revealed by the topological characteristics of the Laplacian of the electronic charge density, Li^+–azole complexes, if they present either a bent or a bridged conformation, are the result of the interaction of two closed-shell systems, no new covalent bonds are formed, and stabilization arises mainly from electrostatic interactions. One can observe, however, the formation of a new covalent N–H bond in the corresponding protonated species.

A consequence of the different nature of H^+– and Li^+–azole interactions is that the charge transferred from the base to the ion is much smaller in the latter as well as the corresponding stabilization energies. More specifically, Li^+ binding energies are predicted to be smaller than the corresponding proton affinities by a factor of 4. This implies that there exists a good linear relationship between both sets of values, for those cases where Li^+ is singly coordinated. On the other hand, the ratio between relative values is about 1.8 as it can be expected from a simple electrostatic model, where the dominant term corresponds to ion–dipole interactions. This would indicate that the trend in relative basicities, at least for these kind of bases, is mainly governed by electrostatic interactions.

Athough it is reasonable to assume that when bases with two atoms having lone-pair electrons are involved Li^+ bridging complexes should be the most stable ones, this is not always the case. Pentazole and 1*H*-tetrazole are significant examples of systems where the expected bridged structures are less stable than the bent ones. From our analysis of the corresponding molecular electrostatic potentials, we can conclude that if the electrostatic minima associated with the two neighboring basic centers are connected by isopotential lines, which are located at a distance from the basic centers similar to or smaller than a typical $N-Li^+$ bond length, the bridged structure will be formed. On the contrary, if these isopotential curves appear at distances greater than the average $N-Li^+$ bond length, the Li^+ ion will be trapped in one of the minima yielding a bent conformation.

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Photoselection Studies of Cis/Trans Isomers of $[Ru(bpy)_2(L)_2]^{2+}$: Evidence for Exciton Interactions in Singlet Metal–Ligand Charge-Transfer States

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Steady-state excitation photoselection (SSExP), 77 K absorption, and 77 K emission spectra are presented for *cis*- and *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ (bpy = 2,2′-bipyridine; py = pyridine), *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$ (mdpp = methyldiphenylphosphine), *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$ (tpp = triphenylphosphine), and $[Ru(bpy)_2(dppe)](PF_6)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) in ethanol glass. SSExP supports the results of the recent interchromophoric coupling model for the SSExP of ruthenium–bipyridine complexes. Independent evidence of excitonic interaction between the chromophores of such species is obtained from the electronic spectroscopy of trans complexes.

Introduction

The steady-state excitation photoselection (SSExP) of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and other tris-chelate ruthenium species has been important in the assignment of the lowest excited manifold of this series as spatially isolated localized orbital states, similar to those charge-transfer excited states of monomeric species such as $[Ru(bpy)(py)_4]^{2+}$ (py = pyridine).[1] To date, SSExP results obtained for mono-chelate, tris-chelate, and cis-configuration bis-chelate complexes have been reported[1,2] with a variety of different solvents, ligands, and counterions.

A recent model has been presented that rationalizes the polarization results obtained for the above species,[2] based upon the spin–orbit coupling (SOC) interactions of the lowest triplet state with a singlet manifold of mixed (localized/delocalized) character. The results of this analysis compared well with the observed SSExP of bis and tris complexes. In addition, the new model provided a means of relating the SSExP typically seen for most tris chelates to that of the anomalous behavior of $[Ru(biq)_3]^{2+}$ (biq = 2,2′-biquinoline).[2b]

This analysis using the interchromophoric coupling (ICC) model depends partly upon the angles between the monomer axis system and dimer/trimer axis systems in complexes that possess multiple chromophores associated with the same core metal ion. If this model is correct, then significant differences are predicted in the polarization properties of bis chelates between cis and trans geometries because of the different angles involved.

The purpose of this work is to report SSExP and low-temperature absorption/emission data for some cis/trans isomers and to analyze these data in terms of exciton theory and the ICC model.

Experimental Section

The complexes *cis*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, *trans*-$[Ru(bpy)_2](py)_2(ClO_4)_2$, *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$ (mdpp = methyldiphenylphosphine), and *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$ (tpp = triphenylphosphine) were prepared according to literature procedures.[3,4] *cis*-$[Ru(bpy)_2(mdpp)_2]^{2+}$ was synthesized but could not be obtained in sufficient purity to permit its use. Luminescence purity of complexes was monitored by the excitation-wavelength independence of the emission.

