copy, precise structural information, and theoretical calculations for the understanding of the conformational behavior of several 5-sulfur-substituted 1,3-dioxanes. An unprecedented finding, with far-reaching implications, was the discovery of an eclipsed rotamer in the axial 5-*tert*-butylsulfonyl derivative.

The second section relates the determination of a very strong S–C–P anomeric effect in 2-(diphenylphosphinoyl)-1,3-dithiane. While a combination of electrostatic and orbital interactions could account for this effect, no single factor seems to dominate, and it is likely that this phenomenon deserves more attention by theoretical chemists.

The third section shows the participation of dipole-dipole and hyperconjugative effects in the axial preference of 2-substituted 1,3-dithianes and 1,3,5-dithiazines. Analysis of the enthalpic and entropic terms in these equilibria leaves little doubt that second-row anomeric interactions exist.

The Life and Times of [Ru(bpy)₃]²⁺: Localized Orbitals and Other Strange Occurrences

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The utility of and interest in [Ru(bpy)₃]²⁺ and its analogue compounds is attested to by a recent long review[1] focusing primarily on the photochemistry of [RuL₃]²⁺ type compounds. The ability of the colored [Ru(bpy)₃]²⁺ to absorb light and photocatalyze a variety of bimolecular electron transfer reactions at room temperature has served to generate literally hundreds of papers dealing with topics as diverse as the water splitting reaction[2-5] and the photocatalytic snipping of DNA.[6-8] Electrochemists have utilized the photooxidative ability of the [Ru(bpy)₃]²⁺ unit to modify[9-12] the redox capability of metal electrodes. Incorporation of [Ru(bpy)₃]²⁺ into various clays[13-15] results in a photocatalytic system capable of reacting with various redox partners. In the great majority of examples, the key to the utility of the [RuL₃]²⁺ species is the existence of lowest emitting excited states that are reasonably stable to decomposition.

This stability results from the fact that this emitting state is a dπ* excited state rather than a dd* state. In spite of the great quantity of useful bimolecular photochemistry done with these [RuL₃]²⁺ materials, a description of this unique emission was developed only recently. The so-called "localized orbital" description (Figure 1)[16-18] used by us to explain the multiple π-π*

emission from the mixed-ligand [Rh(bpy)₂(phen)]³⁺ and [Rh(bpy)(phen)₂]³⁺ complexes was suggested[16,18] as a reasonable description of the emission of the parent [Rh(bpy)₃]³⁺ and [Rh(phen)₃]³⁺ complexes and, further, as a feasible description of the d–π* emission from [Ru(bpy)₃]²⁺. Certainly, the concept of an orbital localized on one bpy chelate ring but not interacting with adjacent orthogonal π electron systems was reasonable for the Rh(III) complexes but was difficult to comprehend for a system in which the orbital character of the emitting state is described as dπ*. In such a system, the emitting state involves an unpaired electron in an orbital on one atom, Ru(III), which is common to each of the three π chelate rings in the metal complex. Consequently, a series of results from our lab and the labs of others, for solution and crystal media, have been presented to elaborate the localized orbital character

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[Ru(bpy)₃]²⁺ Localized Orbitals

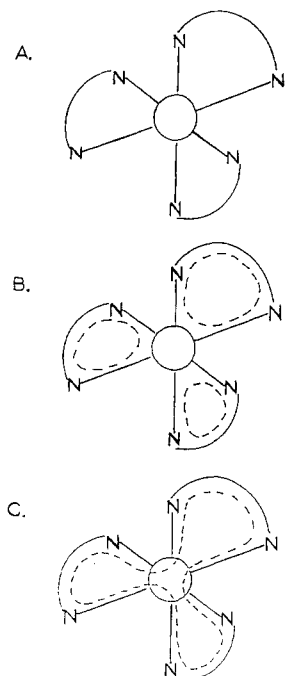Acc. Chem. Res., Vol. 22, No. 10, 1989 365

Figure 1. Localized and delocalized orbitals: (A) propeller structure of D_3 tris system; (B) localized (spatial isolated) orbital; (C) delocalized orbital.

of the emission and to define the emitting state.[19-31] These data and interpretations, although occasionally flawed, have enabled significant progress in establishing the existence of single chelate ring localized orbitals for $[RuL_3]^{2+}$, $[RuL_2L']^{2+}$, $[RuL_2X_2]^{n+}$, and $[RuLX_4]^{n+}$ type complexes (L and L' are π bidentate ligands and X is a monodentate ligand), suggesting a mechanism for generation of "spatially isolated orbital" states and, finally, producing a concise description of the number, spacing, and origin of the emitting manifold of states.

