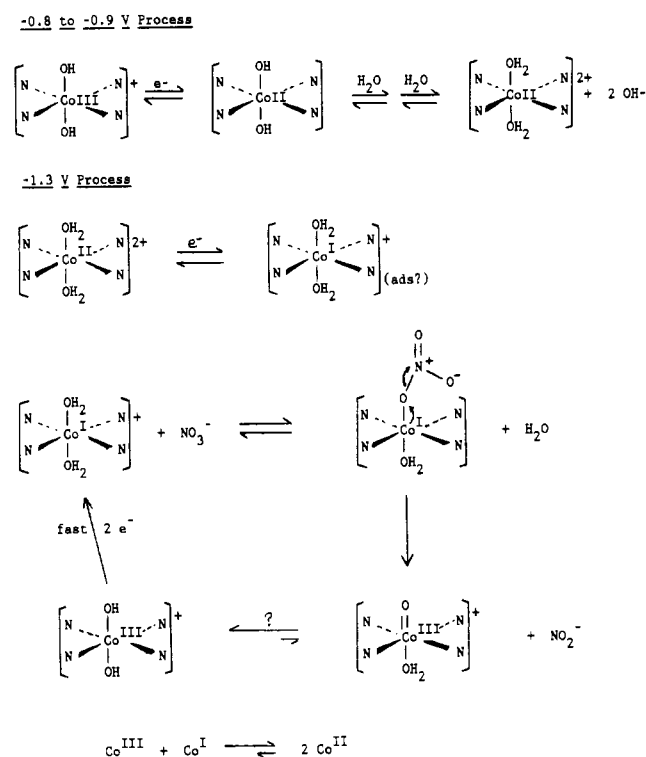


## Scheme I



Since the  $\text{Co}^{\text{III/II}}(\text{cyclam})$  wave is not significantly affected by the addition of nitrate, a key mechanistic role for a  $\text{Co}(\text{I})$  species is indicated in agreement with a variety of other studies in which electrocatalysis by reduced cobalt macrocyclic species has been observed. A plausible mechanistic pathway that entails a two-electron reduction of a coordinated nitrate ion is proposed in Scheme I.

Several aspects of Scheme I deserve comment. First, this mechanism does not address the complete reduction of nitrate or nitrite to hydroxylamine (or other products); only the initial reductive cleavage of a nitrogen-oxygen bond is considered. In this process, no protonations or hydride transfer reactions are suggested to occur. This is consistent with the lack of dependence of the

peak voltammograms of the nitrate reduction process on either the solution pH or the use of  $\text{NaOD}/\text{D}_2\text{O}$  in place of  $\text{H}_2\text{O}$ .

Complexation of nitrate (or nitrite) by the  $\text{Co}^{\text{I}}$  species is suggested in Scheme I. This has precedent in the detection, by Gangi and Durand, of a carbon dioxide-cobalt(I) complex with a related macrocyclic amine ligand that is stable on the cyclic voltammetric time scale.<sup>18</sup> The magnitude of the formation constant reported by these authors is sufficient to account for the shift of the  $\text{Co}^{\text{II/I}}$  wave out of the discharge region. It is interesting to note that electrocatalysis of carbon dioxide reduction by cobalt macrocyclic amines occurs in a potential region close to where the reduction of nitrate occurs and may proceed by a similar mechanism. The possibility that the key  $\text{Co}^{\text{I}}$  intermediate is adsorbed on the working electrode is suggested in Scheme I. A role for the electrode material is indicated by dependence of the catalytic current on the  $\text{Co}^{\text{III}}(\text{cyclam})$  complex concentration, which differs for the various electrodes employed; see Figure 6. If the catalytic process involves only homogeneous reactions in the diffusion layer, without double-layer effects, a similar concentration dependence would be seen for different electrode materials.

In summary, Scheme I accounts for the reductive cleavage of a N-O bond in nitrate or nitrite ions in base and partially explains the electrocatalysis by  $\text{Co}(\text{cyclam})$  ions in these systems. The catalytic action is provided by formation of an oxocobalt bond via reduction of a coordinated nitrate ion. While Scheme I is attractive, it should be stated that it is incomplete with regard to even the nature of the intermediates en route to hydroxylamine and ammonia.

**Acknowledgment.** This work was supported by a contract from E. I. du Pont de Nemours & Co., Inc., Savannah River Plant, Aiken, SC. Helpful discussions with Drs. S. W. Feldberg, C. E. Barnes, and S. Canagaratna are acknowledged. Drs. Mamantov and Orchard are gratefully thanked for the use of their rotating disk instrumentation.

**Registry No.** [*trans*- $\text{Cl}_2\text{Co}^{\text{III}}(\text{cyclam})$ ] $\text{Cl}$ , 15220-74-2; [*trans*- $\text{Cl}_2\text{Co}^{\text{III}}(\text{cyclam})$ ] $^+$ , 19973-61-6; [*trans*- $(\text{OH})_2\text{Co}^{\text{III}}(\text{cyclam})$ ] $^+$ , 64044-37-7; [*trans*- $(\text{H}_2\text{O})_2\text{Co}^{\text{III}}(\text{cyclam})$ ] $^{3+}$ , 46750-08-7; Pb, 7439-92-1; Au, 7440-57-5; Ag, 7440-22-4; Hg, 7439-97-6; NaOH, 1310-73-2;  $\text{NO}_3^-$ , 14797-55-8;  $\text{NO}_2^-$ , 14797-65-0;  $\text{NH}_3$ , 7664-41-7;  $\text{NH}_2\text{OH}$ , 7803-49-8.

