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The Luminescence of Heterobischelated Complexes of Iridium(III). II. Analysis of the Thermally Nonequilibrated Levels in the Luminescence of *cis*-Dichloro(1,10-phenanthroline)(4,7-dimethyl-1,10-phenanthroline)iridium(III) Chloride

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Abstract: The multiple emissions of *cis*-dichloro(1,10-phenanthroline)(4,7-dimethyl-1,10-phenanthroline)iridium(III) chloride, $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$, have been resolved by analysis of luminescence decay curves as a function of emission wavelength. The data are best fit by a model which views the luminescence as the result of three sets of thermally nonequilibrated levels with lifetimes of 6.0, 8.7, and 22 μs. The levels all lie within a 400-cm^{-1} energy region. The 22-μs set of levels arises from a mixed $d\pi^*$-$\pi\pi^*$ orbital parentage localized around the 4,7-Me(phen) ligand. The 6.0 and 8.7 μs levels arise from $d\pi^*$ or d-d orbital parentage. The orbital parentage of the levels produced by excitation is retained to some degree during radiationless deactivation of the complex. The origin of this unique behavior in the heterobischelated complexes of Ir(III) is attributed to the combined effects of charge localization and vibrational deficiencies.

The nonexponential luminescence decay of *cis*-dichloro(1,10-phenanthroline)(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride, $[IrCl_2(phen)(5,6\text{-}Me(phen))]Cl$, at 77 K has been reported.[2] This molecule is the first example of an iridium(III) complex with this unusual property, which is indicative of emission of light from two or more sets of thermally nonequilibrated levels. The decay curves for this complex have been determined as a function of emission wavelength throughout the luminescence spectrum.[3] Analysis of these data on the basis of a model which presumes that two sets of thermally nonequilibrated levels are responsible for the emission indicates that the two sets of levels are split by 200–300 cm^{-1}. The lower set of levels decays with a lifetime of 65 μs and is thought to arise from $\pi\pi^*$ orbital parentage. The upper set decays with a lifetime of 9.5 μs and is thought to arise from $d\pi^*$ orbital parentage. The rate of interconversion of the two sets is thought to be negligible relative to their rates of decay to the ground state. From an analysis of the excitation wavelength dependence of the decay curves and time-resolved spectra of the complex we have formulated the following set of selection rules for radiationless transitions in the molecule: $d\pi^* \leftrightsquigarrow d\pi^*$; $\pi\pi^* \leftrightsquigarrow \pi\pi^*$; $d\pi^* \not\leftrightsquigarrow \pi\pi^*$. That is, there is a tendency toward retention of orbital parentage during radiationless deactivation of the complex.

The formulation of a set of symmetry-based selection rules for radiationless transitions in polyatomic molecules has been attempted by several authors.[4,5] Although these selection rules are of some utility, particularly in the case of small molecules with vibrational deficiencies,[5a] they are difficult to apply to large molecules. This difficulty arises from two major sources. First, the symmetry of the various excited states of large molecules is often not known with sufficient certainty to apply symmetry selection rules with confidence. Second, the abundance of vibrational modes of all possible symmetries in polyatomic molecules usually provides for a vibration of the right symmetry to make the radiationless transition between any two electronic levels allowed by symmetry. In spite of this, the radiationless transition may not occur for other reasons. Robbins and Thomson[4] have had some success in applying symmetry selection rules to complexes of the first-row transition metals by adding certain restrictions to the general symmetry considerations. The treatment was limited to "d–d" transitions from the lowest excited state to the ground state, and required incorporation of restrictions based on the orbital nature of the states as well as their overall symmetry. Thus, while symmetry selection rules for radiationless transitions have a sound theoretical basis, their application to polyatomic molecules is of limited use.

In contrast to the limited utility of symmetry-based selection rules for radiationless transitions in polyatomic molecules, El-Sayed[6,7] has successfully employed a set of selection rules for singlet–triplet transitions in N-heterocycles which are based upon the orbital parentage of the electronic levels. These rules state that radiationless transitions between an nπ^* state and a $\pi\pi^*$ state of different spin multiplicity are about 10^3 times faster than those between two $\pi\pi^*$ or two nπ^* states of different spin multiplicity. That is: $S_{\pi\pi^*} \leftrightsquigarrow T_{n\pi^*}$; $S_{n\pi^*} \leftrightsquigarrow T_{\pi\pi^*}$; $S_{\pi\pi^*} \not\leftrightarrow T_{\pi\pi^*}$; $S_{n\pi^*} \not\leftrightarrow T_{n\pi^*}$, where S and T stand for singlet and triplet, respectively. These results have been confirmed by numerous experimental studies of intersystem crossing in N-heterocycles.[7,8]