Localized or Delocalized Orbital Emission

Subsequent to our suggestion of a localized orbital emission for $[Ru(bpy)_3]^{2+}$, Professor W. Woodruff, then of the University of Texas at Austin, measured the room-temperature excited-state resonance Raman[27] for the emitting state of $[Ru(bpy)_3]^{2+}$ and found that the vibrational spectra observed necessitated the existence of bpy and bpy⁻ ligands for this emitting state, consistent with a localized orbital description of the emitting-state species. Thus $*[Ru^{III}(bpy^-)(bpy)_2]^{2+}$, not $*[Ru^{III}(bpy^{1/3-})_3]^{2+}$, is the best description of this excited

Figure 2. Steady state excitation polarization (SSExP) for $[Ru(bpy)_3]^{2+}$. Note P_{max} at 21 900 cm⁻¹.

state. Most recently Brus and Carroll[29] have extended these results by determining the excited-state resonance Raman (RR) for $[Ru(bpy)_3]^{2+}$ in frozen solution (90 K) as well as fluid room-temperature solvents. These results, done by using time-resolved methods probing to the picosecond domain, will be discussed below.

Shortly after the Woodruff report, we published luminescence photoselection (polarization) results for the $[Ru(bpy)_3]^{2+}$ complex.[20] The photoselection technique initially developed and utilized by Albrecht[32] can provide polarization (P) for randomly oriented solute species dissolved in either glassy or polymer matrices. The ease of sample preparation affords a significant advantage for this method over single crystal polarization methods. The method does, however, provide only the *relative* orientation of the absorber and emitter oscillators. Nevertheless, biochemists[33-36] have utilized the technique, in particular in the time-resolved mode, to characterize protein motion. Chemists have utilized[37-39] the methodology to characterize nonradiative relaxation for organic π electron systems.

Our use of this technique was, in part, motivated by the earlier photoselection results of Fujita and Kobayashi[19] for $[Ru(bpy)_3]^{2+}$. These workers reported data that we did corroborate and extend, but our interpretation of the origin of the high P_{max} ($P_{max} = 0.23$) (Figure 2) differed from that of the Japanese workers[19] and was that localization occurred *at 77 K*, not just at room temperature as for the Woodruff excited state RR work. Subsequently we did also note that the emission energy and structure of mono bpy compounds[20] as $[Ru(bpy)(py)_4]^{2+}$ and bis bpy complexes as $[Ru(bpy)_2(py)_2]^{2+}$ were nearly identical with those of the tris $[Ru(bpy)_3]^{2+}$.

An experimental result[40] that initially seemed to be in contradiction to this localized orbital model for the emission was the spectra and emission decay of the

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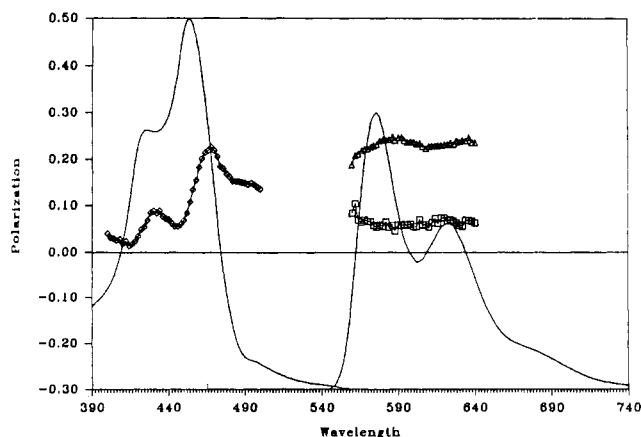(32) Albrecht, A. C. *J. Mol. Spectrosc.* **1961**, *6*, 84.
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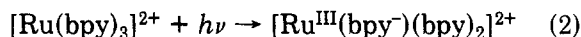(37) El Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.
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mixed-ligand complexes $[Ru(bpy)_2(phen)]^{2+}$ and $[Ru(phen)_2(bpy)]^{2+}$. For these materials only a single exponential decay could be measured; therefore, no time-resolved emission could be measured as for $[Rh(bpy)_2(phen)]^{3+}$. However, it must be noted that the emission spectra and lifetimes of the two parent tris Ru(II) complexes are similar and too close to result in resolved spectra or nonexponential decay for these compounds. Further, the recent identification[41,42] of a bona fide multiple emission (one characteristic of a RuL unit, L = bpy or phen) from the $[Ru(bpy)_2(HDPA)]^{2+}$ and the $[Ru(phen)_2(HDPA)]^{2+}$ complexes, complete with biexponential decay times and time-resolved emission spectra, verifies that the fundamental emitting chromophore is simply a Ru(bpy) or Ru(phen) unit, respectively. By analogy then the $[Ru(bpy)_3]^{2+}$ emitting species is best defined as a trimer with overlapping emission spectra and decay times from the individual Ru(bpy) units.