(18) Gangi, D. A.; Durand, R. R., Jr. *J. Chem. Soc., Chem. Commun.* **1986**, 697-699.

Contribution from the Department of Chemistry,  
University of California, Santa Cruz, California 95064

## Solvent Effects on the Long-Axis Intraligand Transition of $\text{Ru}(\text{bpy})_3^{2+}$ and Related Compounds

Steven J. Milder

Received May 5, 1988

The effect of solvent polarizability on the energy of the intraligand, long-axis-polarized  $\pi\pi^*$  transition of bpy in  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{Ni}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ,  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ , and bpy free in solution and the  $^1\text{L}_a$  transition of anthracene is presented. The energy at the  $\lambda_{\text{max}}$  value of the transition shifts as a linear function of the polarizability,  $(1 - n^2)/(2n^2 + 1)$ , and the slopes of the plots range between  $5.6 \times 10^3$  and  $13.9 \times 10^3 \text{ cm}^{-1}$ . INDO/S CI calculations of the singlet spectra of bpy in the cis and trans conformations are presented. It is shown that a previously reported interpretation of the effect of solvent on the energy of the visible singlet metal-to-ligand charge-transfer ( $^1\text{MLCT}$ ) absorptions of  $\text{Ru}(\text{bpy})_3^{2+}$  is flawed. The current results support previously reported polarized absorption and emission studies, which show that throughout most of the visible  $^1\text{MLCT}$  absorption band of  $\text{Ru}(\text{bpy})_3^{2+}$  the initially produced excited state is delocalized over all three ligands.

### Introduction

The properties of the excited states of  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) have been extensively studied. In particular, much effort has gone into understanding the nature of the long-lived ( $\tau = 640 \text{ ns}$ ,  $\text{H}_2\text{O}$ ,  $20^\circ\text{C}$ ) emissive excited state.<sup>1</sup> A prepon-

derance of evidence from a number of techniques shows that in fluid solution this metal-to-ligand charge-transfer ( $\text{MLCT}$ ) triplet state has the transferred electron localized on one bpy at a time.<sup>2-7</sup>

(1) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(2) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(3) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowless, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.

There is some dispute whether the transferred electron is also localized on a single bpy when the complex is in a rigid environment.<sup>8-14</sup> However, recent absorption and Raman spectra of the excited state support a localized electron model for the excited state of the complex in rigid media as well.<sup>15,16</sup> Ru(bpy)<sub>3</sub><sup>2+</sup> in the single-ligand-localized MLCT state will have C<sub>2</sub> symmetry and thus should have a dipole moment. The ground-state complex has D<sub>3</sub> symmetry and thus will have no dipole moment.

It would be interesting to know how the D<sub>3</sub> ground state comes to be in the C<sub>2</sub> emissive excited state. At least two photophysical routes are possible. First, the initial excitation into the MLCT singlet states might be polar and the single-ligand localization is directly produced. Alternatively, the initial excitation into the MLCT singlet might be to a delocalized D<sub>3</sub> state, which then relaxes to the C<sub>2</sub> symmetry MLCT triplet. In this scheme the localization would take place in either a singlet or a triplet state during the nonradiative decay process to the emissive state. A number of experiments have either directly or indirectly addressed the problem of when localization of the transferred electron occurs. Recent time-resolved resonance Raman studies have given conflicting results.<sup>16,17</sup> In one study it appears that the Raman spectrum characteristic of the single-ligand-localized C<sub>2</sub> emissive state is obtained within 10 ps.<sup>16</sup> This was observed for Ru(bpy)<sub>3</sub><sup>2+</sup> dissolved both in fluid solution and in rigid media. This result implies that the localization must take place on a very fast time scale, though it does not say whether localization occurs directly during the absorption to the singlet MLCT state. On the other hand, another group found there was a lag on a picosecond time scale between the initial excitation and the observation of the resonance Raman spectrum of the C<sub>2</sub> triplet MLCT state.<sup>17</sup> This time lag increased with the viscosity of the solvent and was taken as due to the relaxation time necessary for the excited electron to localize onto one ligand. This result implies there is a relaxation on the picosecond time scale from a delocalized triplet state to a localized triplet state. If this result is correct, it implies that a delocalized singlet state is initially formed, which then inter-system-crosses to a delocalized triplet, which then undergoes the localization process, perhaps at a rate related to the rate of solvent relaxation.

The absorption spectrum of Ru(bpy)<sub>3</sub><sup>2+</sup> has been extensively studied under a number of conditions, including in single crystals and in mixed crystals at cryogenic temperatures.<sup>18-20</sup> These studies show that the strong singlet MLCT absorptions seen in the visible region are primarily polarized perpendicular to the C<sub>3</sub> axis of the complex. This has been interpreted as being consistent with the complex having D<sub>3</sub> symmetry and the two absorption peaks being due to transitions to delocalized bpy orbitals. The exact nature of the bpy orbitals involved in these transitions is not clear. It is generally agreed that the transition dipoles