In this paper we extend our previous study of energy transfer processes in the $[IrCl_2(phen)(5{,}6\text{-}Me(phen))]^+$ ion to the complex ion, $[IrCl_2(phen)(4{,}7\text{-}Me(phen))]^+$. As a result of this study we are able to present a broader-based discussion of radiationless transitions between the states of heavy metal complexes and of the selection rules which govern these transitions. Furthermore, the study represents a step towards the elucidation of the effects of slight changes in ground state molecular structure of the radiationless processes between the electronically excited levels of metal complexes.

Experimental Section

cis-Dichloro(1,10-phenanthroline)(4,7-dimethyl-1,10-phenanthroline)iridium(III) Chloride. $[IrCl_2(phen)(4{,}7\text{-}Me(phen))]Cl$ was prepared from $K[IrCl_4(phen)]$ and 4,7-Me(phen) by the method of Watts and Harrington.[9] This technique is a modification of the Broomhead and Grumley[10] procedure for the preparation of $[IrCl_2(phen)_2]Cl$. The complex was also prepared from $K[IrCl_4(4{,}7\text{-}Me(phen))]$ and phen. Samples of the product prepared by the two routes were found to be identical by uv-visible absorption spectroscopy and visible emission spectroscopy. The purity of the samples of the complex used in this study was established by thin-layer chromatography as described previously for $[IrCl_2(phen)(5{,}6\text{-}Me(phen))]Cl$.[2]

Anal. Calcd for $[IrCl_2C_{26}H_{20}N_4]Cl{\cdot}3H_2O$: C, 41.25; H, 3.46; N, 7.40. Found: C, 41.25; H, 3.63; N, 7.49.

Absolute ethanol (Commercial Solvent Corp., Reagent Quality) and absolute methanol (Matheson Coleman and Bell, spectroquality) were used without further purification. The solvent mixtures used in the study were ethanol–methanol (4:1 v/v) and methanol–water (4:1 v/v). Solutions of the complex at concentrations of 10^{-3} to 10^{-4} M were prepared and stored under refrigeration in dark containers when not in use.

The apparatus and techniques used in the determination of luminescence decay curves as a function of excitation wavelength and emission wavelength, time-resolved emission spectra, and time-integrated emission spectra have been described in a previous paper.[3] In this study, the luminescence decay curves of $[IrCl_2(phen)(4{,}7\text{-}Me(phen))]Cl$ were analyzed at 5-nm intervals over the range between 460 and 660 nm using 337-nm excitation. The region covers the portion of the spectrum in which the luminescence of the complex can be observed under steady-state illumination. The decay curves were analyzed by a nonlinear least-squares fit of a function representing the sum of two exponentials and also by a function representing the sum of three exponentials. The time-resolved emission spectra of the complex were determined as a function of excitation wavelength at 10-nm intervals in the region from 360 to 480 nm, using a pulsed dye laser as an excitation source. The time-resolved emission spectra of the complex were also determined with 337-nm excitation directly from the pulsed nitrogen laser. Excitation wavelengths between 337 and 360 nm and shorter than 337 nm were not available with our apparatus.

Results

A. Analysis of Dependence of Luminescence Decay Curves on Emission Wavelength. The function used in the analysis of luminescence decay curves as the sum of two exponentials have been presented in a previous paper.[3] The generalized form of this function which may be applied to the analysis of decay curves as the sum of any number of exponentials is given by eq 1

$$I(\nu,t) = \sum_{i=1}^{n} A_i(\nu) e^{-t/\tau_i} \qquad (1)$$

In eq 1, the $A_i(\nu)$ represent preexponential factors and the τ_i's represent the lifetimes of the levels whose emissions give rise to the measured luminescence decay curves. As discussed by Zuclich et al.,[11] this equation is applicable to the decay of a set of levels which are not in thermal equilibrium. Although the equation holds for any arbitrary rate of interconversion between the levels, it takes on a particularly simple form in the case where no interconversion occurs. In that case, the A_i's represent the initial emission intensities from the various levels, and each of the terms in the summation in eq 1 represents a normal decay curve for a set of thermally equilibrated levels. When this is the case, the decay curve for each set of levels may be integrated to yield the total luminescent intensity arising from the decay of that set of levels. Thus, by analyzing decay curve measurements as a function of luminescence wavelength, the emission spectrum of each set of levels contributing to the total luminescence may be deduced.