Simultaneous with the accumulation of data pointing to the localization of the emitting excited states, data (spectroscopic primarily) was obtained for the electrochemically reduced species.[43-49] The one electron reduced species (eq 1) could, in a qualitative sense, serve

$$[Ru(bpy)_3]^{2+} + e^- \rightarrow [Ru(bpy^-)(bpy)_2]^+ \quad (1)$$

$$[Ru(bpy)_3]^{2+} + h\nu \rightarrow [Ru^{III}(bpy^-)(bpy)_2]^{2+} \quad (2)$$

as a model for the excited-state species since the reduction electron, as the optical electron, appears to enter spatially isolated orbitals localized primarily on the π ligand portion of the metal complex. The combination of cyclic voltammetry and resonance Raman, electronic absorption, and electron spin resonance spectroscopy for the reduced species did demonstrate that both L and L$^-$ ligands were present in the reduced $[RuL_3]^{n+}$ species, the reduction electrons in orbitals on adjacent ligands do exhibit a minimum interaction, and the reduction electrons do move between the π ligands, i.e., intramolecular electron hopping occurs.

However, quantitative comparison of the interaction energies of the reduced and optical species should be approached with caution.

With all of the cumulative evidence that "localized" excited states exist, some spectroscopic data[25,50-55] for

dilute and pure single crystals has been presented that indicates that absorption occurs to excited states that are best classified within the D_3 symmetry system, a result requiring that the excited states are "delocalized"! These data and the conclusions derived from polarized absorption studies seem reasonable and even correct (at least for the *dilute* single crystal systems),[54,55] yet such conclusions would appear to contradict the conclusions reached from the luminescence polarization data and the excited-state resonance Raman.

Two general possibilities exist to resolve the dilemma: first, one of the two types of experiments has given incorrect data or data not relevant to the problem, or, second, both experimental approaches are correct and the conclusions obtained are not complete.

Certainly, dilute single crystal data[54,55] for $[Ru(bpy)_3]^{2+}$ in an appropriate D_3 host lattice should give good data; thus, the D_3 symmetry conclusion is likely correct. Recall, though, these absorption results relate only to the spin-allowed MLCT transition, not to the spin-forbidden transition associated with the emitting state.

But what of the possibility that the glassy solution used by the Japanese workers[19] and us to obtain the original $P_{max} = 0.23$ for $[Ru(bpy)_3]^{2+}$ resulted in inhomogeneity,[56-57] i.e., a *classical* red-edge effect? This red-edge effect[58,59] is more common in polar solvents; therefore, the original work by Carlin,[20] in which both the excitation polarization spectra and the excitation spectra were found to be unaffected by solvent polarity, argued against this red-edge effect. Indeed, most recently, this same $P_{max} = 0.23$ was measured for $[Ru(bpy)_3]^{2+}$ in a dichloromethane–ether solvent mixture, a nonpolar solvent mixture significantly different from the alcohol–water glasses in which $P_{max} = 0.23$ can also be measured. Further, these most recent polarization results[30] indicate that the excitation polarization structure and the magnitude of P_{max} are primarily determined, in most cases, by the *complex structure*. Thus, the tris Ru(II) complexes typically produce a $P_{max} \sim 0.23$, the bis complexes $[Ru(bpy)_2X_2]^{n+}$ give $P_{max} \sim 0.34$, and the $[Ru(bpy)X_4]^{n+}$ complexes produce $P_{max} \sim 0.42$. Further, all of these P_{max} results, including some for mixed-ligand complexes, can be rationalized by a model in which interchromophoric coupling, that is, coupling between the π ligand units in a $[RuL_3]^{2+}$ complex, results in a reduction of the P_{max} from the 0.5 limit of a monomeric $[Ru(bpy)X_4]^{n+}$ complex. Thus the anomalous P_{max} occurring on the red edge of the single MLCT band for bis and tris complexes as $[Ru(bpy)_2(bpz)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ derives from the same localized transition that occurs in $[Ru(bpy)(py)_4]^{2+}$. The intensity components perpendicular to the direction of the original localized chromophore of $[Ru(bpy)(py)_4]^{2+}$ are generated by the two additional Ru(bpy) chromophores in the $[Ru(bpy)_3]^{2+}$ complex. The observation of a time-resolved P_{max} decay[30] at 77 K for the $[Ru(bpy)_3]^{2+}$ complex that results from spin–lattice relaxation is verification of this mechanism. The time dependence of P_{max} for $[Ru(bpy)_3]^{2+}$ in various solvents