transverse the short axis of the bpy ligands.<sup>18,21,22</sup>

The polarization of the excitation spectrum of Ru(bpy)<sub>3</sub><sup>2+</sup> in rigid glasses has been extensively studied.<sup>8-10,13,14,19,23</sup> Here it can be shown that if one has a purely delocalized absorption from a D<sub>3</sub> complex that is polarized perpendicular to the C<sub>3</sub> axis and then emission occurs from a short-axis, single-ligand-localized (or delocalized) transition, the polarization ratio should be 1/7 (0.14).<sup>24</sup> The polarization ratio through most of the singlet MLCT absorption band is near this value. However, at the red edge of the absorption it climbs to greater than 0.2. This "red edge" effect has been interpreted in different ways. It has either been attributed to direct absorption into a localized singlet at the red edge of the singlet transitions<sup>9,10</sup> or to a distribution of ground-state geometries, with those that are distorted from pure D<sub>3</sub> symmetry absorbing primarily at the red edge of the singlet transition.<sup>8,19</sup> For the postulated case of distorted Ru(bpy)<sub>3</sub><sup>2+</sup> complexes absorbing at the red edge of the spectrum, the distorted complexes (in C<sub>2</sub> symmetry) might be expected to be distorted in a similar way in the excited state. This could, in principle, lead to an emission polarization as large as 0.5.<sup>24</sup> Whatever the interpretation of the "red edge" effect, the low polarization through most of the excitation spectrum seems to argue for a delocalized charge-transfer absorption assignment for most of the spectrum.<sup>23</sup>

One group looked at the absorption maximum of the singlet MLCT bands of Ru(bpy)<sub>3</sub><sup>2+</sup> and related complexes as the solvent refractive index and dielectric constant were varied.<sup>25</sup> For Ru(bpy)<sub>3</sub><sup>2+</sup> they saw significant shifts with changes in refractive index (polarizability), and they attributed this to changes in the dipole moment of the complex between the ground and <sup>1</sup>MLCT states. From this they made the inference that the <sup>1</sup>MLCT states that give the strong visible absorption are directly single-ligand-localized charge-transfer states.

In the current work the solvent effects on the absorption spectrum of Ru(bpy)<sub>3</sub><sup>2+</sup> are extended to the intraligand (IL) ππ\* bands in the near-ultraviolet region. For comparison, similar solvent effects on the absorption spectrum are determined for other complexes with bpy ligands, for the free ligand, and for anthracene. Also, INDO/S CI calculations are presented for bpy in the C<sub>2v</sub> conformation found in metal complexes and for the C<sub>2h</sub> conformation found free in solution. These are all used to show that the solvent effects for both the ππ\* and the MLCT bands are similar in magnitude. It is discussed how the previously reported data on the solvent effects on the visible <sup>1</sup>MLCT bands of Ru(bpy)<sub>3</sub><sup>2+</sup> can be considered consistent with these bands being due to excitations to delocalized charge-transfer states.

## Experimental Section

Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was purchased from Aldrich and was recrystallized three times from H<sub>2</sub>O. Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>,<sup>26</sup> Ru(bpy)<sub>2</sub>Cl<sub>2</sub>,<sup>27</sup> and Ni(bpy)<sub>3</sub>Cl<sub>2</sub><sup>28</sup> were made by published procedures. Anthracene and 2,2'-bipyridine were obtained from Aldrich and were used as received. The solvents used in the study were reagent grade or better. DMSO, DMF, and DMA were dried over molecular sieves. All spectra were taken on an IBM 9420 spectrophotometer.

Calculations of the spectrum of 2,2'-bipyridine were done by using the all-valence-electron INDO/S method.<sup>29-32</sup> Two-centered repulsion integrals were evaluated by using an empirical Mataga-Nishimoto-Weiss formula. Transition energies and intensities were obtained from CI wave

- (4) Gold, J. S.; Milder, S. J.; Lewis, J. W.; Klinger, D. S. *J. Am. Chem. Soc.* **1985**, *107*, 8285.
- (5) Milder, S. J.; Gold, J. S.; Klinger, D. S. *Chem. Phys. Lett.* **1988**, *144*, 269.
- (6) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.
- (7) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.
- (8) Ferguson, J.; Krausz, E. *Inorg. Chem.* **1987**, *26*, 1383.
- (9) Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.
- (10) Blakley, R. L.; Myrick, M. L.; DeArmond, M. K. *Inorg. Chem.* **1988**, *27*, 589.
- (11) Ferguson, J.; Krausz, E. *Chem. Phys.* **1987**, *112*, 271.
- (12) Ferguson, J.; Krausz, E. *J. Phys. Chem.* **1987**, *91*, 3161.
- (13) Carlin, C. M.; DeArmond, M. K. *J. Am. Chem. Soc.* **1985**, *107*, 53.
- (14) Myrick, M. L.; Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 2841.
- (15) Milder, S. J.; Gold, J. S.; Klinger, D. S. *J. Phys. Chem.* **1986**, *90*, 548.
- (16) Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613.
- (17) Chang, Y. J.; Orman, L. K.; Anderson, D. R.; Yabe, T.; Hopkins, J. B. *J. Chem. Phys.* **1987**, *87*, 3249.
- (18) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.
- (19) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.
- (20) Yersin, H.; Gallhuber, E.; Hensler, G. *Chem. Phys. Lett.* **1987**, *134*, 497.

- (21) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683.
- (22) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238.
- (23) Myrick, M. L.; Blakley, R. L.; DeArmond, M. K.; Arthur, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 1325.
- (24) Albrecht, A. C. *J. Mol. Spectrosc.* **1961**, *6*, 84.
- (25) Kober, E. M.; Sullivan, B. P.; Meyer, T. *J. Inorg. Chem.* **1984**, *23*, 2098.
- (26) Demas, J. N.; Turner, T. F.; Crosby, G. A. *Inorg. Chem.* **1969**, *8*, 674.
- (27) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.
- (28) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1931**, 2213.
- (29) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.
- (30) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.
- (31) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223.
- (32) Mataga, N.; Nishimoto, K. *Z. Phys. Chem. (Wiesbaden)* **1957**, *13*, 140.

functions constructed from a basis of 197 configurations including all single excitations between the 14 highest occupied and the 14 lowest unoccupied MOs. Atomic coordinates for the  $C_{2v}$  conformation were taken from the published crystal structure of  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>33</sup> Hydrogens were placed at a distance of 1.10 Å from their bonding partner and at equal angles to the aromatic ring. For the  $C_{2A}$  conformation, the same coordinates were used, except that one of the bipyridine rings was rotated 180°.