The emission spectra generated by the application of eq 1 for two sets of emitting levels to our experimental decay curves are shown in Figure 1. In the two-level analysis, lifetimes of 8.7 and 22 μs (vide infra) were fixed for τ_1 and τ_2 in eq 1, and the values of the initial intensities from each of the two sets of levels were established by the least-squares fitting routine. If the energy of each set of emitting levels is taken as the peak of the highest energy emission band, then the 8.7 μs set of levels is found at 20.9 kK and the 22 μs set is at 21.2 kK.

Analysis of our decay curves on the basis of three sets of emitting levels was accomplished by using lifetimes of 6.0, 8.7, and 22 μs for the three states. The emission spectra of the three states resulting from the least-squares determination of intensities as a function of wavelength are presented in Figure 2. From the highest energy emission peaks in these spectra, the 6.0 μs set of levels is found to lie at 21.1 kK, the 8.7 μs set at 20.7 kK, and the 22 μs set at 21.2 kK.

B. Time-Resolved Luminescence Spectra. The results of our studies of the time-resolved spectra of this complex via box-car averaging techniques are illustrated in Figure 3. This figure shows that the intensity distribution in the emission spectrum of the complex has a pronounced functional dependence of the delay time used in the measurement when the complex is excited at 337 nm. In the spectrum measured 2 μs after excitation, the three peaks at 478, 511, and 544 nm have intensities in the ratio 1:1.5:0.79. At 40 μs after excitation the three peaks are located at 472, 507, and 543 nm and are in the ratio of 1:0.93:0.39. Thus, as the delay time is increased the relative intensity in the first peak increases while that in the second and third peaks decreases. This trend continues as the delay time is increased to our

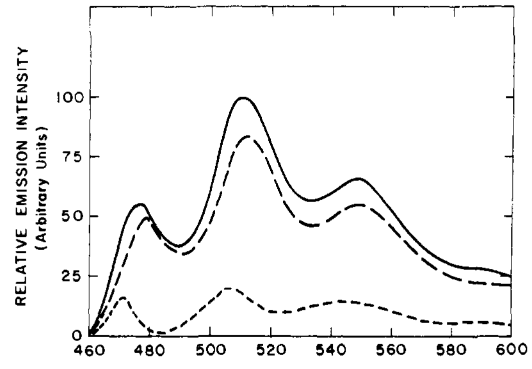

Figure 1. Results of two-level analysis of emission spectrum of [Ir-Cl_2(phen)(4,7-Me(phen))]Cl excited at 337 nm in ethanol-methanol (4:1 v/v) at 77 K: (—) total time-integrated emission spectrum; (- -) time-integrated emission spectrum of the 8.7-μs set of levels; (- - - - -) time-integrated emission spectrum of the 22-μs set of levels.

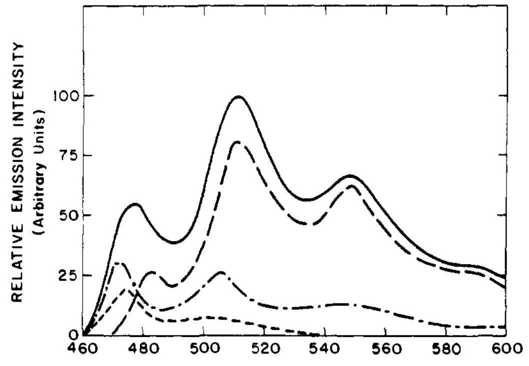

Figure 2. Results of three-level analysis of emission spectrum of [Ir-Cl_2(phen)(4,7-Me(phen))]Cl excited at 337 nm in ethanol-methanol (4:1 v/v) at 77 K: (—) total time-integrated emission spectrum; (- -) time-integrated emission spectrum of the 8.7-μs set of levels; (- • -) time-integrated emission spectrum of the 22-μs set of levels; (- - - - -) time-integrated emission spectrum of the 6.0-μs set of levels.