$[Ru(bpy)_2(dppe)](PF_6)_2$ (dppe = 1,2-Bis(diphenylphosphino)ethane). This complex was synthesized by combining 100 mg of $[Ru(bpy)_2Cl_2]\cdot 3H_2O$ and 400 mg of dppe ligand in 60

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(1) (a) Carlin, C. M.; De Armond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297. (b) Carlin, C. M.; De Armond, M. K. *Chem. Phys. Lett.* **1985**, *107*, 53.

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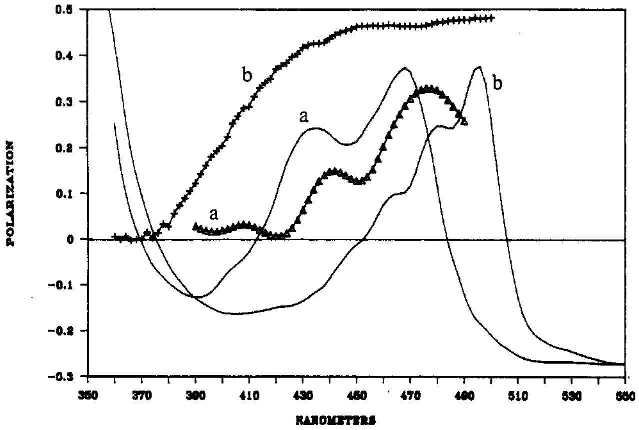

Figure 1. Absorption and SSExP at 77 K of (a) *cis*- and (b) *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ in ethanol.

mL of a 1:1 ethanol/water mixture. The reaction mixture was purged with N_2 for 15 min before refluxing. Refluxing was continued for 2 weeks. The reaction mixture was filtered and $KPF_6(aq)$ added to form a yellow precipitate. This was filtered and washed with 2-propanol and ether. The complex is purified by recrystallization from H_2O/2-propanol. The shorter reaction time of Durham[4] appeared to produce low yields and complicated purifications.

Trans isomers and the cis pyridine complex were photochemically unstable in fluid solution and appeared to undergo solvolysis under irradiation. Indeed, the room-temperature absorbance of *trans*-$[Ru(bpy)_2(py)_2(ClO_4)_2$ reported by Krause[5] shows strong evidence of the presence of a photodecomposition product in solution. However, when frozen in ethanol glass at 77 K, all complexes were photochemically inert and no change could be detected in emission or absorption spectra of the frozen species after $^1/_2$ h of intense illumination. Fresh samples were prepared and frozen in complete darkness for the pyridine complexes and under low illumination from a Kodak Safelight for the trans phosphine complexes in order to assure the absence of photochemical products in the studies.

Photoselection was performed on an instrument previously described,[6] now automated with a Zenith Z-158 computer. Studies were performed in ethanol glasses at 77 K. Absolute ethanol was provided by Fisher Scientific Co. and USI Chemicals Co. and was used without further purification. Excitation was provided by a 450-W xenon/mercury lamp. For all complexes SSExP was performed by detecting luminescence at the maximum of the emission band.

Absorption studies were performed on either a Cary 14 or a Cary 2300 spectrometer.

Results

Figure 1 shows the 77 K absorption and SSExP spectra of *cis*-and *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ in ethanol. Absorption spectra are uncorrected for solvent contraction and are scaled arbitrarily. Figure 2 gives the 77 K emission spectra for *cis*- and *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ in ethanol glass. Intensities are relative.

Features to note in Figures 1 and 2 are the similarity of emission bands for the cis/trans pair and the distinctly different energies and bandshapes of absorption in the ^{1}MLCT region. The "vibronic" structure of the transition is significantly different, with the cis isomer displaying a pair of transitions separated by 1700 cm^{-1}, a form common to the Ru–bpy unit and observed for $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)(py)_4]^{2+}$, and others.[2] The trans isomer, however, exhibits a vibronic progression of 670-cm^{-1} magnitude. Also, the profiles of the SSExP spectra are significantly different across the MLCT bpy absorption, the trans isomer possessing a simple profile that approaches $P = 0.5$. The profile of the cis isomer is similar to that observed for many cis complexes, attaining a value of $P = 0.33$ on the red edge of the absorption.