## Results and Discussion

Before the current results on the solvent effects on the absorption spectrum of the  $\text{bpy } \pi\pi^*$  bands of  $\text{Ru}(\text{bpy})_3^{2+}$  and related species are presented, previous work on solvent effects on the absorption spectrum of the  $^1\text{MLCT}$  bands of  $\text{Ru}(\text{bpy})_3^{2+}$  will be discussed. This will place the present work in perspective and outline the relevant theoretical issues.

Previously reported work shows that the  $\lambda_{\text{max}}$  value of the visible  $^1\text{MLCT}$  absorption of  $\text{Ru}(\text{bpy})_3^{2+}$  shifts significantly when the solvent refractive index is varied.<sup>25</sup> It was found that for 19 solvents there was a high correlation ( $r = 0.939$ ) between the energy at the absorption maximum and the function  $F(n^2) = (1 - n^2)/(2n^2 + 1)$ , where  $n$  is the refractive index of the solvent. From a plot of  $E_{\text{max}}$  ( $E_{\text{max}}$  is the transition energy at  $\lambda_{\text{max}}$  in  $\text{cm}^{-1}$ ) versus  $F(n^2)$  a slope of  $3670 \pm 690 \text{ cm}^{-1}$  and a  $y$  intercept of  $22830 \pm 140 \text{ cm}^{-1}$  were obtained. The authors attempted to understand this result by using expressions previously derived from a semi-classical theory that correlates absorption shifts for a solute in solvents of differing refractive index and dielectric constant.<sup>34-37</sup> They presented two expressions for the absorption shift. One was the generalized red shift and applies for all solutes, including nonpolar solutes. The other depends on the solute's dipole moment in the ground and excited states involved in the transition. From the work of McRae,<sup>34</sup> they obtained an expression for the solvent shift of a nonpolar solute as  $\Delta E_{\text{max}} = (3.30Lf/b^3)[F(n^2)]$  ( $L \approx 80000 \text{ cm}^{-1}$ ,  $f$  = oscillator strength,  $b$  = radius of solute). They showed that for the  $^1\text{MLCT}$  absorption of  $\text{Ru}(\text{bpy})_3^{2+}$  this gave a slope for the plot of  $\Delta E_{\text{max}}$  versus  $F(n^2)$  of  $91 \text{ cm}^{-1}$ . This value is obviously less than the slope obtained for the  $^1\text{MLCT}$  absorption of  $\text{Ru}(\text{bpy})_3^{2+}$ , so the authors looked at other terms in McRae's expression that take into consideration the solute's dipole moment. They presented the expression  $\Delta E_{\text{max}} = ((\bar{\mu}_1 - \bar{\mu}_0)^2/b^3)[F(n^2)] + (2\bar{\mu}_0(\bar{\mu}_1 - \bar{\mu}_0)/b^3)((1 - D)/(2D + 1))$ , where  $D$  is the static dielectric constant.<sup>25</sup> In this expression,  $\bar{\mu}_0$  is the ground-state dipole moment and  $(\bar{\mu}_1 - \bar{\mu}_0)$  is the transition dipole.<sup>38</sup> Since the calculation of the dipole moment of a charged species depends on the origin of the coordinated system, it appears from their discussion that the authors took the Ru atom as the center of the coordinate system.<sup>39</sup> In the ground state the dipole moment is zero and the second term will not contribute. Consistent with this, no dependence of the solvent shift on  $D$  is observed. From the first term they get a value of  $14.1 \pm 6.1 \text{ D}$  for the transition dipole. From this they say there is a "dipole length" of  $(3.0-3.6) \pm 1.3 \text{ Å}$ .<sup>25</sup> This leads the authors to say that the  $^1\text{MLCT}$  absorption is directly to a state that has a dipole moment, and thus this state already represents the localization of the transferred electron on one of the bpy ligands.<sup>38</sup>

The authors ignore the influence of other terms in McRae's expression for the shift in  $E_{\text{max}}$  of a nonpolar solute in solvents of varying refractive index.<sup>40</sup> McRae describes how the solvent shift depends not only on the qualities of the transition being

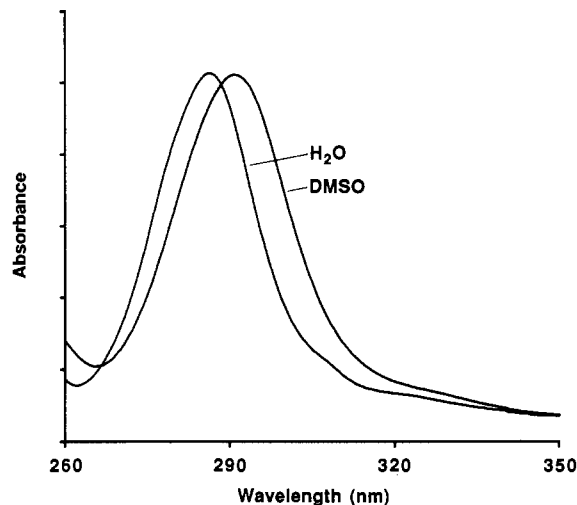


Figure 1. Absorption spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in  $\text{H}_2\text{O}$  and  $\text{DMSO}$  in the long-axis-polarized  $\pi\pi^*$  intraligand absorption region of the spectra.