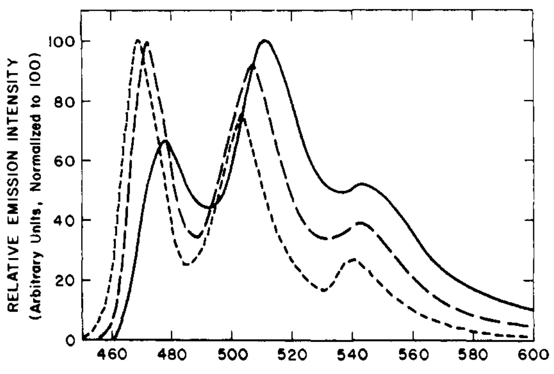

Figure 3. Time-resolved emission spectra of [$IrCl_2$(phen)(4,7-Me-(phen))]Cl excited at 337 nm in ethanol-methanol (4:1 v/v) at 77 K: (—) emission spectrum 2 μs after excitation; (- -) emission spectrum 40 μs after excitation; (- - -) emission spectrum 180 μs after excitation.

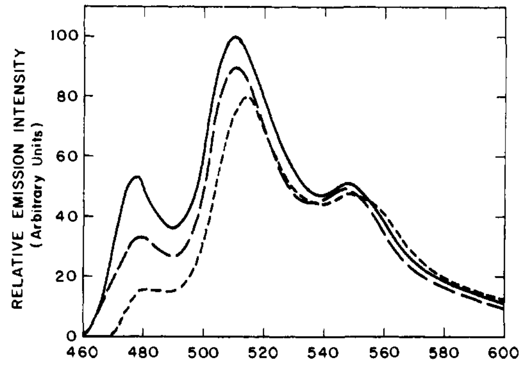

Figure 4. Time-resolved emission spectra of [$IrCl_2$(phen)(4,7-Me-(phen))]Cl 2 μs after excitation in ethanol-methanol (4:1 v/v) at 77 K as a function of excitation wavelength: (—) excited at 360 nm, (- - -) excited at 420 nm, (- - - -) excited at 470 nm.

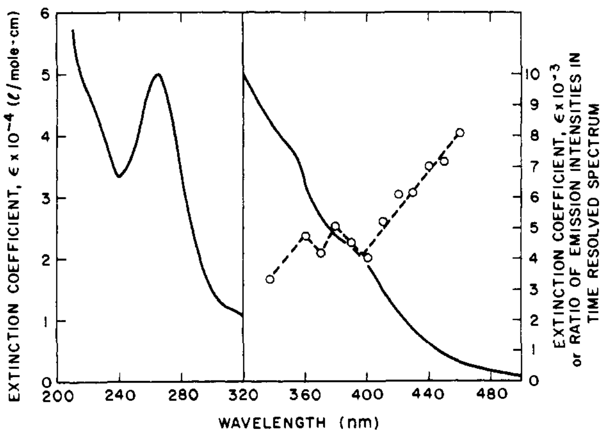

Figure 5. Ratio of emission intensities in the first two bonds of the time-resolved emission spectra of [$IrCl_2$(phen)(4,7-Me(phen))]Cl 2 μs after excitation in ethanol-methanol (4:1 v/v) at 77 K as a function of excitation wavelength and absorption spectrum in ethanol-methanol at 25 °C: (—) absorption spectrum, (- - -) ratio of emission intensities.

limit of 180 μs. At this time the three peaks are found at 469, 503, and 540 nm with an intensity ratio of 1:0.8:0.25.

The dependence of the time-resolved spectrum of the complex on excitation wavelength is illustrated in Figure 4 for a 1.5-μs delay time. This figure shows that the second peak in the spectrum increases in intensity relative to the first peak as the excitation wavelength is increased. The time-resolved emission spectrum could be determined for excitation wavelengths as long as 485 nm. The increase in the ratio of the intensity of the second peak to the first peak with increasing excitation wavelength is not monotonic, and this effect is illustrated in Figure 5. This figure shows that there are maxima in this ratio at 380 nm and between 337 and 360 nm. These maxima correspond closely to two shoulders in the absorption spectrum of the complex which is also shown in Figure 5.

The effect of solvent polarity on the time-resolved emission spectra of the complex in ethanol-methanol and in methanol-water glasses is illustrated in Figure 6. This figure shows that the emission spectrum at long time (50 μs) is shifted to only slightly higher energy in the methanol-water glass. A much larger blue shift in the short-time (2 μs) emission spectrum is observed for the methanol-water glass.