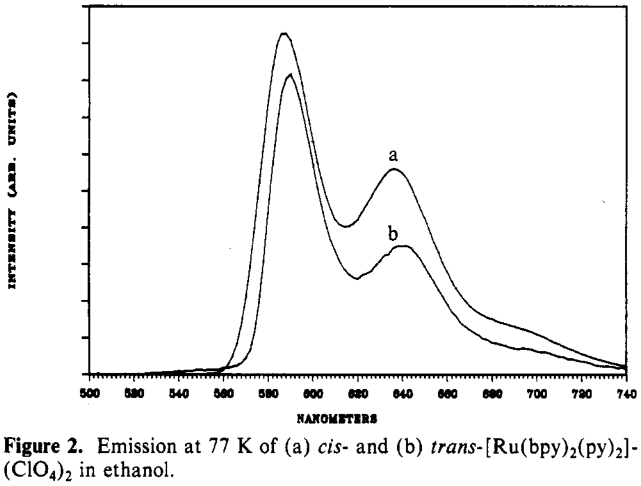

Figure 2. Emission at 77 K of (a) *cis*- and (b) *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ in ethanol.

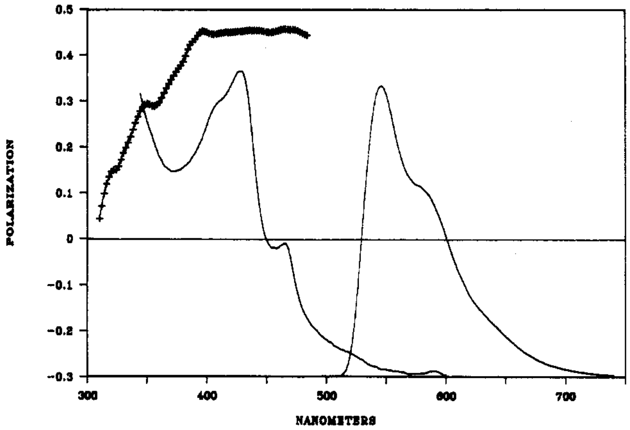

Figure 3. Absorption, SSExP, and emission at 77 K of *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$ in ethanol.

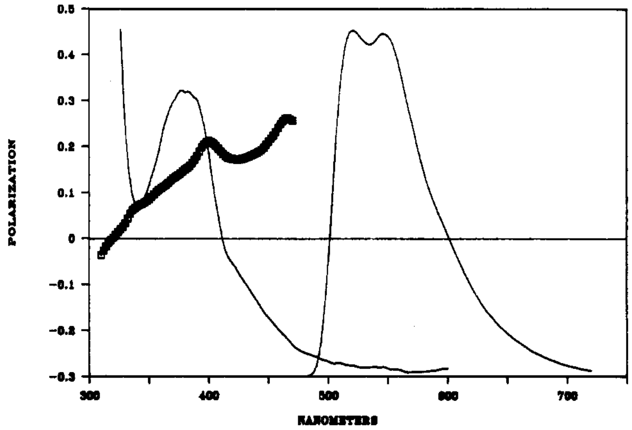

Figure 4. Absorption, SSExP, and emission at 77 K of $[Ru(bpy)_2(dppe)_2](PF_6)_2$ in ethanol.

Figure 3 gives the 77 K absorption, SSExP, and emission for *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$ in ethanol. Preliminary studies on the cis isomers of this complex have indicated behavior analogous to that of the pyridine cis/trans pair, with emission energy differences small in comparison to the discrepancies in ^{1}MLCT absorbances.

The 77 K absorbance, SSExP, and emission for $[Ru(bpy)_2(dppe)](PF_6)_2$ are shown in Figure 4. Note that the position of the emission maximum disagrees with that previously reported for this complex by Meyer.[7] Further work in this laboratory on related cis-configuration phosphine complexes is consistent with

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TABLE I: Luminescence Decay Times for Complexes

complex	solvent	wavelength,[a] nm	lifetime, μs
trans-$[Ru(bpy)_2(py)_2](ClO_4)_2$	4:1 EtOH/MeOH	580	4.14 ± 0.02
	4:1 EtOH/MeOH	640	3.92 ± 0.03
cis-$[Ru(bpy)_2(py)_2](ClO_4)_2$	4:1 EtOH/MeOH	580	5.92 ± 0.10
	4:1 EtOH/MeOH	640	5.93 ± 0.11
trans-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$	EtOH	545	5.50 ± 0.06
	EtOH	585	5.80 ± 0.04
$[Ru(bpy)_2(dppe)](PF_6)_2$	EtOH	515	20.0 ± 0.10
	EtOH	550	20.0 ± 0.10
trans-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$	4:1 EtOH/MeOH	548	5.12 ± 0.05
	4:1 EtOH/MeOH	585	5.34 ± 0.05

[a] Wavelengths of analysis correspond to emission maximum and shoulder.

