Inorg. Chem. **1987**, *26*, 3950–3952

Notes

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Dual Emissions from Cu(dmp)(PR$_3$)$_2^+$ Systems in a Rigid Glass: Influence of the Phosphine Donor Strength

Dominick J. Casadonte, Jr., and David R. McMillin*

Received May 21, 1987

Because internal conversion processes connecting neighboring excited states are usually quite rapid in condensed media, emission is typically observed solely from the lowest energy excited state of a given multiplicity.[1,2] Simultaneous emissions from states of the same multiplicity can, however, be observed if the levels are in thermal equilibrium[3-5] or if interconversion between the levels is slow compared to the individual radiative rates.[5,6] Cases in which interconversion is hindered include molecules that exhibit a large energy gap between successive excited states[7,8] as well as systems involving proximate excited states with different geometrical structures. In the latter there is a barrier against internal conversion that is especially pronounced in low-temperature, rigid media.[5,6]

Previously, we have observed emission from proximate ^{3}d–π^* and $^3\pi$–π^* states in mixed-ligand copper(I) complexes of the type Cu(NN)(PPh$_3$)$_2^+$ where NN denotes 1,10-phenanthroline or a derivative thereof.[6,9,10] In these systems two types of triplet emission are observed, each with a similar excitation spectrum, because the interconversion between the vibrationally relaxed ^{3}d–π^* and $^3\pi$–π^* excited states is inhibited in rigid glasses. When 5-substituted phenanthrolines are used, the energy of the ^{3}d–π^* state remains approximately constant while the energy of the $^3\pi$–π^* state varies.[6] Although a Boltzmann equilibrium is not established, the intensities of the emissions reflect the energy separation between states. In particular, the relative intensity of the intraligand emission increases as the energy of the $^3\pi$–π^* state decreases with respect to the ^{3}d–π^* state.[6] In the series described below the phenanthroline derivative, namely 2,9-dimethyl-1,10-phenanthroline (dmp), is held constant while the phosphine ligand is varied. As before, thermally nonequilibrated $^3\pi$–π^* and ^{3}d–π^* emissions are observed in the glass, and the $^3\pi$–π^* emission responds systematically to changes in donor strength of the phosphine.

Experimental Section

Materials and Methods. The phosphines were purchased from Strem Chemicals, Inc., while the dmp ligand was purchased from G. F. Smith Chemical Co. The mixed-ligand complexes were prepared by the previously reported method[10] from Cu(BF$_4$)$_2$·xH$_2$O. Ethanol was obtained from U.S. Industrial Chemicals Co., and methanol was distilled-in-glass grade from Burdick and Jackson.

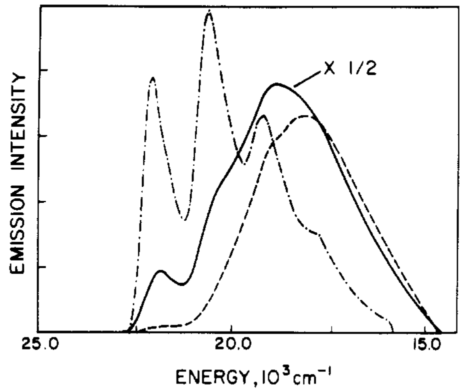

Figure 1. Corrected total emission spectra in 4:1 ethanol/methanol at 77 K: Cu(dmp)(P(p-Cl-Ph)$_3$)$_2^+$ (–··–); Cu(dmp)(PPh$_3$)$_2^+$ (—); Cu(dmp)(P(p-Me-Ph)$_3$)$_2^+$ (---). The excitation wavelength was 365 nm, and the excitation and emission slits were set at 5 and 4 nm, respectively. The areas reflect the relative quantum yields.

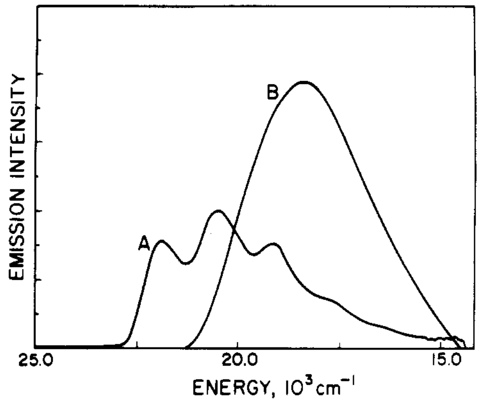

Figure 2. Emission components from Cu(dmp)(PPh$_3$)$_2^+$ in 4:1 ethanol/methanol at 77 K: (A) $^3\pi$–π^* component excited at 365 nm and resolved with the phosphoroscope with the emission slit set at 8 nm; (B) ^{3}d–π^* component obtained by subtracting spectrum A from the total emission spectrum. Both spectra are corrected for the instrumental response.

