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Communications

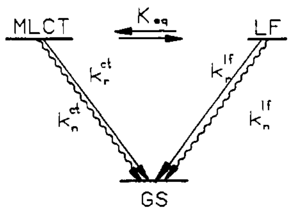
Pressure Tuning of Excited-State Equilibria As Probed by Photoemission Properties of Iridium Complexes

Sir:

We and others have demonstrated the effectiveness of using ligand substituents and solvent effects in "tuning" the photophysical and photochemical properties of transition-metal complexes.[1-3] Such tuning is most effective when the complex of interest has two or more low-lying excited states of different orbital parentages, so that variation of systematic parameters will influence the relative energies of these states differently. Recent reports from this laboratory and other laboratories have demonstrated the usefulness of studying pressure effects on the excited-state reaction dynamics in delineating the photosubstitution mechanisms of d^6 transition-metal complexes.[4] We have also shown that pressure perturbs the equilibrium concentrations and relaxation rates of certain iron(II) complexes that exist in high-spin ↔ low-spin equilibrium in solution.[5] The latter pressure effects are the result of volume differences between the two "ground" states of the iron(II) complexes; thus, similar effects should be applicable in probing the volume differences between two *excited states* in equilibrium. Here we describe the effect of pressure on the photoluminescence properties of the iridium(III) ions $IrL_2Cl_2^+$ (L = 5,6-dimethyl-1,10-phenanthroline (Me_2phen) or 2,2′-bipyridine (bpy) in solution. For each of these complexes we demonstrate volume differences of ~4 cm^3/mol between two emitting excited states, the lowest energy ligand field (LF) state and a mixed metal-to-ligand charge-transfer/ligand-localized (MLCT/$\pi\pi^*$) or MLCT state of comparable energy.[3] These observations constitute the first report of the use of pressure to probe the relative volume changes between two excited states of a single metal complex.

Figure 1 (inset) illustrates the emission spectra of $Ir(Me_2phen)_2Cl_2^+$ in DMF solution at ambient pressure and at 300 MPa[6] (~3 kbar). It is clear from these spectra that at higher pressure there is a decrease in the intensity of the band centered at 720 nm, which has been assigned as LF emission,[3] relative to that centered at 550 nm, which has been assigned[3] as emission from a mixed MLCT/$\pi\pi^*$ state in thermal equilibrium with the LF state. A similar spectral change due to pressure is seen for $Ir(bpy)_2Cl_2^+$ in DMF, although in this case the higher energy band has been assigned to MLCT emission. For each complex there is no apparent pressure-induced shift in the energies of the band maxima, and emission lifetimes, τ, are independent of the observation wavelengths, indicating that the two emitting states are in thermal equilibrium at all pressures. For each complex a plot of ln (I^{ct}/I^{lf}) vs. P is linear. (Figure 1 (T = 295 K); I^{ct} and I^{lf} are the intensities of the MLCT/$\pi\pi^*$ (or MLCT) and LF emission bands, respectively.) From the average of the slopes ($-\Delta V/RT$) obtained for three or more runs with each complex, the ΔV_{app} values −4.1 ± 0.8 and −4.2 ± 0.5 cm^3/mol were calculated for the bpy and Me_2phen complexes, respectively.

Scheme I. Qualitative Illustration of the Excited-State Processes for the Complexes $IrL_2Cl_2^{+\,a}$



[a] The rate constants for nonradiative deactivation are k_n^{ct} and k_n^{lf} and for radiative deactivation are k_r^{ct} and k_r^{lf}.