studied but also on other transitions in the solute molecule, including excited-state transitions. His expression can be written as

$$\Delta E = 3.30((Lf_0/b^3) + \sum_{j \neq 0,i} [(v_{j0} - L)f_{j0}^2/b^3 - (v_{ji} - L)f_{ji}/2b^3])[F(n^2)]$$

where the first part of the second term represents contributions from other ground-state transitions in the solute and the second part of the second term represents excited-state transitions emanating from the excited state involved in the transition of interest. McRae, in his paper, gave the example of the effect of solvent on the absorption maximum of two transitions in benzene. In both these transitions it is shown that the dominant contribution to the solvent shift is not from the transition experiencing the shift. In fact, for the  $^1\text{B}_{2u}$  transition near 250 nm, other terms contribute up to a factor of 400 more to the solvent frequency shift than the term representing the transition itself. Because of the complexity of directly calculating all the terms in his expression, McRae advocated the use of an empirical function for determining the solvent shift of the absorption for nonpolar solutes,  $\Delta E_{\text{max}} = (AL + B)[F(n^2)]$ . From the previously reported results it is obvious that the  $^1\text{MLCT}$  bands fit this empirical function, and the solvent shifts of the  $^1\text{MLCT}$  absorption bands may be considered consistent with an interpretation that neither the ground nor the excited state has a dipole moment.

Tests were made of the effect of solvent on the maximum of the transition energy of the  $\pi\pi^*$  long-axis intraligand ( $^1\text{IL}$ ) transitions in  $\text{Ru}(\text{bpy})_3^{2+}$  and three related complexes. These transitions usually lie between 280 and 310 nm, the exact position depending on the metal complex.<sup>18,41</sup> When tris(bipyridine) complexes are resolved into their enantiomers, these  $^1\text{IL}$  transitions exhibit very large circular dichroisms ( $\Delta\epsilon > 100$ ). This implies that there is a large amount of exciton coupling between the transition moments of the  $\pi\pi^*$  transitions.<sup>42</sup> However, even with the interaction between the ligands, the  $\pi\pi^*$  transitions will not give rise to a dipole moment in the excited state of the tris(bipyridine) complexes.<sup>43</sup> A more complex situation occurs for complexes such as  $\text{Ru}(\text{bpy})_2\text{X}_2$ . Here the complex has  $C_2$  symmetry in the ground state and can have a significant dipole moment. Here one would expect an MLCT transition to the two bpy ligands to exhibit a large change in dipole moment. For the  $^1\text{IL}$  transitions, however, there will probably only be a small change in the dipole moment, and the effect of solvent can be considered

(33) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* 1979, 849.

(34) McRae, E. G. *J. Phys. Chem.* 1957, 61, 562.

(35) Marcus, R. A. *J. Chem. Phys.* 1965, 43, 1261.

(36) Marcus, R. A. *J. Chem. Phys.* 1963, 39, 1734.

(37) Bayliss, N. S. *J. Chem. Phys.* 1950, 18, 292.

(38) The designation in ref 25 of  $\bar{\mu}_0 - \bar{\mu}_1$  as the transition dipole is obfuscating, as the transition dipole is not the same as the difference between the dipole moments of the ground state and the excited state.

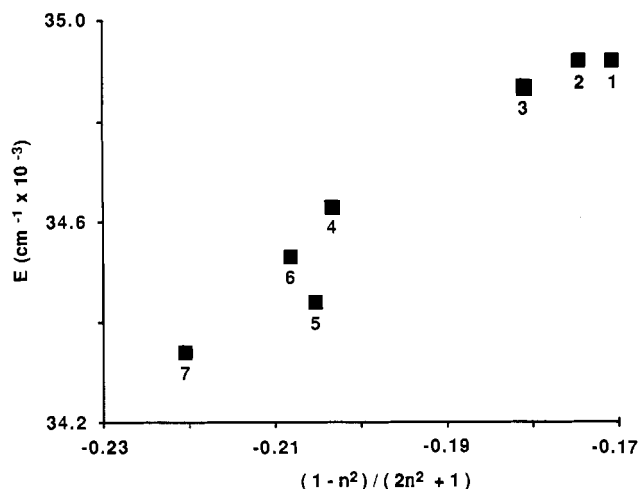
(39) A dipole moment in a complex occurs when there is a nonsymmetric placement of charge. For a charged species, the calculation of the dipole moment will depend on the origin of the coordinate system used.

(40) See eq 16 in ref 34.

(41) Mason, S. F.; Peart, B. J. *J. Chem. Soc., Dalton Trans.* 1973, 949.

(42) Bosnich, B. *Acc. Chem. Res.* 1969, 2, 266.

(43) A molecule that is in a symmetry group whose totally symmetric representation does not transform as  $x$ ,  $y$ , or  $z$  cannot have a dipole moment in any state: Jaffe, H. H.; Orchin, M. *Symmetry in Chemistry*; Wiley: New York, 1965; pp 68-69.



**Figure 2.** Plot of the energy at the  $\lambda_{\max}$  value of the long-axis-polarized  $\pi\pi^*$  intraligand absorption in Ru(bpy)<sub>3</sub><sup>2+</sup> versus a function of solvent polarizability,  $(1 - n^2)/(2n^2 + 1)$  ( $n$  = refractive index): (1) water; (2) acetonitrile; (3) ethanol; (4) methylene chloride; (5) *N,N*-dimethylformamide; (6) *N,N*-dimethylacetamide; (7) dimethyl sulfoxide.