The fluorometer was operated in the dc mode for all low-temperature emission measurements taken with a quartz finger Dewar flask. In order to obtain corrected spectra and to determine quantum yields, the $^3\pi$–π^* and ^{3}d–π^* emissions were resolved from the total emission spectra by subtraction of the $^3\pi$–π^* components. The latter were measured independently with a phosphoroscope. Before plotting, spectra were converted from a wavelength representation to an energy representation after pointwise multiplication of the intensity by the wavelength squared, in order to compensate for the energy dependence of the instrumental band-pass function.[11] Lifetimes were calculated from standard log plots of the decay data.

Instrumentation. Steady-state luminescence spectra were measured with a Perkin-Elmer MPF-44B fluorometer interfaced to an Apple IIE microcomputer as described previously.[6] The $^3\pi$–π^* phosphorescence was isolated with a rotating-can phosphoroscope; millisecond decay curves were photographed from oscilloscope traces obtained at low rpm's. The microsecond components and time-resolved ^{3}d–π^* emission spectra could be obtained with a pulsed N$_2$ laser system in conjunction with a boxcar detector as described previously.[6]

Results

In a low-temperature glass the absorption spectra of all three complexes parallel the spectra previously reported for Cu-

---

(1) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14–19.

(2) Porter, G. B. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 37–79.

(3) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262–7270.

(4) Watts, R. J. *Inorg. Chem.* **1981**, *20*, 2302–2306.

(5) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325–355.

(6) Casadonte, D. J., Jr.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331–337 and references therein.

(7) Viswanath, G.; Kasha, M. *J. Chem. Phys.* **1956**, *24*, 574–577.

(8) Kobayashi, H.; Kaizu, Y. *ACS Symp. Ser.* **1986**, *No. 321*, 105–117.

(9) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846–5848.

(10) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J., Jr.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906–5912.

(11) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983; pp 42–43.

0020-1669/87/1326-3950$01.50/0

Table I. Photophysical Data in 4:1 Ethanol/Methanol at 77 K

	$^3\pi-\pi^*$ emission			^{3}d$-\pi^*$ emission		
system	$\bar{\nu}_{max}$, cm^{-1}	$\Delta\bar{\nu}$,[a] cm^{-1}	Φ[b]	$E^{abs}_{max}(^1\text{d}-\pi^*)$, cm^{-1}	$E^{em}_{max}(^3\text{d}-\pi^*)$, cm^{-1}	Φ[b]
dmp	22 170 20 660 19 190 17 730	1500 1470 1460				
$\text{Cu(dmp)(P(}p\text{-Cl-Ph)}_3)_2^+$	22 140 20 670 19 220	1470 1460	1.9	27 400	18 620	c
$\text{Cu(dmp)(PPh}_3)_2^+$	21 930 20 530 19 160	1400 1370	1.0	27 250	18 420	2.5
$\text{Cu(dmp)(P(}p\text{-Me-Ph)}_3)_2^+$	21 890 20 450 19 160	1380 1290	0.17	26 800	18 250	1.6

[a] Separations between successive vibronic maxima. [b] Yield relative to $^3\pi-\pi^*$ component of PPh$_3$ complex; estimated error ±10%. [c] Too weak to measure.

Table II. Zero–Zero Energies and Lifetimes at 77 K in 4:1 EtOH/MeOH

system	$\tau(^3\pi-\pi^*)$, ms	$\tau(^3\text{d}-\pi^*)$, μs	$E_{0-0}(^3\pi-\pi^*)$, cm^{-1}	$E_{0-0}(^3\text{d}-\pi^*)$,[a] cm^{-1}	Δ,[b] cm^{-1}
$\text{Cu(dmp)(P(}p\text{-Cl-Ph)}_3)_2^+$	12.2	c	22 140	22 510	400
$\text{Cu(dmp)(PPh}_3)_2^+$	8.0	250	21 930	22 340	400
$\text{Cu(dmp)(P(}p\text{-Me-Ph)}_3)_2^+$	6.2	220	21 890	22 030	100

[a] Calculated from eq 1. [b] $\Delta = E_{0-0}(^3\text{d}-\pi^*) - E_{0-0}(^3\pi-\pi^*)$. [c] Signal too weak to measure.