Given that I^{ct}/I^{lf} is proportional to the concentration ratio [MLCT]/[LF], then according to Scheme I[7]

$$\Delta V_{app} = -RT\frac{\delta \ln (k_r^{ct}/k_r^{lf})}{\delta P} + \Delta V_{eq}^*$$

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(6) In a typical emission intensity experiment, the emission spectra were measured on a lock-in apparatus previously described[3] where the pressure was varied from 0.1 to 300 MPa. The lifetimes were measured on a Nd-YAG laser/Tektronics 7912AD digitizer apparatus previously described[4] (λ = 355 nm). Emission spectra and lifetime measurements agreed (within experimental uncertainty) with those published.[3] Spectra and lifetimes were recorded ascending and descending in pressure to monitor reproducibility. The emission intensities were corrected for phototube response. Typically the intensity of the LF emission was monitored at 720 nm while the intensity of the MLCT emission was measured at 550 nm. Emission lifetimes were also recorded at these wavelengths. The emission decays remained linear in all cases, and the values at the respective wavelengths (720 and 550 nm) remained equal. Low laser light levels were used to reduce the possibility of photochemistry.

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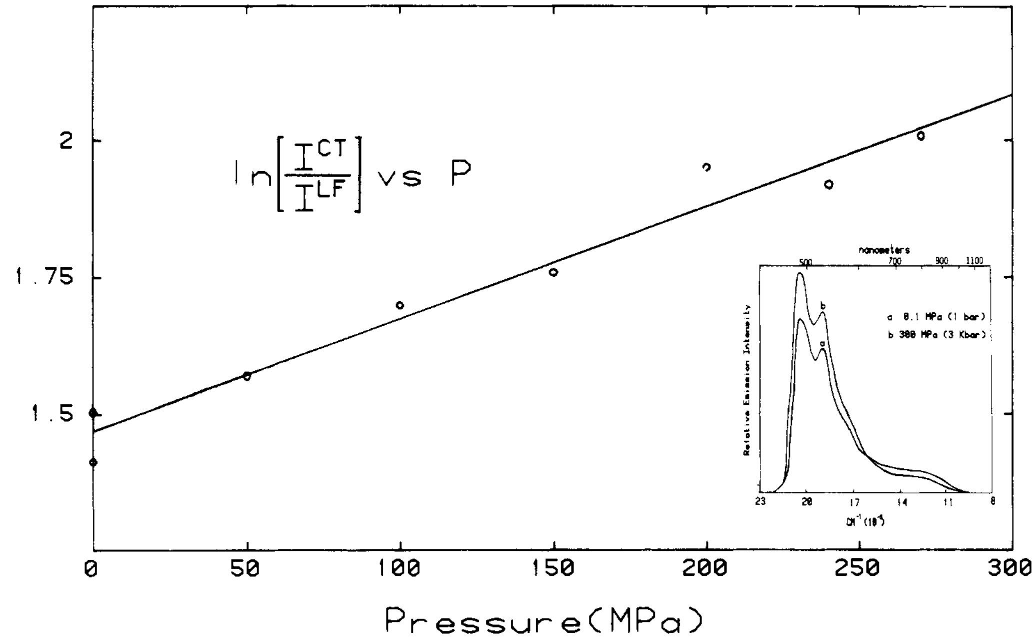

Figure 1. Example plot of ln (I^{ct}/I^{lf}) vs. P for the emission intensity at 550 nm (ct) and 720 nm (lf) for $[Ir(5,6\text{-}Me_2phen)_2Cl_2]ClO_4$ in DMF solution at 295 K. The corrected emission spectra of this complex at 0.1 and 300 MPa are shown in the inset.

where $\Delta V_{eq}{}^*$ is the volume difference between the two excited states. If it is assumed that the $k_r{}^{ct}/k_r{}^{lf}$ ratio is essentially pressure insensitive (see below), this simplifies to

$$\Delta V_{app} = \Delta V_{eq}$$

and the pressure-induced changes in spectral intensity can be attributed to shifts in the relative populations of the two excited states resulting from the difference in partial molar volume between the LF and MLCT/$\pi\pi^*$ states. That the former state is the larger by ~4 cm^3/mol is consistent with the population of $\sigma_{M-L}{}^*$ orbitals in the LF state, the result being bond length extensions[8] and volumes estimated as much as 10 cm^3/mol larger than the ground state for some d^6 complexes.[4] The MLCT/$\pi\pi^*$ states would be expected to be much less distorted from the ground-state configuration. The present results are in agreement with this expectation and provide the first direct evidence for the volume differences between two excited states of a transition-metal complex in fluid solution.