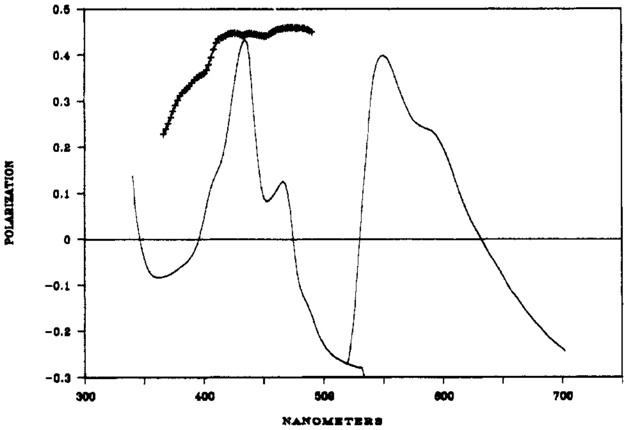

Figure 5. Absorption, SSExP, and emission at 77 K of *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$ in ethanol.

our identification of this complex, as are data for other such complexes reported by Meyer.[7]

^{1}MLCT transitions of the dppe complex are blue-shifted in comparison with *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$, in part due to the bidentate nature of this ligand which allows it to bind more strongly to the central metal ion than the monodentate mdpp. The emission for the dppe complex is also blue-shifted relative to that of the trans isomer, though not displaced so much as the spin-allowed transitions.

The SSExP of the trans mdpp complex is similar to that of the trans py complex, while that of the dppe complex exhibits lower values than other cis complexes and exhibits a structured wave pattern that is not typical of other cis and tris species. The normal three-wave pattern frequently observed in cis complexes, such as that seen for *cis*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ reported here, is apparently absent or obscured. The maximum SSExP value obtained, $P = 0.28$, is somewhat lower than other cis species, which normally attain $P = 0.34$ on the red edge of the absorbance. Instead, a region of reduced polarization is observed extending from approximately 405 to 465 nm, roughly correlating with a slight shoulder observed in that region in the 77 K absorbance.

Figure 5 gives the 77 K absorption, SSExP, and 77 K emission of *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$ in ethanol. Though this phosphine ligand is monodentate, the cis isomer of this complex could not be produced. This is consistent with the observations of Durham[4] and, as he suggests, is likely due to steric hindrance. Comparison with Figure 4 reveals differences in energy of the ^{1}MLCT manifolds between trans isomers with tpp and mdpp ligands, as well as variations in intensity distributions. However, despite this variation in ^{1}MLCT bandshapes, the photoselection profile reported in Figure 5 is remarkably similar to those of the other trans isomers and indicates that such SSExP spectroscopy is a phenomenon generally observable for bis chelates of bipyridine in a trans configuration.

The 77 K luminescence decay lifetimes for the complexes are listed in Table I for emission wavelengths that correspond to the maximum and shoulder of the emission envelope. With the exception of $[Ru(bpy)_2(dppe)](PF_6)_2$, lifetimes are similar to the approximately 6-μs lifetimes of $[Ru(bpy)_3]^{2+}$ and other complexes.[8]

The decay of $[Ru(bpy)_2(dppe)](PF_6)_2$ in ethanol is somewhat longer than other decays of Ru–bpy CT luminescence, near 20 μs. Studies at room temperature have shown the luminescence of this complex to be nearly quenched in fluid ethanol, though the complex is apparently photochemically inert in this fluid medium.