Discussion

A. Analysis of the Decay Curves by the Two-Level Model. Our two-level analysis of the luminescence decay curves of [$IrCl_2$(phen)(4,7-Me(phen))]Cl as a function of emission wavelength was carried out in a manner analogous to that reported for [$IrCl_2$(phen)(5,6-Me(phen))]Cl.[3] Just as low-energy excitation (450–505 nm) of that complex resulted in a single exponential luminescence decay curve with a lifetime of 9.5 μs, low energy excitation of [$IrCl_2$(phen)(4,7-Me(phen))]Cl led to a single exponential luminescence decay curve with a lifetime of 8.7 μs. Thus, the lifetime of the short-lived level in the two-level model is determined directly by an experimental result. The 22-μs lifetime of the long-lived level in this model was taken from the lifetime observed for [IrCl$_2$(4,7-Me(phen))$_2$]Cl under similar conditions.[12] By using these two values for τ_1 and τ_2 in eq 1 and treating $A_1(\nu)$ and $A_2(\nu)$ as adjustable parameters, we were able to fit all experimental decay curves to within ±5% of each data point. We found, however, a systematic deviation between the calculated and observed decay curves in the low intensity tails which could not be remedied by adjustments of τ_1 and τ_2.

As we have pointed out in a previous paper,[3] the physical interpretation of $A_1(\nu)$ and $A_2(\nu)$ in this model is dependent upon the degree of coupling between the two sets of levels responsible for the luminescence of the complex. If the two sets of levels are coupled by rate constants which are comparable to those for the return to the ground state, then $A_1(\nu)$ and $A_2(\nu)$ have a complicated functional dependence on the initial intensities and rate constants for the levels. However, in the case where the two sets of levels are not coupled by radiationless processes, $A_1(\nu)$ and $A_2(\nu)$ are equal to the initial emission intensities, $I_1{}^0(\nu)$ and $I_2{}^0(\nu)$. Our observation of a single, 8.7-μs decay curve under low-energy excitation establishes that the short-lived set of levels does not convert to the long-lived set of levels. (Interconversion would lead to a nonexponential decay curve.) However, we found no evidence that the long-lived set of levels could be excited without simultaneously exciting the short-lived emission. This suggests either that the long-lived set of levels may be converted to the short-lived set by a radiationless transition or that there are absorption bands of other states which overlap the absorption of the long-lived set of levels at all possible excitation wavelengths. Since we have obtained a good fit to our experimental decay curves by using a 22-μs lifetime taken from the results on [IrCl$_2$(4,7-Me(phen))$_2$]Cl, we favor the latter interpretation. This 22 μs value suggests that there is an excited state of the hetero-bischelated complex which decays at the same rate as the luminescent set of levels in the homobischelated complex. Since conversion of the set of levels with the 22 μs lifetime to a lower energy set of levels does not occur in the homobischelated complex, we infer that this conversion does not occur in the heterobischelated complex either.

In the case where $A_1(\nu)$ and $A_2(\nu)$ for the two-level model are equal to $I_1{}^0(\nu)$ and $I_2{}^0(\nu)$, Figure 1 represents the time-integrated emission spectra of the two independent sets of levels. This establishes that the short-lived set of levels lies about 300 cm^{-1} below the long-lived set and is consistent with our observation of emission from the short-lived set of levels under low-energy excitation. This result is in contrast to our previous observation that the long-lived set of levels lies lowest in the [IrCl$_2$(phen)(5,6-Me(phen))]Cl complex. Thus, according to the two-level model, replacement of the 5,6-methyl substituents by 4,7-methyl substituents leads to a shortening of the lifetimes of both sets of levels, and an inversion of their relative energies.

Although consideration of the goodness-of-fit obtained by applying the two-level model to the decay curves of [IrCl$_2$(phen)(4,7-Me(phen))]Cl indicates that all decay curves may be fit within our limits of experimental error, we believe that we have additional data which indicates that three sets of levels are responsible for the observed luminescence. This point is illustrated best by examination of the time-resolved emission spectrum taken 180 μs after the initial excitation in Figure 3. Since this spectrum was recorded more than 20 decades after initial excitation of the 8.7-μs set of levels, but only about 8 decades after initial excitation of the 22-μs set of levels, it should very nearly represent the emission spectrum of the 22-μs levels. However, comparison of this spectrum to the spectrum of the 22-μs set of levels obtained from the two-level fitting procedure (Figure 1) indicates that the two are not identical. Although both spectra originate at higher energy than the total emission spectrum, the intensity distribution in the time-resolved spectrum is not matched by that obtained from the curve-fitting procedure. *In fact, no combination of the spectra in Figure 1 can reproduce the 180-μs time-resolved spectrum in Figure 3.* Thus, we conclude that our two-level model does not lead us to an adequate representation of the spectrum of the long-lived set of levels.