**Table I.** Results of Plots of  $E_{\max}$  of the Long-Axis  ${}^1\pi\pi^*$  Absorption versus a Function of Solvent Polarizability,  $(1 - n^2)/(2n^2 + 1)$

species	slope, $10^3 \text{ cm}^{-1}$	$y$ intercept, $10^3 \text{ cm}^{-1}$	$r$
Ru(bpy) <sub>3</sub> <sup>2+</sup>	12.2	37.0	0.974
Ru(bpy) <sub>2</sub> Cl <sub>2</sub>	13.9	36.3	0.897
Ru(bpy) <sub>2</sub> (CN) <sub>2</sub> <sup>a</sup>	13.3	36.7	0.932
Ni(bpy) <sub>3</sub> <sup>2+</sup>	5.6	34.7	0.911
bpy	8.3	37.0	0.955
anthracene (0-0) <sup>b</sup>	7.5	27.9	0.948
anthracene (0-1)	7.2	29.3	0.976
anthracene (0-2)	6.5	30.6	0.945
anthracene (0-3)	6.3	32.0	0.975

<sup>a</sup>The value in water was excluded since Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> is known to strongly interact with this solvent.<sup>47,48</sup> <sup>b</sup>These represent the plots obtained for the first four vibrational bands of the short-axis  ${}^1L_a$  ( ${}^1B_{2u}$ ) transition. Anthracene is not soluble in water, and so this solvent was not used.

essentially as in the case when there is no change in dipole moment. This conclusion can be, and has been, tested by determining if the solvent effect can be well described by a linear fit of  $E_{\max}$  with  $F(n^2)$ .

Seven solvents were used for the study: water, acetonitrile, dimethyl sulfoxide, *N,N*-dimethylformamide, methylene chloride, *N,N*-dimethylacetamide, and ethanol. The  ${}^1IL$  transitions of the complexes Ru(bpy)<sub>3</sub><sup>2+</sup>, Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, and Ni(bpy)<sub>3</sub><sup>2+</sup> were tested as well as the lowest energy  ${}^1\pi\pi^*$  transition of free bpy and anthracene. Figure 1 shows the difference in the long-axis IL spectra for Ru(bpy)<sub>3</sub><sup>2+</sup> in water and DMSO. It can be seen that not only does the spectrum shift but also other features, such as the half-bandwidth, change. Bandwidth changes could be due to effects the solvent has on the exciton coupling. Figure 2 shows the plot of  $E_{\max}$  versus  $F(n^2)$  for Ru(bpy)<sub>3</sub><sup>2+</sup>. Clearly, a linear fit is reasonable, and linear-regression analysis gives  $r = 0.974$ ,  $y$  intercept  $37.0 \times 10^3 \text{ cm}^{-1}$ , and slope  $12.2 \times 10^3 \text{ cm}^{-1}$ . Similar plots were made for the other species studied, and the resultant parameters obtained are shown in Table I. While there is some variability in the value of the slope, in all cases it is larger than the slope reported for the  ${}^1MLCT$  band of Ru(bpy)<sub>3</sub><sup>2+</sup>. Since these transitions are nonpolar or only give small changes in the dipole moment, it is clear on empirical grounds that the results for the solvent effects on the  ${}^1MLCT$  are consistent with a transition which does not give rise to a dipole moment. The comparison that most clearly shows the probable nonpolar nature of the  ${}^1MLCT$  transition is the one between it and the various bands in the vibrational progression of the  ${}^1L_a$  ( ${}^1B_{2u}$ ) transition in anthracene. The  ${}^1L_a$  transition, like all transitions for a non-distorted  $D_{2h}$  anthracene, does not involve a dipole moment in either the ground or excited state. It does involve a change in

**Table II.** INDO/S CI Calculated Absorption Spectrum for bpy in the Cis ( $C_{2v}$ ) Conformation<sup>a</sup>

transition <sup>d</sup>	energy, $10^3 \text{ cm}^{-1}$	$f^b$	polariz <sup>c</sup>
S <sub>1</sub> ( $n\pi^*$ , ${}^1A_2$ )	31.34	0.0000	
S <sub>2</sub> ( $n\pi^*$ , ${}^1B_2$ )	33.72	0.0244	$y$
S <sub>3</sub> ( $\pi\pi^*$ , ${}^1B_1$ )	36.16	0.3621	$x$
S <sub>4</sub> ( $\pi\pi^*$ , ${}^1A_1$ )	38.23	0.0373	$z$
S <sub>5</sub> ( $n\pi^*$ , ${}^1A_2$ )	41.23	0.0000	
S <sub>6</sub> ( $\pi\pi^*$ , ${}^1B_1$ )	42.14	0.3847	$x$
S <sub>7</sub> ( $n\pi^*$ , ${}^1B_2$ )	42.68	0.0001	$y$

<sup>a</sup>All transitions below  $50\,000 \text{ cm}^{-1}$  are reported. <sup>b</sup>Oscillator strength. <sup>c</sup>The coordinate system of the molecule is as follows:  $x$ , long axis;  $z$ , short axis;  $y$ , out of plane. <sup>d</sup>From  $S_0$  to the level shown.