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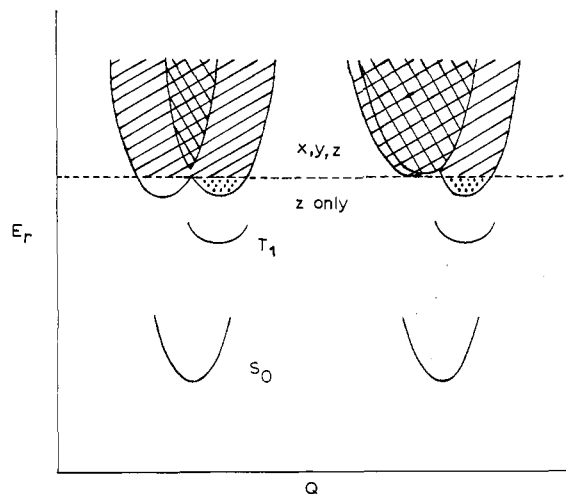(59) Castelli, F.; Forster, L. S. *J. Am. Chem. Soc.* **1973**, *95*, 7223.

Figure 3. Singlet MLCT potential surface for tris diimine complexes demonstrating localized and delocalized regions.

at 77 K thus indicates that a decay of P_{max} from the localized (experimental) limit of $P_{max} = 0.4$ to the steady state $P_{max} = 0.23$ occurs with nanosecond decay times. This decay corresponds to the spin-state relaxation from the Z polarized spin level ($P_{max} \sim 0.4$) to the X or Y spin states producing the steady-state $P_{max} = 0.23$. Consequently, the emitting state for $[RuL_3]^{2+}$ complexes is *localized* but of mixed polarization, unlike that of the mono bpy Ru complex which derives from a pure Z emission state. That this "interchromophoric coupling" is an appropriate description is made creditable by the calculation of P_{max} consistent with experimental data for a variety of additional mixed-ligand complexes with altered emitting-level spacings.[60]

But, if the solvent media perturbation does *not* determine the localization, how can the single crystal polarized absorption and the photoselection results be consistent? The key, of course, is that the excited singlet potential surface (Figure 3) has a localized (C_2) portion near the minimum, but above this minimum the singlet state can be "delocalized"! The polarized absorption spectra for single crystals must, necessarily, reflect only the "delocalized" portion of the spectrum across most of the absorption band. Across the extreme red edge of the singlet absorption, localized transitions occur; however, the relative contribution of the localized and delocalized portions of the potential surface cause the appearance of a near D_3 intensity distribution in the polarized absorption. And what of the excitation polarization spectra? At shorter wavelengths than the P_{max}, the P drops rapidly to ~ 0.1, consistent with a planar (E symmetry) absorber and a mixed-polarization emitter (Figure 2). Thus, both localized and delocalized states are present in the singlet manifold, but the emitting spin triplet is "localized" and of mixed polarization. This accounts for P greater than 0.14 for the localized portion of the singlet.

The origin of the *small* excitation dependence[20] of the emission and excitation spectra can now be rationalized. Some of this dependence can result from exciting the different regions of the singlet potential surface. Alternatively, some of this dependence may be the result of excitation of the *near* isoenergetic equivalent chromophores. The structure observed (Figure 2) in the

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excitation polarization of a typical $[RuL_3]^{2+}$ system is not directly the result of underlying vibrational structure, but must have its origin in the overlap of the "localized" and "delocalized" portions of the potential surface. Further, the emission polarization spectra[60] show structure that can be interpreted as an indication of the presence of multiple emission for mixed-ligand compounds as $[Ru(bpy)_2(phen)]^{2+}$ that have near degenerate energy levels.