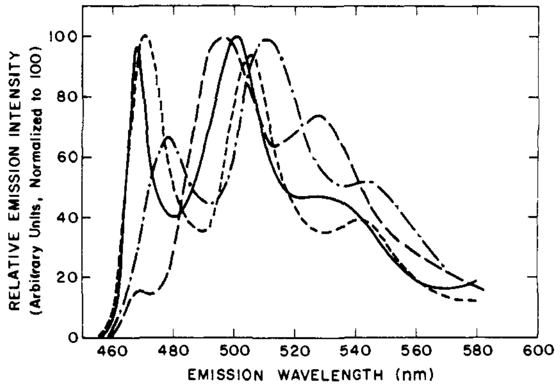

Figure 6. Time-resolved emission spectra of [IrCl$_2$(phen)(4,7-Me(phen))]Cl excited at 337 nm at 77 K: (—) 50 μs after excitation in MeOH–H$_2$O (4:1 v/v), (- - - -) 40 μs after excitation in EtOH–MeOH (4:1 v/v), (– –) 2 μs after excitation in MeOH–H$_2$O (4:1 v/v), (- - - ·) 2 μs after excitation in EtOH–MeOH (4:1 v/v).

B. Analysis of the Decay Curves by a Three-Level Model. The application of eq 1 to a three-level model for the emission of [IrCl$_2$(phen)(4,7-Me(phen))]Cl is complicated by several factors. First, the fitting procedure may be done with as many as six variable parameters (three $A_i(\nu)$'s and three τ_i's). However, one cannot hope to obtain physically meaningful results with a computer fit which varies this number of parameters. We therefore chose to retain the values of 22 and 8.7 μs which were consistent with the two-level model and to vary the third τ_i manually. For each value of the third τ_i we tried, a computer fit of our decay curves was achieved by least-squares variation of the three $A_i(\nu)$'s. This procedure was continued for different values of the third τ_i until a value of 6.0 μs was found to give the best fit to our decay curves.

The second major difficulty encountered in the treatment of our data by a three-level model is in accounting for the possible interconversion of any of the three sets of levels. We feel that our previous conclusion that the 8.7-μs set of levels and the 22 μs set of levels do not interconvert remains valid. Furthermore, we conclude that no interconversion of the 22-μs set of levels and the 6.0-μs set of levels occurs for the same reasons we suggested to rule out interconversion of the 22- and 8.7-μs levels. However, interconversion of the 6.0-μs set of levels to the 8.7-μs set is difficult to rule out. In fact, we feel that this conversion is quite feasible (vide infra).

In spite of this difficulty, the spectral distribution curves shown in Figure 3 contain significant information. *In particular, the spectrum of the 22-μs set of levels now matches the time-resolved spectrum at 180 μs after excitation.* This result was obtained without direct consideration of the 180-μs time-resolved spectrum in the curve fitting procedure. Thus, we feel that this improvement provides rather strong evidence in support of the three-level model.

C. The Orbital Parentage of the Emitting Levels. The lifetime data from both our two-level and three-level models for the emission of $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$ is consistent with one set of levels with a mean lifetime of 22 μs. This set of levels is the longest-lived set in both models, and the lifetime is identical with that of $[IrCl_2(4,7\text{-}Me(phen))_2]Cl$ under similar conditions. We therefore conclude that the 22-μs set of levels arises from a mixture of ππ* and dπ* orbital parentage.[12] The π-orbitals in these configurations are localized on the 4,7-Me(phen) ligand of the heterobischelated complex. This assignment is reinforced by the solvent effect which we observed in the 50-μs time-resolved spectrum (Figure 6). This spectrum, which represents primarily the emission of the 22-μs set of levels, is shifted to only slightly higher energy by changing the solvent from EtOH–MeOH to $MeOH\text{–}H_2O$. This small shift correlates well with the small shift previously reported in the luminescence of $[IrCl_2(4,7\text{-}Me(phen))_2]Cl$ under a similar solvent perturbation.[12]

The identity of the two short-lived levels is more difficult to ascertain. From their lifetimes we anticipate that they are probably of d–π* or d–d orbital parentage. The relatively large solvent shift observed in the 2-μs time-resolved spectra, which contain large contributions from these short-lived levels, is indicative of a large contribution from d–π* orbital parentage in at least one set of levels. The 8.7-μs set of levels lies about 400 cm^{-1} below the 6.0-μs set of levels, and it is therefore unlikely that conversion of the 8.7-μs set to the 6.0-μs set occurs at 77 K. However, conversion of the 6.0-μs set to the 8.7-μs levels may occur, and this could account for the relatively low emission intensity we observe for this set of levels. Such an interconversion would complicate the interpretation of the A_i's in our decay curve analysis, and the 6.0- and 8.7-μs spectral distribution curves in Figure 3 would not represent the emission spectra of independent sets of thermally equilibrated levels. We feel that there is insufficient evidence to further characterize the nature of the two short-lived sets of levels at the present time.