For both complexes in DMF, lifetime measurements[10] show that higher pressure leads to decreased deactivation rates, with $\delta(\ln \tau^{-1})/\delta P$ plots giving the ΔV^* values +0.3 ± 0.1 cm^3/mol for $Ir(bpy)_2Cl_2{}^+$ and +4.0 ± 0.2 cm^3/mol for $Ir(Me_2phen)_2Cl_2{}^+$. According to Scheme I, the τ^{-1} value can be expressed by

$$\tau^{-1} = \frac{K(k_r{}^{ct} + k_n{}^{ct}) + k_n{}^{lf} + k_r{}^{lf}}{1 + K}$$

Given that emission quantum yields are small and that nonradiative deactivation from the LF state is much more rapid than from the MLCT/$\pi\pi^*$ state,[9] this simplifies to $\tau^{-1} = k_n{}^{lf}(1 + K)^{-1}$. For the limiting case $K \ll 1$, $\Delta V^* = -\delta(RT \ln k_n{}^{lf})/\delta P$ while for $K \gg 1$, $\Delta V^* = \delta(RT \ln K)/\delta P$. For the latter, ΔV^* would be equal in magnitude but opposite in sign to $\Delta V_{eq}{}^*$. The present cases should lie somewhere between these extremes. For $Ir(Me_2phen)_2Cl_2{}^+$ the MLCT/$\pi\pi^*$ state apparently lies at lower energy than does the LF state (i.e., $K > 1$);[3] thus, a larger ΔV^* would be expected than for $Ir(bpy)_2Cl_2{}^+$ for which the MLCT state has a relatively higher energy ($K < 1$).

The assumption that the $k_r{}^{ct}/k_r{}^{lf}$ ratio is pressure insensitive must be examined given the earlier conclusion[11] that pressure effects on emission from the rhenium(I) complex $Re(CO)_3Cl(phen)$ are the result of changes in the k_r value owing to the modest pressure-induced increase in solvent dielectric constant. Whether both $k_r{}^{ct}$ and $k_r{}^{lf}$ would respond to such a perturbation equally (hence making the ratio pressure insensitive) is doubtful given the different orbital parentages of the emitting states. However, examination of the emission spectra for both $Ir(Me_2phen)_2Cl_2{}^+$ and $Ir(bpy)_2Cl_2{}^+$ in different solvents shows the I^{ct}/I^{lf} ratio to decrease in solvents of higher dielectric constant (e.g., Me_2SO), a change opposite from that induced by pressure (Figure 1). Thus, if the $k_r{}^{ct}/k_r{}^{lf}$ ratio is indeed sensitive to dielectric constant perturbations, these may well serve to decrease the overall effect of pressure on the emission spectrum, so that the ΔV_{app} represents only the lower limit for $\Delta V_{eq}{}^*$. This question is the subject of a more detailed investigation.

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Registry No. $Ir(Me_2phen)_2Cl_2{}^+$, 68842-70-6; $Ir(bpy)_2Cl_2{}^+$, 52612-80-3.

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(7) Since $I^{ct} = k_r{}^{ct}[MLCT]$ and $I^{lf} = k_r{}^{lf}[LF]$, then $\ln(I^{ct}/I^{lf}) = \ln(k_r{}^{ct}/k_r{}^{lf}) + \ln K$, where $K = [MLCT]/[LF]$ and $k_r{}^i$ is the radiative rate constant for state i. The pressure dependence relationships are defined by $\delta \ln K/\delta P = -\Delta V_{eq}{}^*/RT$ and $-\delta \ln(I^{ct}/I^{lf})/\delta P = -\Delta V_{app}/RT$. (In this treatment transition-state theory is used to derive the activation volumes from the pressure dependencies.)

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(10) Lifetime measurements show that for the Me_2phen complex τ varied from 790 ns at 0.1 MPa to 1.3 μs at 300 MPa while for the bpy complex τ varied only slightly, from 340 to 350 ns over the same pressure range.

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