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Dipole Moment of the Excited Tetracarbonyl(2,2′-bipyrazine)molybdenum

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Synopsis. Visible absorption maxima of [Mo$(CO)_4$(bpz)] and [Mo$(CO)_4$(bpy)] depend on solvent, while their emission maxima are less sensitive to solvent. These molybdenum carbonyl complexes have a large dipole moment in the ground state, but a small dipole moment in the MLCT excited state. These results suggest that π back donation from metal to CO ligands occurs in the ground state, whereas a counter migration of the other electron from the ligands to metal accompanied by photoexcitation occurs in the MLCT state.

Solvato-chromism of several transition metal complexes has been reported, for example, [Fe$(CN)_2$$(bpy)_2$],[1)] [Fe$(CN)_2$$(phen)_2$],[1)] and [M$(CO)_4$(L)] (M=Cr, Mo, W; L=bpy, phen, etc.),[2)] where bpy and phen denote 2,2′-bipyridine and 1,10-phenanthroline, respectively; while usually the visible metal-to-ligand charge-transfer (MLCT) absorption band of an isotropic compound such as $[Fe(bpy)_3]^{2+}$ is fairly insensitive to solvent effect. Maxima of these intense visible absorption bands were correlated with solvent parameters, E_T-value,[3)] Z-value,[4)] and the acceptor number.[5)] Solvato-chromism of emissive complexes such as [Ru$(CN)_2$$(bpy)_2$] and [Ru$(CN)_2$$(phen)_2$] was also investigated in the ground and the emitted states.[6,7)] The correlation between the absorption maxima with the acceptor number was discussed on the basis of the donor–acceptor interaction in the second coordination sphere.[7)] On the other hand, the dipole moments of metal complexes have never been attended to in the MLCT state, since it has been considered that the dipole moment in the MLCT excited state is larger than that in the ground state. This opinion is based on the MLCT state being a charge-separated state composed of an oxidized central metal ion and a trapped electron in the π^* orbital of ligand. However, recently, the DV-Xα molecular orbital calculation on [Cr$(CO)_4$(bpy)] predicted a smaller dipole moment in the metal-to-bpy charge-transfer state than in the ground state.[8)]

In this paper, the solvent-induced spectral shifts of [Mo$(CO)_4$(bpz)] and [Mo$(CO)_4$(bpy)] are discussed as being due to a difference of the molecular dipole moments in the ground and excited states, since the solvent effect has been explained in terms of dipole–dipole interaction between solute and solvent in aprotic solvents.

Results and Discussion

[M$(CO)_4$(L)] (M=Cr, Mo, W; L=bpy, phen) emits phosphorescence from the lowest MLCT (metal-to-bpy or -phen CT) state at 77 K without dissociation of CO.[9)] [Mo$(CO)_4$(bpz)] also exhibits the metal-to-bpz charge-transfer band in the visible region and emits from the triplet MLCT state at 77 K. The absorption band is red-shifted in non-polar solvents, but blue-shifted in polar solvents. Figure 1 shows plots of the maximum of the visible absorption spectrum of [Mo$(CO)_4$(bpz)] versus that of [Mo$(CO)_4$(bpy)]. Since the electron affinity of bipyrazine is stronger than that of bipyridine, the MLCT absorption band for [Mo$(CO)_4$(bpz)] is in the lower energy compared with that for [Mo$(CO)_4$(bpy)]. The linear relation obtained except for CCl_4 implies that the origin of the solvent effect for [Mo$(CO)_4$(bpz)] and [Mo$(CO)_4$(bpy)] is the same. Manuta and Lees obtained a linear relationship between the maximum of the lowest MLCT band of [W$(CO)_4$(bpy)] and the E_T value with the exception in alcohols. They concluded that the deviation from linearity for alcohol solutions is caused by the hydrogen-bonding with CO