D. Analysis of the Dependence of the Emission of $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$ on Excitation Wavelength. In view of our analysis of the emission of $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$ by a three-level model, the interpretation of the dependence of the emission properties on excitation wavelength is more complicated than our previous analysis of $[IrCl_2(phen)(5,6\text{-}Me(phen))]Cl$.[3] However, Figure 3 indicates that the predominant emission intensity from the long-lived set of levels occurs in the first (highest energy) band of the vibrational progression. Thus, a comparison of the emission intensities in the first and second bands of the time-resolved spectrum of the complex as a function of excitation wavelength provides a rough estimate of the relative population of the long- and short-lived levels. Thus, the increase in the intensity of the second band relative to the first band in the time-resolved emission spectra of Figure 4 with increasing excitation wavelength is indicative of an increase in population of the short-lived levels.

The dependence of the ratio of the emission intensity in these two bands on the excitation wavelength, which is illustrated in Figure 5, indicates that there is also an increase in the relative population of the short-lived levels when the complex is excited at 360 and 380 nm. These wavelengths correspond to two shoulders in the absorption spectrum of the complex which correspond to the region where charge transfer bands appear in the absorption of all of the homobischelated complexes of Ir(III) which have been studied.[13] By analogy with these assignments, we assign the two shoulders in the absorption spectrum of $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$ to charge transfer transitions. Thus, we conclude that excitation of the complex into higher energy charge transfer states leads to preferential population of the short-lived levels. Conversely, excitation of higher energy ππ* levels, which are presumably responsible for the absorption which underlies the charge-transfer bands, leads to preferential population of the long-lived levels.

Conclusion

The complex, $[IrCl_2(phen)(4,7\text{-}Me(phen))]Cl$, represents the second case of a heterobischelated complex of Ir(III) which has a nonexponential luminescence decay curve at 77 K. Our experimental results indicate that this is due to light emission from several thermally nonequilibrated sets of levels of different orbital parentage. Thus, the heterobischelated complexes of Ir(III) appear to form an unusual class of complexes in which the radiationless transitions which would lead to thermal equilibration of the emitting sets of levels are slow relative to the rates for return to the ground state. This property is in contrast to the conclusion that the luminescence of heavy metal complexes generally originates from a single set of thermally equilibrated levels which constitutes the "lowest excited state" of the complex.[14]

We feel that there are several factors which contribute to the origin of this unique property in the heterobischelated complexes of Ir(III). According to the current theoretical description of radiationless transitions in both heavy-atom and light-atom molecules,[15,16] the rate for a radiationless transition between different electronic states depends upon both electronic factors and vibrational factors. The electronic factors include contributions from spin-orbit coupling and from vibronic perturbations introduced by either breakdown of the Born–Oppenheimer approximation or by Herzberg-Teller coupling.[17] The vibrational terms are generally expressed as Franck-Condon factors.

We feel that the following two factors are most pertinent in determining the origin of the different luminescence properties of these hetero- and homo-bischelated complexes of Ir(III): (1) the degree of localization of the transition density in the nuclear framework of the molecule; (2) the relative magnitude of the energy gaps between the two electronic levels involved in a radiationless transition and the vibrational frequencies of the nuclei in the region of the nuclear framework where the changes in electron density occur. The effects of factor 1 may be illustrated by considering the excitation of one of two isolated molecular fragments in the vapor phase. Since the transition density would be completely localized on one of the two isolated fragments, no radiationless transition leading to excitation of the second fragment could occur. However, if the two fragments were brought together to form a single molecule, the states of the two fragments would be mixed to some degree. The degree of mixing would depend upon the interaction of the charge clouds of the two fragments and the energy gaps between the states of the fragments. If the two fragments were identical, the degeneracies of the states of the two fragments would cause mixing of fragment states to form completely delocalized molecular states. Provided that the requisite matching of energy gaps and vibrational frequencies were present in such a molecule (vide infra), the transition densities of the delocalized excited states would be expected to overlap, and rapid ratiationless transitions between the various electronic states would be anticipated. In drawing this conclusion we rule out the possibility that spin or symmetry selection rules would prevent such transitions. These problems are unlikely to arise in the types of complexes with which we are dealing due to the presence of large spin-orbit coupling terms induced by the heavy metal and the multitude of vibrational modes present. If the two fragments were not identical, only partial mixing of the levels would be anticipated. This would lead to various degrees of localization of transition density in one of the two fragments which would influence the rate of energy migration between them.