**Table III.** INDO/S CI Calculated Transition Energies for bpy in the Trans ( $C_{2h}$ ) Conformation<sup>a</sup>

transition <sup>c</sup>	energy, $10^3 \text{ cm}^{-1}$	$f^b$	polariz <sup>c</sup>
S <sub>1</sub> ( $n\pi^*$ , ${}^1A_u$ )	32.46	0.0204	$y$
S <sub>2</sub> ( $n\pi^*$ , ${}^1B_g$ )	33.51	0.0000	
S <sub>3</sub> ( $\pi\pi^*$ , ${}^1B_u$ )	35.95	0.4113	$x, z^d$
S <sub>4</sub> ( $\pi\pi^*$ , ${}^1A_g$ )	38.03	0.0000	
S <sub>5</sub> ( $n\pi^*$ , ${}^1A_u$ )	41.48	0.0022	$y$
S <sub>6</sub> ( $\pi\pi^*$ , ${}^1B_u$ )	42.53	0.3813	$x, z^d$
S <sub>7</sub> ( $n\pi^*$ , ${}^1B_g$ )	43.36	0.0000	
S <sub>8</sub> ( $\pi\pi^*$ , ${}^1A_g$ )	49.04	0.0000	

<sup>a</sup>All transitions below  $50\,000 \text{ cm}^{-1}$  are reported. <sup>b</sup>Oscillator strength. <sup>c</sup>The coordinate system of the molecule is as follows:  $x$ , long axis;  $z$ , short axis;  $y$ , out of plane. <sup>d</sup>Primarily  $x$  polarized. <sup>e</sup>From  $S_0$  to the level shown.

sign in the wave function along the short axis of the molecule.<sup>44,45</sup> Thus, this transition in anthracene illustrates that McRae's empirical linear correlation of  $E_{\max}$  with  $(AL + B)[F(n^2)]$  for a nonpolar molecule can give rise to a slope  $(AL + B)$  that is as large as  $7000 \text{ cm}^{-1}$  and probably (as illustrated by the  $\pi\pi^*$  transitions of the bpy complexes) much larger.

To gain further insight into the  $\pi\pi^*$  transitions in bpy when it is complexed or free in solution, INDO/S CI calculations were performed. The structure of chelated bpy is planar, and it has  $C_{2v}$  symmetry.<sup>34</sup> Each individual bpy will have a dipole moment when considered independently, and it is calculated to be 4.91 D and directed along the short axis of the molecule. When three bpy ligands are complexed in a symmetric fashion to form a tris complex, these dipoles will cancel and the molecule will have no net dipole moment.<sup>43</sup> However, in a case where one of the bpy ligands is substituted (such as by two X<sup>-</sup> species or by ethylenediamine), a dipole moment will occur in the complex due both to the differing electronegativities of the ligands and to the inherent dipole moment of the remaining bpy ligands whose dipoles are not symmetrically balanced. In free bpy the lowest energy conformation is when the nitrogens are trans.<sup>46</sup> This is due to the reduced steric crowding of hydrogens at the 5-position since the nitrogens do not have a bound hydrogen.

Tables II and III present some of the results of the calculations for bpy in the cis ( $C_{2v}$ ) and trans ( $C_{2h}$ ) conformations. For the cis species (Table II) a strong transition is calculated to be at  $36\,160 \text{ cm}^{-1}$  and it is long-axis-polarized. This represents the strong  $\pi\pi^*$  transitions in metal bpy complexes observed between 280 and 310 nm. Its transition dipole is calculated to be 4.40 D and it is directed completely along the long axis of the molecule. There is a small change in the dipole moment of bpy in this transition, and the change is 0.51 D along the short axis of the molecule, in the same direction as the ground-state dipole moment. Thus, though the transition dipole is in one direction, the change in the

(44) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

(45) Moffitt, W. *J. Chem. Phys.* **1954**, *22*, 320.

(46) Barone, V.; Leji, F.; Cauletti, C.; Piancastelli, M. N.; Russo, N. *Mol. Phys.* **1983**, *49*, 599.

(47) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 6571.

(48) Kitamura, N.; Sato, M.; Kim, H.-B.; Tazuke, S. *Inorg. Chem.* **1988**, *27*, 651.

dipole moment is in a perpendicular direction. Thus, for this  $\pi\pi^*$  bpy transition there will be a small change in dipole moment for the metal complex if the bpy ligands are not symmetrically placed.

In Table III are some of the results of the calculation of the transition energies for bpy in its trans conformation, the conformation of bpy free in solution. In  $C_{2h}$  symmetry neither the ground state nor any excited states will have a dipole moment.<sup>43</sup> The lowest strong transition is at 35 950  $\text{cm}^{-1}$ , and it is primarily long-axis-polarized with a transition dipole directed 4.82 D along the long axis and 1.08 D along the short axis. This transition is analogous to the long-axis transition in trans bpy, as both are primarily long-axis-polarized and represent primarily the promotion of an electron from the HOMO to the LUMO.

It is interesting that the slope of the  $E_{\text{max}}$  versus  $F(n^2)$  plot of the  $\pi\pi^*$  long-axis transition for free bpy lies within the values for the cis, exciton-coupled bpy ligands in the complexes reported. It thus appears that the dispersive effect of the solvent is qualitatively about the same for bpy in the two conformations. However, there is a large variation in the slope obtained for the cis bpy in the different metal complexes ( $(5.6-13.3) \times 10^3 \text{ cm}^{-1}$ ). Thus, the specific nature of the coordination of the bpy has a significant influence on how its  $\pi\pi^*$  long-axis transition is perturbed by the polarizability of the solvent.