An additional feature of interest in the case of the phosphine complexes is the high energy of the emitting states relative to other Ru–diimine complexes. For $[Ru(bpy)_2(dppe)](PF_6)_2$, the energy of luminescence begins to approach the energy expected for the π–π^* state of coordinated bipyridine.[9] The greenish luminescence is likely due to increased crystal-field stability of the phosphine–Ru bonds. Previous electrochemical studies on the oxidation potentials of cis/trans pairs have also indicated this.[4]

Discussion

Trans isomers of $[Ru(bpy)_2(L)_2]^{2+}$ have only recently been synthesized, first by Krause[5] and more recently by Durham.[4,10,11] Structural confirmation has been obtained from X-ray crystal studies. Due to these efforts, a number of trans isomers have been synthesized and characterized by their room-temperature electronic absorption spectra,[4,5] electrochemistry,[4] IR,[5] and NMR.[11] These previous studies found that the singlet MLCT manifolds of trans species absorb radiation at lower energies than the corresponding cis species,[4] originally attributed solely to destabilization of the metal d–π orbital levels in the trans geometry. This is a reasonable expectation supported to an extent by differences in +3/+2 oxidation potentials reported for cis and trans isomers,[4] but it cannot be the only cause of the systematic trend in the absorption because the luminescence reported here for trans species is nearly isoenergetic with that of the corresponding cis species. Indeed, the emission maxima for the cis/trans pyridine pair are separated by less than 100 cm^{-1} while their singlet absorbances are separated by nearly 1200 cm^{-1}. The variation of emission maxima is consistent with the small separation of oxidation potentials between *cis*- and *trans*-$[Ru(bpy)_2(py)_2]^{2+}$ reported by Durham and Walsh;[4] the large variation in absorption maxima is likely due to other processes. Comparison of the phosphine complexes as $[Ru(bpy)_2(dppe)](PF_6)_2$ and *trans*-$[Ru(bpy)_2(mdpp)_2(PF_6)_2$ is not so straightforward because the ligands are different; however, even for these the emission separation is 1100 cm^{-1} while that of the singlet MLCT absorbances is 3200 cm^{-1}.

The red shift in the absorption and the modification of the absorption bandshape present in *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$, and *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$ suggest the presence of excitonic interactions in the singlet manifold. Exciton theory[12] indicates that molecules such as trans complexes may have distorted and red-shifted absorption spectra. The extent of red shift would be dependent upon the strength of the interaction producing the exciton levels, which for most dimers

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is considered to be primarily the pseudo-Coulombic repulsion of the two monomer transition moments.[13-15] Thus, transitions that possess a large moment also generate the greatest interaction and red shift; this is likely the cause of the changes in the absorption envelope, while the "spin-forbidden" emission is virtually identical with that of the monomer because the transition moments are relatively small.

In the absence of effects due to wave function overlap, exciton theory predicts that the magnitude of the interaction between monomers in a trans complex should be slightly smaller than in a corresponding cis complex, due to the increased distance between the monomer centers. Since the reverse ordering is found experimentally, overlap effects must be important here. Qualitatively, this seems plausible since the monomers share a common central ion.

Mason[13] has pointed out that simple exciton theory has difficulty accounting for the interactions of π–π^* states in tris-chelate metal complexes of the form $[M(L)_3]^{n+}$ (L = 2,2′-diimine ligand) due to the small interligand separation. In general, he found that the simple exciton approach provided the correct ordering of exciton levels in such molecules but was unable to provide spacings that matched those determined experimentally.

The procedure that Mason utilizes to obtain a better correlation between prediction and experiment is to discard the approximate point–dipole interaction in favor of the general two-electron Coulombic repulsions of the dimer. This reduces the energy terms to summations of electron repulsions of atomic orbitals localized on separate monomers, such as that shown in eq 1, an alternate form of eq 21 of ref 13:

$$v = \sum_{s(a)} \sum_{t(b)} (C_{sd}C_{s\Pi^*})_a (C_{td}C_{t\Pi^*})_b \times \left\langle X_{s(a)}(i)\, X_{t(b)}(j) \left| \frac{e^2}{r_{ia,jb}} \right| X_{s(a)}(i)\, X_{t(b)}(j) \right\rangle \quad (1)$$

where s indicates atomic basis functions of monomer a, t indicates atomic basis functions of monomer b, d and π^* indicate the respective molecular orbitals, C_{no} indicates the participation of the atomic function n in the molecular function o, and i and j are electrons of monomer a and monomer b, respectively. Dominant terms then would be those involving metal orbitals of each monomer, and the extent to which these contribute will depend partly upon the extent of overlap between the half-filled metal orbital of one ligand-localized coordinate system with that of equivalent systems. This in turn indicates that the energy separations will be strongly dependent upon orientation of ligands, more so than the simple exciton theory allows. An additional factor is the removal of the near orthogonality of ligand π^* functions in the trans geometry.

