol, and  $E_{\text{th}} \approx E'_{\text{th}}$ ; *i.e.*, these quantities are nearly equal within the expected precision of our estimates. It is useful to take Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup> as a prototype of the class of compounds; for this complex we estimate  $E_{\text{th}} = 22$  kK/mol,  $E'_{\text{th}} = 22$  kK/mol, and  $\Delta H_c^\circ = 24$  kK/mol. Allowing for some small Franck-Condon contribution to  $E'_{\text{th}}$ , this quantity may be taken to be an approximation to the vibrationally thermalized energy of potential energy manifold describing the spectroscopic CTTM excited state (<sup>1</sup>CT), and  $\Delta H_c^\circ$  may be taken as an approximation of the minimum energy required to form a geminate "radical pair" of net singlet spin multiplicity<sup>1</sup> [<sup>1</sup>Co(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup>, ·Br]. It may also be estimated that a radical pair of net triplet spin multiplicity containing high-spin cobalt(II), [<sup>3</sup>Co(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup>, ·Br], lies about 4 kK lower in energy than [<sup>1</sup>Co(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup>, ·Br].<sup>7,8b</sup> A qualitative representation of a potential energy surface connecting points corresponding to these estimated energy differences is shown in Figure 1.

**2. Franck-Condon Components.** The spectroscopic transition Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup>(<sup>1</sup>A<sub>1</sub>) → Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup>(<sup>1</sup>CT) generates the Franck-Condon excited state in a ground-state solvation environment and with ground-state metal-ligand bond distances. Both of these factors contribute repulsively to cause the initial Franck-Condon state to be higher in energy than a thermally equilibrated CTTM excited state with the same electronic configuration. If no other factors intervened, one would expect the initial Franck-Condon state to relax smoothly (along an "antibonding" trajectory) to primary radical-pair products, [<sup>1</sup>Co(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup>, ·Br]. An approach to generating such a trajectory is available if one considers the back-reaction, *i.e.*, the compression of the bonds in the radical-pair species and repolarization of the solvent to regenerate metal-ligand distances and solvation appropriate to the ground state. Very similar processes have been considered in detail for electron-transfer reactions<sup>13,14</sup> and in charge-transfer transitions in mixed dinuclear complexes.<sup>15</sup> The total free energy change involved in this process may be estimated from,  $\Delta G_{\text{R}} = (\lambda_i + \lambda_o)/4$ , with  $\lambda_i \approx 2k(\Delta r)^2$ , where  $k$  is a force constant and  $\Delta r$  the difference in bond lengths between equilibrated radical pair and initial excited-state species, and with  $\lambda_o$  given by (3)<sup>13,14,16</sup> at any distance of separation  $r$  of cobalt(II) and

$$\lambda_o = \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{el}}} \right) e^2 \quad (3)$$