The Mechanism of Localization: Intrinsic or Extrinsic?

The question of the mechanism of the localization will next be considered. Although attempts have been made to obtain photoselection data for oriented single crystals[57] of $[Ru(bpy)_3]^{2+}$, no appropriate determination of this data for oriented samples is yet available. However, Brus and Carroll[28] have succeeded in determining excited state resonance Raman for dilute crystals of $[Ru(bpy)_3]^{2+}$ that demonstrate localization of the emission for the $[Ru(bpy)_3]^{2+}$ complex in single crystals. These data and low temperature lifetime data discussed below make it apparent that the localization (or delocalization) is not affected by the physical state of the complex. However, the suggestion has been made that the "localization" is a solvent-driven effect.[57,61-64] That is, at low temperatures in a glassy (frozen) solvent, the emitting state would be "delocalized". This conclusion was based primarily upon the large shift and change in the emission spectra upon thawing of the glassy solution for $[Ru(bpy)_3]^{2+}$. This conclusion overlooked the fact that, in general, the emission spectra for most chromophores changes dramatically at the solvent melting point.[33,33a] Meyer and co-workers[65] have determined that an emission shift comparable to that observed for the frozen $[Ru(bpy)_3]^{2+}$ complex occurs for a mono complex of Os(II). Finally, a key piece of evidence for the localization is the original polarization data.[19,20] These data were determined at *77 K*, while the recent excited-state resonance[28] of Carroll and Brus at *90 K* in glassy solution indicates that, under these conditions, bpy⁻ and bpy ligands can be identified. Since gross movement of the solvent is very unlikely at 77 or 90 K, the localization must be intrinsic. Such an intrinsic process is best described as a "vibronic" effect and must occur on the time scale of a vibration, 10^{-14} s.

The Number and Spacing of the Emitting Levels: Spin–Orbit Levels or Spin Triplet?

The early temperature dependent lifetime and quantum yield data[22] for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ and many analogous tris derivatives (glassy solution) of general formula $[ML_3]^{2+}$ could be fit to equations permitting the calculation of the spacing of the emitting energy levels as well as the individual rate constants for these emitting levels. This fit is, however, dependent upon the assumption of equilibration among the emitting levels in the range of 77–1.2 K. Given the limitations of the Crosby measurement system,[66,67] this

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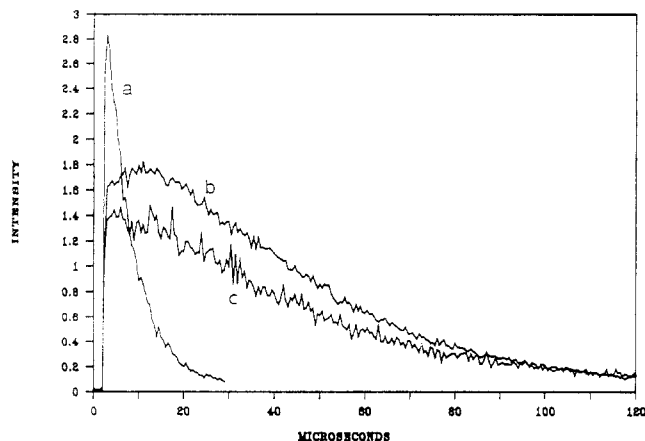(66) Harrigan, R. W.; Crosby, G. C. *J. Chem. Phys.* **1973**, *59*, 3468.

Figure 4. Decay curve for $[Ru(bpy)_3]^{2+}$ in ethanol: (a) 77 K, zero field; (b) 7 K, zero field; (c) 7 K, 15 kG.

Figure 5. General description of excited-state phenomena. A nonluminescent level is populated via ISC from the singlet manifold. Population is transferred to a luminescent level with a rate k_1, and decay to the ground state occurs with a rate k_2.

appeared to be a valid assumption. However, the validity of this assumption, in hindsight, should have been questioned earlier. First, Halper[17] had determined that, at 7 K, the decay of emission from $[Rh(phen)_3]^{3+}$ became multiexponential and did obey the simple relationships presented earlier by El Sayed[68,69] and van der Waals[70,71] for systems in which slow spin–lattice relaxation prevents equilibration of the spin states for emitting spin triplets of heterocycles. The magnetic field dependence of the $[Ru(bpy)_3]^{2+}$ emission at 2 K produced by Crosby[72] and Krausz[73] did produce evidence that the spin states are not equilibrated at this temperature. Electron spin resonance measurements performed at He(I) temperature[29] provided direct evidence of the lack of thermal equilibrium.