The presence of larger exciton splittings in trans complexes suggests that weak exciton interactions occur in cis complexes but are too small to affect the bandshape of the absorption significantly. Such a weak interaction may affect polarizations of transitions, however, and is a key factor in the ICC model. This model assumed the presence of weak exciton coupling in bis and tris complexes which produces some spatial delocalization in the ^{1}MLCT manifold.

Analysis of the SSExP for cis/trans pairs is also instructive. The behavior of trans isomers predicted by the ICC model is radically different from that of cis isomers, due to the collinearity of the monomer axes.

X-ray crystallography of *trans*-$[Ru(Mebpy)_2(py)_2]^{2+}$ (Mebpy = 4,4-dimethyl-2,2′-bipyridine) and *trans*-$[Ru(bpy)_2(tpp)_2]^{2+}$ has shown these complexes to be distorted in the single crystal.[17] In both cases, a "bowed" type of deformation occurs, rather than the "twisted" deformation of *trans*-$[Ru(bpy)_2(H_2O)(OH)](ClO_4)_2$.[10] That these deformations may not significantly affect the electronic properties of the ligands is suggested by the similarity of the emission oscillators in trans and cis isomers. For this reason, we analyze these complexes assuming the monomeric chromophores of the trans complexes to be perfectly coplanar.

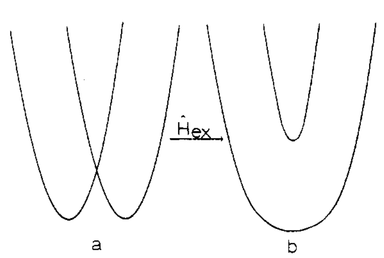

Figure 6. (a) Potential energy surfaces of a dimer assuming weak exciton coupling and (b) the same surfaces assuming strong exciton coupling. Note that the lower surface in (a) possesses two minima, while that of (b) has only a single minimum.

As for cis complexes, we assume the ^{1}MLCT transitions possess intensity polarized only in the metal–ligand (z) axis direction for the individual chromophores. Exciton theory[12] then shows that, for the trans isomer, all transition moment is concentrated along the collinear monomer z and dimer Z axes.

For this reason, the metastable localized triplet state, which is composed of three spin levels of differing total symmetries,[18] can borrow only z-polarized intensity by spin–orbit coupling to the ^{1}MLCT manifold. This is in contrast to the result for cis isomers given previously,[2b] which indicates that two different polarizations occur for these species in emission, resulting in lowered SSExP values. In addition, the previous calculation for cis species indicated structure in the SSExP profile, since absorption polarization depended upon the weak exciton coupling of the monomers and was therefore a function of wavelength. For trans species, exciton coupling does not affect the polarization of the absorption because the monomer units are in a special geometry, and thus no structure is expected for the SSExP of a trans isomer across the MLCT bands.

Both of these conclusions are confirmed by the experimental data presented here.

A large exciton interaction implies delocalization in the states concerned. That is, the ability to differentiate excitations between different monomeric moieties is lost since excitation transfers between monomers occur so rapidly that nuclear motions are impossible.[16] The effect of a large exciton interaction on the potential energy surfaces concerned is illustrated in Figure 6. The ICC model requires that even in cis species, where excitonic interactions are less evident, localization within the ^{1}MLCT manifold is only indicated for a small, lower energy region of the relevant potential energy surface. Most visible singlet excitation for cis species occurs to a delocalized portion of the singlet manifold. Possibly, the singlet manifolds of trans isomers are of the delocalized type illustrated in Figure 6b, since a large coupling of chromophores is indicated. The emitting triplet state exhibits no such energy effect in the trans species and is most likely spatially localized on individual ligands.

Interestingly, comparison of data for the three trans isomers reported here reveals both the striking similarities already discussed and marked differences. The principal example of the latter is the visible electronic absorption of these complexes, arising from the charge-transfer transition of the Ru–bpy chromophore. Apparently, the detailed nature of the exciton coupling present in these species is modulated to some extent by the nonchromophoric axial ligands. The 670-cm^{-1} progression apparent in the pyridine complex is absent in both of the phosphine analogues, replaced by a 1600-cm^{-1} spacing. Intensity components are different between the two trans phosphine complexes. Indeed, some trends seem evident. For axial phosphines, the Stokes shift

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between the relatively sharp low-energy feature at approximately 2.13 μm^{-1} and the emission maximum nearly equals that between the sharp maximum and emission of *trans*-$[Ru(bpy)_2(py)_2]^{2+}$ reported here. However, the separation of absorption and emission maxima is more similar to that of the cis pyridine analogue. Indeed, the MLCT absorption spectra of the phosphine seems to illustrate an intermediate magnitude between weak and strong exciton interaction. As eq 1 shows, electron density on the metal should be a key determining factor in the extent of exciton coupling for these species. Thus, ligands with good acceptor properties will tend to reduce the magnitude of this coupling by removing electron density from the metal. The slightly higher energy of the emission for axial mdpp relative to axial tpp is indicative of greater acceptor ability for this ligand and accounts for the slightly lower exciton interaction apparent for that complex.