We expect that the degree of localization of transition density in the homo- and heterobischelated complexes of Ir(III) will be significantly different. In the homobischelated complexes, the π-orbitals of the two bidentate ligands are identical. Thus, when they are brought together in complex formation with Ir(III), complex π-orbitals which are delocalized over both bidentate ligands will be formed. Since the d orbitals of the metal are not expected to mix completely with the complex π-orbitals, states of "d–d", "d–π^*", and "π–π^*" orbital parentage will occur. However, states of dπ^* and $\pi\pi^*$ orbital parentage could be coupled relatively efficiently due to the overlap of transition densities through the delocalized π^* orbitals. On the other hand, the nondegenerate π-orbitals of two dissimilar bidentate ligands in the heterobischelated complexes are expected to form complex π-orbitals which are localized on one of the two ligands to some degree. Although "d–d", "d–π^*", and "π–π^*" states will still occur, certain of these states may have transition densities which overlap only slightly. For example, we anticipate that in [IrCl$_2$(phen)(4,7-Me(phen))]Cl, there will be a mixed $\pi\pi^*$-dπ^* state localized on the 4,7-Me(phen) ligand and a dπ^* state localized on the Ir(III)–phen fragment. The overlap in the transition densities of these two states may be very small, and this would be an important contributing factor to the failure of this molecule to attain thermal equilibration.

The second factor which we feel may contribute to the unique properties of the heterobischelated complexes are the small values of the energy gaps between the thermally nonequilibrated levels. There are relatively few vibrational frequencies of the nuclear framework in the 200–300-cm^{-1} region[18] necessary to accept the electronic energy lost in going from one set of levels to the other. Furthermore, the nuclear vibrations which do have this frequency may not involve nuclei in the region where the small overlap in the transition densities of the two sets of levels occurs, as is required for the electronic–vibrational energy transfer.[15] Thus, we feel that it is the combined effect of factors 1 and 2 which is responsible for the failure of the heterobischelated complexes of Ir(III) to attain thermal equilibration of the dπ^* and $\pi\pi^*$ sets of levels.

Although the tendency for retention of orbital parentage is undoubtedly mitigated by more favorable energy gaps and vibrational frequency matching when dπ^* and $\pi\pi^*$ states of higher energy than the luminescent levels are excited, our results indicate that orbital-parentage remains an important consideration. We feel that this is probably due to factor 1 as applied to dπ^* and $\pi\pi^*$ levels. Thus, we believe that the overlap between dπ^* and $\pi\pi^*$ transition densities in these complexes is small enough to render interconfigurational radiationless transitions less favorable than intraconfigurational processes which preserve orbital parentage. Recent results in this laboratory[19] as well as in other laboratories[20] suggest that even the homobischelated complexes of Ir(III) may have slightly nonexponential luminescence decay curves. This may suggest that the selection rules for radiationless transitions in heterobischelated complexes of Ir(III) may remain somewhat operative in the homobischelated complexes. These complexes are currently being studied carefully, and the results of this study will be reported at a later date.[19]

Recent studies[19] of the time-resolved emission spectra of [IrCl$_2$(phen)$_2$]Cl and [IrCl$_2$(5,6-Me(phen))$_2$]Cl in glycerol between −196 and 0 °C indicate that the emission of these complexes becomes decidedly nonexponential as the temperature is raised above −196 °C. Our results indicate that this is due to population of a low-lying "d–d" set of levels via a thermally activated radiationless process. These levels are responsible for a small portion of the emission at −196 °C, but are responsible for most of the emission in fluid solutions at 0 °C. This suggests that one of the emissions of the [IrCl$_2$(phen)(4,7-Me(phen))]Cl complex reported in this paper is due to a low-lying set of "d-d" levels, and reinforces our conclusion that selection rules for radiationless transition in this and similar complexes are largely determined by orbital parentage.

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