(NN)(PPh$_3$)$_2^+$ systems.[6] Thus, in the near-UV region there is a broad, structureless ^{1}d–π^* charge-transfer (CT) absorption that maximizes in the vicinity of 370 nm. To higher energy, vibronic components of the lowest energy $^1\pi-\pi^*$ absorption of the ligand, the ^{1}L$_b$ bands,[12] are resolved on the low-energy edge of more intense $^1\pi-\pi^*$ absorptions. The energy maxima of the ^{1}d–π^* absorption are presented in Table I.

As can be seen in Figure 1, the emission spectra also have a complex band shape, and they can be resolved into two main components. One component has a submillisecond lifetime and can be time-resolved with the laser system. This emission is broad band, analogous to the d–π^* absorption, and it is assigned to a corresponding ^{3}d–π^* state. The other component persists for several milliseconds such that it can be viewed through the phosphoroscope. Here the band shape is characteristic of $^3\pi-\pi^*$ emission from the dmp ligand, and the lifetimes indicate that the emission occurs from a coordinated ligand. Spectra of the two components from Cu(dmp)(PPh$_3$)$_2^+$ are depicted in Figure 2. Band energies and relative emission yields are compiled in Table I; the lifetimes are listed in Table II.

Discussion

Figure 3 depicts a system with two excited states having distinct equilibrium geometries.[4–6,13] The excited states are assumed to undergo vibronic mixing along the nuclear displacement coordinate Q, which describes the reorganization of the solvent medium as well as structural changes that occur within the complex itself. Q can also be viewed as the "reaction coordinate" for internal conversion, and when the barrier along Q is large compared to thermal energies, internal conversion is hindered. Although there is a dominant configuration at each minimum, the surface in Figure 3 cannot be identified with a particular electronic configuration because it reflects an admixture of the $^3\pi-\pi^*$ and ^{3}d–π^* excited configurations. The mixing influences the energetics and the dynamics of the system; the energetic consequences, which are more readily identified, are considered first.

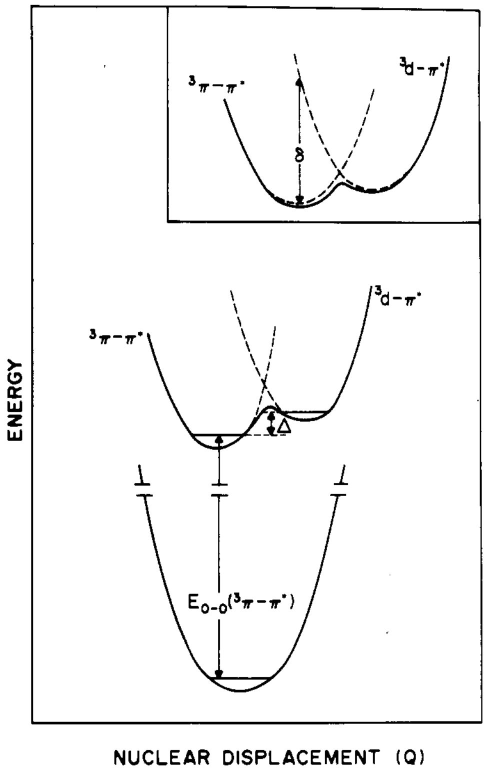

Figure 3. Potential energy surfaces for the ground state and the lowest energy excited state of a Cu(dmp)(PR$_3$)$_2^+$ system. The dashed lines indicate the zero-order $^3\pi-\pi^*$ and ^{3}d–π^* surfaces. A vibronic interaction occurs along the nuclear displacement coordinate Q. The zero–zero energy of the $^3\pi-\pi^*$ state and Δ, the difference between the zero–zero energies of the $^3\pi-\pi^*$ and ^{3}d–π^* excited states, are also depicted. The insert shows a vertical separation of δ between the zero-order states at the equilibrium geometry of the $^3\pi-\pi^*$ state.