Our recognition[30] that the time-resolved P_{max} data obtained at 77 K resulted, not from exciton hopping, but from spin–lattice relaxation, was a stimulus to search for spin–lattice relaxation effects at liquid He temperatures. The first series of experiments done were a determination of the excitation polarization spectra[31] over the temperature range 7–77 K. The startling observation that these spectra are essentially invariant over this temperature range necessitated reexamination of the Crosby results. If the 10- and 50-cm^{-1} spacing of Crosby's picture were valid, then large changes in the photoselection spectra are expected due to change in the Boltzmann populations of these levels. Additional verification of the absence of thermal equilibrium due to slow SLR was obtained from the determination[31] (using laser excitation and boxcar integrator detection in the range 7–10 K) that a rise time could be measured for the decay of the emitting levels of $[Ru(bpy)_3]^{2+}$. Application of a moderate-strength magnetic field removes the slow rise time as predicted for a spin system controlled by slow SLR (Figure 4). The decay curve observed can be modeled by a sequential first order decay scheme (Figure 5) in which the intermediate species concentration (here the emitting species) reaches a maximum at some delay time after the pulse initia-
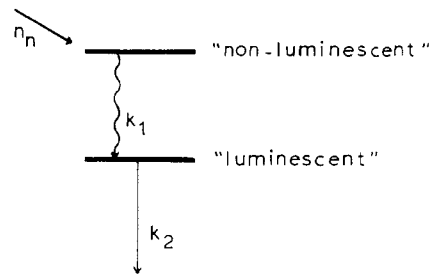
tion. The manipulation of the series first order decay equations indicates that the rise time is very sensitive to temperature. Thus, at slightly higher or lower temperature than that used, the rise time cannot be observed. All of these conclusions and data are consistent with the excited-state ESR obtained by Hirota and co-workers[29] for the $[Ru(bpy)_3]^{2+}$ complex in glassy solution and single crystal. Here $g \sim 2.00$ and $D = 0.1$ cm^{-1} were calculated from the data. Such a zero field splitting is totally incompatible with the $\sim$10- and 60-cm^{-1} splitting calculated by Crosby. Most recently Hirota and co-workers[74] have determined the decay time as a function of temperature for the mono bpy complex $[Ru(bpy)(CN)_4]^{2-}$, which gave a curve shape nearly identical with that of $[Ru(bpy)_3]^{2+}$. No first order spin orbit coupling is, however, possible for the mono bpy complex since no orbital degeneracy ($L = 0$) can occur. The only possible rationale for the calculated spacings would be as a result of spin–spin interaction. Yet no case of such large spin–spin splitting for a transition-metal complex or a heterocycle is known. Therefore, the emitting manifold for tris, bis, and mono bpy complexes of Ru(II) must be a typical spin-state manifold as found in most organic π-electron heterocycles with the spacing of magnitude -0.1 cm^{-1}, not 10–50 cm^{-1} as calculated in the Crosby studies.

The pure single crystal emission results of Yersin and co-workers[50–53] require comment since these crystals give sharp line emissions with spacings of 10 and 50 cm^{-1}, nearly identical with that predicted by Crosby's calculation from lifetimes and quantum yields. Yersin has, using polarized absorption and emission data, suggested that two of these emission lines are E orbital symmetry and the third is nondegenerate. If this were true, then the total degeneracy of these three states *alone* would be 15 (spin × orbital), and at least one additional level has been identified by Yersin some $\sim$200 cm^{-1} above this. This does then exceed the total degeneracy (9) possible for the triplet manifold. Add to this the fact that the low-temperature decay[75] of the pure crystal is different from that of the dilute crystal or the glassy solution (the latter two behave similarly) and the conclusion must be that these anomalous pure crystal data must result from solid-state (exciton) effects. Indeed, the $[Os(bpy)_3](ClO_4)_2$ doped single crystal data[52] have been obtained by Yersin and co-workers, and the 60- and 200-cm^{-1} splittings measured are much larger than the 8- and 57-cm^{-1} spacings calculated by Crosby[76] from

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lifetime data for $[Os(bpy)_3]^{2+}$. Recently, Hirota and co-workers[77] have succeeded in measuring the sharp line emission for a dilute single crystal of $Ru(bpy)_3^{2+}$, but as yet the glassy solution medium does not yield the sharp line emission. A key to this puzzling experimental result may be the determination by Bernal[78] that upon crystallization the structures of $[Ru(bpy)_3X_2]$ (X = PF_6^-, BF_4^-, and ClO_4^-) change with time (as in so-called "plastic" crystals). These single sharp line crystal results are unique, and this exciton effect should be explored further, but the sharp line emission spectra for crystals likely is not related to the molecular localized emission occurring from $[Ru(bpy)_3]^{2+}$. However, as noted previously, the localized emission is characteristic of the Ru(bpy) chromophore and does occur for these solid-state species as for the solution species.