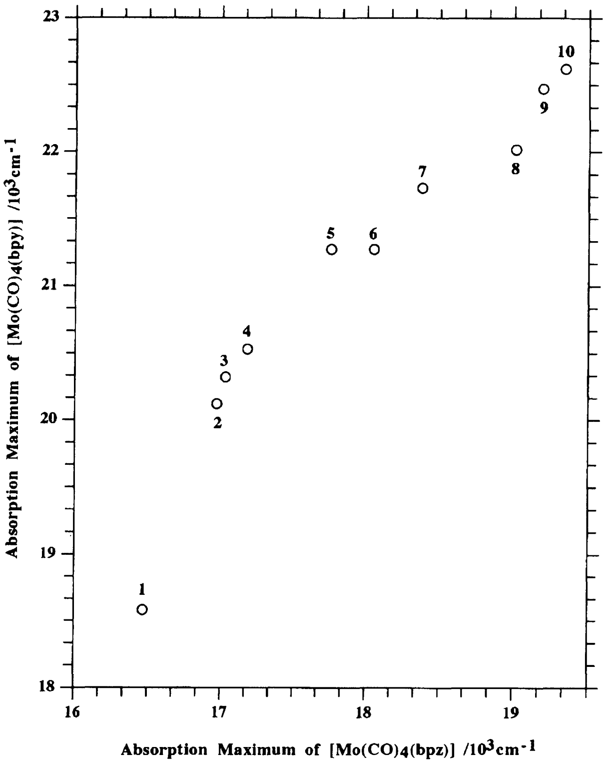

Fig. 1. Plots of visible absorption maximum of [Mo$(CO)_4$(bpz)] against that of [Mo$(CO)_4$(bpy)]. 1: CCl_4, 2: toluene, 3: benzene, 4: $CHCl_3$, 5: CH_2Cl_2, 6: EtOH, 7: MeOH, 8: acetone, 9: CH_3CN, 10: DMF

and alcohol.[10] In the present work, the same correlation was obtained between the absorption maximum of the lowest MLCT band of [Mo(CO)$_4$(bpz)] and the E_T value. Therefore, both dipole–dipole interaction between solute and solvent and the acid-base interaction between CO and protic solvent play an important role in the solvent effect on the charge-transfer band of [Mo(CO)$_4$(bpz)] in protic solvent. However, the results obtained in this work show that the hydrogen-bonding to the peripheral nitrogen atoms of bipyrazine is weak in the ground state.

The luminescence of [Mo(CO)$_4$(bpz)] is phosphorescence from the triplet MLCT state at 77 K, and cannot be observed at room temperature. Since the dielectric constant and the refractive index of solvent depend on temperature, the reaction field at 77 K will be different from that at room temperature. The absorption spectrum at 77 K is distinguished from that at room temperature. Even in a rigid glass, the absorption spectrum is blue-shifted in polar solvent, while the phosphorescence spectrum is independent of solvent. This result suggests that [Mo(CO)$_4$(bpz)] in the MLCT excited state has a very small dipole moment.

According to Ooshika's presentation,[11] the solvent effect on absorption and emission maxima are represented as follows:

$$hc\tilde{\nu}_{\text{abs}} = E^0_{\text{ex}} - E^0_{\text{g}} + \frac{2(D-1)}{2D+1} \times \frac{\mu_{\text{g}}^2 - \mu_{\text{e}}\cdot\mu_{\text{g}}}{a^3} - \frac{n^2-1}{2n^2+1} \times \frac{(\mu_{\text{g}}-\mu_{\text{e}})^2}{a^3},$$

$$hc\tilde{\nu}_{\text{em}} = E^0_{\text{ex}} - E^0_{\text{g}} - \frac{2(D-1)}{2D+1} \times \frac{\mu_{\text{e}}^2 - \mu_{\text{e}}\cdot\mu_{\text{g}}}{a^3} - \frac{n^2-1}{2n^2+1} \times \frac{(\mu_{\text{g}}-\mu_{\text{e}})^2}{a^3},$$

where $E^0_{\text{ex}} - E^0_{\text{g}}$ is the excitation energy without the solute–solvent interaction, $\tilde{\nu}_{\text{abs}}$ and $\tilde{\nu}_{\text{em}}$ are absorption and emission maxima respectively, and D and n are the dielectric constant and the refractive index of solvent, respectively. μ_{g}, μ_{e}, and a are dipole moments in the ground state and excited state and a radius of the complex, respectively. When μ_{e} is negligibly small, the equation can be rewritten as

$$hc\tilde{\nu}_{\text{abs}} = E^0_{\text{ex}} - E^0_{\text{g}} + \left\{\frac{2(D-1)}{2D+1} - \frac{n^2-1}{2n^2+1}\right\} \times \frac{\mu_{\text{g}}^2}{a^3},$$

$$hc\tilde{\nu}_{\text{em}} = E^0_{\text{ex}} - E^0_{\text{g}} - \frac{n^2-1}{2n^2+1} \times \frac{\mu_{\text{g}}^2}{a^3}.$$

Since the solvent constant of $(n^2\text{-}1)/(2n^2+1)$ scarcely depends on solvent, the emission maximum is less sensitive to solvents than the absorption maximum.