### Conclusion

Previous work has shown that the energy of the <sup>1</sup>MLCT transitions observed in the visible part of the spectrum shifts as

a function of the solvent refractive index.<sup>25</sup> This was interpreted as consistent with the transitions being polar and leading directly to a single-ligand-localized charge-transfer state. Solvent shifts that are larger than those reported for the <sup>1</sup>MLCT absorptions are observed for the long-axis-polarized <sup>1</sup> $\pi\pi^*$  absorption of bpy in metal complexes and free in solution and for the <sup>1</sup> $L_a$  absorption of anthracene. It is concluded that the shifts in the absorption maximum with solvent refractive index for the <sup>1</sup>MLCT transitions do not show that this transition leads directly to a single-ligand-localized,  $C_2$  symmetry state. Most evidence from other studies, such as from absorption polarization<sup>18-20</sup> and emission polarization<sup>9,10,23</sup> studies, are consistent with the <sup>1</sup>MLCT bands representing a delocalized transition. Thus, it seems reasonable to conclude that through most of the <sup>1</sup>MLCT visible bands the absorption is probably to a delocalized orbital and that both the ground and the initially populated excited states are symmetric. The nature of the absorption at the "red edge" of the visible bands is a matter of some discussion in the literature,<sup>8-10,19,23</sup> which the current work does not touch upon. While relevant to a description of the nature of the initial singlet produced, the current work does not reveal the details of the subsequent localization process.

**Acknowledgment.** I thank Dr. Robert Goldbeck for providing the output from the INDO/S CI calculations and for many useful discussions and Dr. David Kliger for his encouragement and support. The National Institutes of Health supplied financial support under Grant GM 35158.

Contribution from the Departments of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada, and The Ohio State University, Columbus, Ohio 43210

## Electronic Structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3$ and $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Pt}(\text{CH}_3)_3$ from UV Photoelectron Spectra

D. S. Yang,<sup>†</sup> G. M. Bancroft,<sup>\*,†</sup> R. J. Puddephatt,<sup>\*,†</sup> B. E. Bursten,<sup>\*,‡</sup> and S. D. McKee<sup>†</sup>

Received July 22, 1988

Gas-phase He I and He II photoelectron spectra for  $\text{CpPtMe}_3$  and the new complex  $\text{Cp}^*\text{PtMe}_3$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{Me} = \text{CH}_3$ ) have been obtained. The valence orbitals responsible for the ionizations have been assigned to the corresponding molecular orbitals with the aid of Fenske-Hall molecular orbital calculations. The ordering of the molecular orbitals (in order of increasing binding energy) is  $\text{Pt } 5d < \text{Pt-Me} < \text{Pt-Cp}$ . From the photoelectron results, it is apparent that the  $\text{Cp } e_{11}'$  orbitals interact strongly with the metal orbitals.

### Introduction

Gas-phase UV photoelectron spectroscopy (PES) has proved an invaluable tool for studying the nature of the bonding between a central metal atom and the ancillary ligands of inorganic compounds.<sup>1</sup> PES has been useful for understanding the electronic structure of "sandwich" compounds<sup>1b-d</sup> and more recently has been extended to include "half-sandwich" or piano-stool compounds.<sup>1de,2</sup> In this second class of compounds, the metal is bound to a single carbocyclic ring, with the other ligands (either inorganic or organic) bound to the metal and comprising the "legs" of the stool. The ubiquitous  $\eta^5$ -cyclopentadienyl (Cp) ligand is the most common "bench" in these systems, and thus most of these studies have been devoted to metal cyclopentadienyl carbonyls and their derivatives. In contrast to metal cyclopentadienyl carbonyl compounds, metal cyclopentadienyl alkyls have not been examined in great detail.<sup>2d</sup> Because of differences in the bonding characteristics of carbonyl (a neutral  $\pi$  acceptor) versus alkyl (an anionic  $\sigma$ -only donor), significant changes between the electronic structures of these complexes may be expected. This perturbation is most evident in the high oxidation state of the metal generally found in cyclopentadienyl alkyl complexes.

There has been little activity regarding the chemistry of cyclopentadienylplatinum(IV) complexes. Robinson and Shaw first reported the synthesis of  $\text{CpPtMe}_3$  and deduced from IR and NMR results that the compound was indeed a  $\pi$  complex,<sup>3</sup> a point later substantiated by X-ray structure analysis.<sup>4</sup> Maitlis has reported the synthesis of  $[\text{Cp}^*\text{PtBr}_3\text{PtCp}^*]\text{Br}_3$ , the structure of which was suggested to be an ionic triply bridged binuclear  $\pi$  complex.<sup>5</sup> Interest in chiral organometallic complexes prompted Shaver and co-workers to prepare  $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3$ -

- (1) (a) Fenske, R. F. *Prog. Inorg. Chem.* **1976**, *21*, 179. (b) Caulletti, C.; Furlani, C. *Struct. Bonding (Berlin)* **1978**, *35*, 119. (c) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 46. (d) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37. (e) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.
- (2) (a) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839. (b) Calabro, D. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6846. (c) Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics* **1984**, *3*, 1623. (d) Dudeney, N.; Kirchner, O. N.; Green, J. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1877. (e) Lichtenberger, D. L.; Hubbard, J. L. *Inorg. Chem.* **1985**, *24*, 3835. (f) Caulletti, C.; Furlani, C.; Puliti, C.; Werner, H. *J. Organomet. Chem.* **1985**, *289*, 417. (g) Terpstra, A.; Louwen, J. N.; Oskam, A.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *260*, 207.
- (3) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1965**, 1529.
- (4) Adamson, G. W.; Bart, J. C. J.; Daly, J. J. *J. Chem. Soc. A* **1971**, 2616.
- (5) Taylor, S. H.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *139*, 121.

<sup>†</sup>University of Western Ontario.

<sup>‡</sup>The Ohio State University.