Muddy Water: Confusion and Contradiction

That the study of the photophysics of $[Ru(bpy)_3]^{2+}$ has generated a large and frequently contradictory body of literature over the past two decades, and that the research continues apace even today, is indication of the difficulty and intractability of the problem faced. However, substantial progress has been made toward the understanding of the excited-state energetics and dynamics of this series of complexes, with results of potentially wide applicability for the basic understanding of similar metal complex systems. This, however, is often not visible to the casual observer of this literature.

Much of this confusion has been a natural result of having a large number of research groups throughout the world approaching the study of excited states of $[Ru(bpy)_3]^{2+}$ from different perspectives, i.e., using different techniques, different time scales for experimentation, different temperatures, different matrices and different complexes and studying different portions of the excited manifold. Indeed the situation can be likened to that in the classic "blind men and elephant" parable.

The first blind man, approaching the huge beast and grabbing the tail, said, "Ah yes, the elephant is truly like a rope!" The second, clutching at a mighty leg, said, "Aha, he is none of these things, but the animal is as a huge snake." And so it goes for our "elephant", $[Ru(bpy)_3]^{2+}$. Should localization in a dilute medium imply localization in pure crystals? Or should conclusions obtained with any one experimental approach necessarily apply to other, much different approaches? It is perhaps impractical to expect results from optical spectroscopy, magnetic resonance, electrochemistry, etc., performed on every possible permutation of complex, solvent, concentration, viscosity, and temperature to be 100% in agreement, due to the possibility that the complex may behave differently under grossly different conditions.

Even in light of this natural source of disagreement, however, it remains possible to find examples of contradictory data or improper analysis of data in the literature. Fortunately few instances of this are still extant, as such occurrences have normally been identified quickly. Numerous examples of this process have occurred, such as the following.

First, the fast time-dependent depolarization of the luminescence of $[Ru(bpy)_3]^{2+}$ was originally attributed to exciton hopping by this laboratory.[79] This was reconsidered and corrected in a subsequent publication by the same authors, who attributed the phenomenon to spin–lattice relaxation of the emitting triplet state.[30] Second, the time-dependent shift in the emission energy of $[Ru(bpy)_3]^{2+}$ at the solvent melting point was originally attributed to a delocalized–localized transition of the chromophore,[62,63] but was corrected by Meyer[65] and Tazuke[80] and shown to be the result of simple solvation effects. Third, erroneous time-resolved resonance Raman data were reported by Krausz,[24] but were retracted by him and corrected by Brus and Carroll.[28] Fourth, erroneous excitation photoselection data were reported by Krausz[57] and were quickly rebutted by this laboratory.[81] Fifth, a small solvent dependence of the spin-allowed MLCT absorption maxima at room temperature was analyzed by Meyer as indicative of localization in the singlet manifold,[82] but has been recently revised by Milder[83] as improper interpretation of data. Finally, narrow-line emission spectra were originally obtained by Yersin for neat crystals of $[Ru(bpy)_3]^{2+}$.[51] Krausz reported his inability to reproduce these data,[84] but quickly retracted this in a subsequent report of the phenomena.[85]

Thus the appearance of confusion in the literature is not completely merited. A full examination of work to the present reveals that few areas of serious disagreement still exist and that those in existence may be due to time scale or matrix effects. In this latter category comes the question of consistency of neat crystalline[26,50,84,85] and dilute solution data.[20,21,23,27–31] An ultimate solution to this problem may only come from studies of isolated cold molecules of $[Ru(bpy)_3]^{2+}$, with methods such as supersonic beam spectroscopy. The low vapor pressure of this relatively large complex has prevented this in the past; however, the recent observation of free molecular $[Ru(bpy)_3]^{2+}$ following fast atom bombardment of a powdered sample in a mass spectrometer[86] gives hope that such studies will be possible in the near future.