A different type of interaction is likely responsible for the unusual behavior of $[Ru(bpy)_2(dppe)](PF_6)_2$. Its rather long luminescence lifetime at 77 K sets it apart from other species with a Ru–bpy luminophore. In addition, the high energy of the luminescence, produced by the large crystal-field splitting induced by the phosphine ligand, indicates that the ^{3}MLCT states of this complex lie at higher energy than in most other complexes of ruthenium and bipyridine reported to the present. Consistent with this is the report for a similar bidentate phosphine complex, $[Ru(bpy)_2(dppene)]^{2+}$ (dppene = *cis*-1,2-bis(diphenylphosphino)ethylene).[7] Likewise, the SSExP is inconsistent with that reported for any previous complex of the form $[Ru(L)_2(L')]^{2+}$ (L = 2,2′-diimine ligand; L′ = nonchromophoric ligand).[2]

The skewed appearance of the ^{1}MLCT transition noted by Meyer[19] as evidence for greater distortion in the excited states may indicate that localized parts of the singlet are inaccessible by interaction with a radiation field due to reduced Franck–Condon factors. Alternatively, the relatively high energy of the emitting states may result in appreciable vibronic coupling to the higher lying, triplet $\pi\pi^*$ states. Numerous such coupling pathways exist, as has been indicated by Lim[20–22] for the interaction of $\pi\pi^*$ states with n–π^* states in azaaromatic compounds. Such an interaction may in this case couple the $^1\pi\pi^*$ state of bpy with the ^{1}MLCT.

One further remark concerning the spectroscopy of trans isomers is in order. Though synthesis of several such complexes has been achieved, spectroscopic (other than X-ray) confirmation of the geometry has been elusive. ^{1}H NMR is often ambiguous in these cases due to the large number of aromatic protons present. Methyl substitution has helped but may be impractical. IR analysis is complicated by the large number of vibrations expected for such a large molecule. Electronic absorption is more informative, but due to the variability of exciton effects presented here, the cis analogue is also required in order to reach any definitive conclusions. However, the present work reveals a simple method for such geometry determinations. Trans complexes quite generally exhibit a very simple and highly distinctive photoselection profile, regardless of the magnitude of exciton coupling, which contrasts markedly with all other complexes with the exception of pure monomeric species. In instances where the presence of a monodiimine complex can be ruled out, SSExP is the ideal tool for geometry determinations of the Ru–diimine complexes.

Conclusion

Data for cis/trans isomer pairs support the conclusions of the ICC model which involves exciton effects to explain polarization properties of Ru–diimine complexes. The unique behavior of trans species predicted by this model is observed for these complexes.

Evidence for exciton interactions within the manifold of excited states of the cis/trans pairs is found, which is consistent with the general predictions of exciton theory in dimers. However, spacings of exciton levels predicted by simple exciton theory are inconsistent with experimental results and indicate that a more complex approach is necessary in d–π^* dimers with common central metal ions.

In addition, the systematic differences in the electronic absorption spectra of cis/trans pairs result only in part from destabilization of metal orbitals, though some evidence for this effect is found in small variations of emission maxima. The major cause of this systematic variation is the enhanced excitonic interaction present in species with a trans geometry.

Finally, complete delocalization is possible within the trans singlet manifold, though likely not within the emitting since these are similar states to such states in cis analogues. Final clarification of this point awaits further data, such as circular dichroism or electron spin resonance of the reduced complexes.

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Registry No. *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, 63358-69-0; *cis*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, 63338-39-6; *trans*-$[Ru(bpy)_2(mdpp)_2](PF_6)_2$, 119679-83-3; $[Ru(bpy)_2(dpp)](PF_6)_2$, 119679-84-4; *trans*-$[Ru(bpy)_2(tpp)_2](ClO_4)_2$, 119679-85-5.

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