Figure 2 shows plots of absorption maximum of [Mo(CO)$_4$(bpz)] and [Mo(CO)$_4$(bpy)] against $[2(D-1)/(2D+1)-(n^2-1)/(2n^2+1)]$ for aprotic solvents, since the protic solvent causes an additional solvent effect due to the hydrogen-bonding between CO and solvent. Nearly linear relations were obtained, suggesting that the dipole moments of [Mo(CO)$_4$(bpz)] and [Mo(CO)$_4$(bpy)] in the excited state are small. The dipole moments of the complexes in the ground state were estimated to be 10—12 debyes for [Mo(CO)$_4$(bpz)] and 14—16 debyes for [Mo(CO)$_4$(bpy)] assuming a=5—6 Å and μ_{e}=0. It is likely that the large dipole moment of the ground-state complex is provided by π back donation from metal to CO ligands.

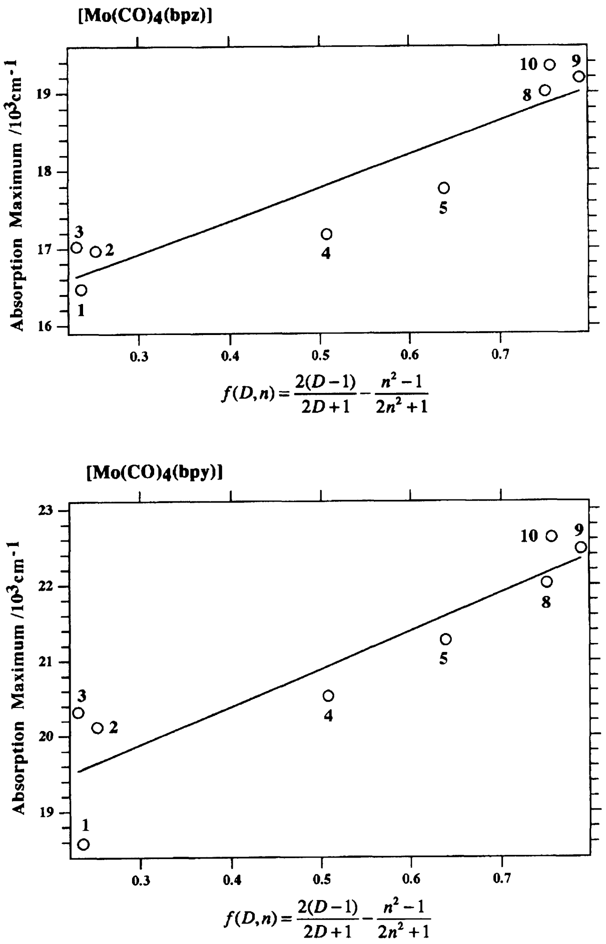

Fig. 2. Plots of visible absorption maxima of [Mo(CO)$_4$(bpz)] (upper) and [Mo(CO)$_4$(bpy)] (lower) against $f(D,n){:=}2(D-1)/(2D+1)-(n^2+1)/(2n^2+1)$.

The DV-Xα calculation on [Cr(CO)$_4$(bpy)] predicted that the dipole moments in the ground and the lowest MLCT states are 6.6 and 0.1 debyes, respectively.[8] In spite of charge separation caused by photoexcitation, the excited complex has a small dipole moment. This can be explained in such a way that the electron population (net charge of C and O are +0.05 and −0.17e, respectively) in the trans CO ligands with respect to the bipyridine is provided by π back donation in the ground state and the charge-transfer excitation increase the chromium charge only by 0.05e and decreases the bipyridine charge by 0.43e due to enhancing the counter electron-migration from the ligand to the central metal ion.[8]

Experimental

The ligand bipyrazine was prepared by the literature method[12] and recrystallized from toluene. [Mo(CO)$_4$(bpy)] and [Mo(CO)$_4$(bpz)] were prepared by the methods in the literature.[13,14] Absorption and luminescence spectra were measured on a Hitachi spectrophotometer model 330 and a Hitachi spectrofluorometer model 850, respectively. Low temperature absorption spectra were recorded on a Shimadzu MPS-50L in a dewar assembly with the sample in rigid glass media at 77 K. Solutions were purged with solvent saturated nitrogen gas for 20—30 min before the luminescence measurements.

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