Thus research on the photophysics of $[Ru(bpy)_3]^{2+}$ presently contains few existing conflicts. Those that do exist are likely related to environmental factors,[78] themselves an interesting aspect of the work.

Summary: What Do We Know?

The discussion indicates that the following conclusions can be made about the emitting state of Ru(II) diimine complexes (mono, bis, and tris). First, the emission is a phosphorescence localized on a single RuL unit with potential barriers (Figure 2) existing between the adjacent spatially isolated optical orbitals. Second, multiple state emission necessarily occurs for all

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$[RuL_3]^{n+}$ and many $[RuL_2L']^{n+}$ complexes since the individual RuL units have near degenerate emitting energy levels. Third, the "spatially isolated optical orbital" implies that only noninteracting relaxation channels exist in the spin-triplet channel. However, *delocalized* MLCT excited states exist for the singlet manifold such that low *P* values, consistent with the presence of E symmetry states, are present (localized singlets also exist). Such a situation accounts for the observation that the *singlet* MLCT states have polarization properties largely determined by D_3 symmetry. Fourth, the localization occurring in the triplet manifold is fast and intrinsic, a vibronic effect. (The solvent, at most, may play a role in the rate of intramolecular exciton hopping between chelate rings.) Finally, the emitting levels are triplet spin levels that behave as the spin states in a typical aromatic heterocycle, so the spacing of the three spin states is ~ 0.1 cm^{-1}, indicating a very small spin-orbit interaction. Slow spin-lattice relaxation results in the failure of these spin states to equilibrate at low temperatures ($T < 20$ K).

Lead in Petrol. The Isotopic Lead Experiment

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Introduction

When cars were first introduced, fuel petrols were obtained by distillation of crude oil. These consisted of hydrocarbons formed over thousands and thousands of years and were composed of alkanes, mainly normal, some aromatics, and no olefins. The octane number (ON), which defines a scale to evaluate the antiknock quality of petrol, was low (around 60), as was the compression ratio of the engines, while the fuel consumption was high. Together with improvements in engines, new conversion processes have led to the production of relatively low cost fuels with ON values increased to 85–90. The discovery of the performance of lead alkyls, $Pb(C_2H_5)_4$ and/or $Pb(CH_3)_4$, allowed a further increase of ON (98–100) when lead was added to petrols at the level of 0.6–0.8 g/L. Therefore around 1970 the most favored refining processes were those leading to the isoparaffins, which had a high susceptibility to lead, and to aromatics to produce petrols with high ON at relatively low cost.

Starting from 1960, under pressure from ecologists, studies were undertaken all over the world to evaluate the impact of the gaseous emissions (CO, NO$_x$, HC, etc.) and of airborne lead particulates on the environment and on humans. However, the uncertainties regarding

the possible effects of hydrocarbon emissions were so great that a chemical characterization of the individual hydrocarbons was necessary. Vehicle exhaust emissions were found to consist of about 1000 different chemical compounds, most of which are or may be assumed to be injurious to human health. There is probably no harmless level of emission and exposure for these substances, lead included. This means that the risk can be reduced only by lowering the emission levels.

Many studies were dedicated to the evaluation of the impact of automotive lead on the environment and to the assessment of its absorption in the human population. They can be subdivided into two groups, those based on changes of air and blood lead concentrations[1-7] and those based on changes of air and blood lead isotopic compositions.[8-12]

Sergio Facchetti was born on December 5, 1931, in Borgo Ticino, Novara, Italy. He received a Doctorate in chemistry in 1955 at the University of Pavia. During 1957–1959, he was engaged in research in the field of structural analysis of mineral oils at Milan Polytechnic. Since 1959 he has worked at the Ispra Establishment of the European Communities. Since 1967 he has taught mass spectrometry and instrumental techniques in many Italian universities, at present at Sassari University, and has been course coordinator of Ispra-Courses on analytical techniques. He has been active in the Italian Chemical Society. He was Chairman of the VII International Mass Spectrometry Conference (Florence, 1976). He is a member of the Editorial Board of the journal *Biomedical & Environmental Mass Spectrometry*. He has been deeply involved in the Safeguards activity and in the identification of environmental pollutants at trace levels. Of particular significance are the environmental studies carried out in connection with the Seveso disaster and the Isotopic Lead Experiment (ILE project, 1974–1985) to determine the automotive lead contribution to total lead in human blood and to airborne lead and to follow the pathway of lead through the environmental compartments.

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