Zero–Zero Energy. For a particular excited state the zero–zero energy—the energy difference between the lowest vibrational level of the excited state and the corresponding level of the ground state—is the proper measure of energy. For the $^3\pi-\pi^*$ states this can be identified with the highest energy vibronic component of the emission. On the other hand, for the CT state, where no vibronic structure is resolved, eq 1 has been used,[6] where

---

(12) Bray, R. F.; Ferguson, J.; Hawkins, C. J. *Aust. J. Chem.* **1969**, *22*, 2091–2103.

(13) Dellinger, B.; Kasha, M. *Chem. Phys. Lett.* **1975**, *36*, 410–414.

$$E_{0-0}(^3\text{d}-\pi^*) = \tfrac{1}{2}[E^{\text{abs}}_{\text{max}}(^1\text{d}-\pi^*) - 1000 + E^{\text{em}}_{\text{max}}(^3\text{d}-\pi^*)] \qquad (1)$$

$E^{\text{abs}}_{\text{max}}(^1\text{d}-\pi^*)$ and $E^{\text{em}}_{\text{max}}(^3\text{d}-\pi^*)$ are the energy maxima in cm^{-1} from the CT absorption and emission spectra, respectively. As illustrated in Figure 3, Δ is defined as the energy difference between the ^{3}d–π^* and the $^3\pi$–π^* excited states. The estimates based on eq 1 are approximate; for example, we have neglected the complications that occur if the CT band envelopes reflect more than one state.[6] Nevertheless, the numbers are useful because the discussion is based on *trends* rather than the absolute energies themselves.

Inductive Effect. The most obvious energy trends are that the ^{1}d–π^* absorption and the ^{3}d–π^* emission energies decrease as the para substituents on the phosphine range from Cl to H to CH_3. This correlates with the trend of increasing basicity established by Tolman:[14]

$$\text{P}(p\text{-Cl-Ph})_3 < \text{PPh}_3 < \text{P}(p\text{-Me-Ph})_3 \qquad (2)$$

Thus, the variation in the band energies can be explained as a simple inductive effect: Stronger phosphine donors increase the electron density at copper and lower the energy of the CT excited states.

The ordering in (2) is based on the effect that phosphine variation has on the carbonyl stretching frequencies of $Ni(CO)_3(PR_3)$ systems.[14] A similar phosphine-induced perturbation of the ring-stretching mode(s) of the dmp ligand is apparent in the $^3\pi$–π^* phosphorescence spectra (Table I). In line with high-resolution studies of the phosphorescence spectrum of the free 1,10-phenanthroline ligand,[15,16] the high-frequency modes in the $^3\pi$–π^* emission are assigned to totally symmetric ring-stretching modes as well as overtones and combination bands involving the same. Since dmp is a π-acceptor ligand, the frequencies are expected to decrease on complex formation just like the carbonyl stretching frequencies in $Ni(CO)_3(PR_3)$ complexes.[14] Consistent with this reasoning, the higher the donor strength of the phosphine, the greater the observed frequency shift. Parenthetically, we may note that the same synergistic interaction between the ligands has previously been invoked to explain the favorable formation constants of $Cu(NN)(PPh_3)_2^+$ species.[17]

Although the effect is quite small, the data in Table II also suggest that the energy of the $^3\pi$–π^* state tends to decrease with increasing donor strength of the phosphine.[18] This trend can be understood in terms of the configurational mixing alluded to earlier. In the insert to Figure 3 the zero-order, i.e., noninteracting, $^3\pi$–π^* and ^{3}d–π^* excited states differ in energy by δ at the equilibrium geometry of the $^3\pi$–π^* configuration. When mixing is accounted for, the energy of the (preponderantly) $^3\pi$–π^* state and, as a result, the energy of the $^3\pi$–π^* emission decrease. Therefore, δ and $E_{0-0}(^3\pi-\pi^*)$ are expected to decrease as more basic phosphines are introduced into the complex. Although configurational mixing between the charge-transfer and intraligand excited states is a well-recognized phenomenon,[4-6,19,20] the $Cu(dmp)(PR_3)_2^+$ systems are noteworthy because it is possible to assess the energies of each state involved.

Dynamic Effects of Mixing. There is also a concomitant decrease in lifetime of the $^3\pi$–π^* emission as the energy of the ^{3}d–π^* state decreases. Although a variety of processes may affect the lifetime, this trend is probably due to the increasing importance of configuration interaction as well. Configurational mixing should promote relaxation because spin–orbit interactions at the metal center facilitate the spin change that is formally required for crossing to the ground state. In the same way the $^3\pi$–π^* lifetimes are shorter for $Cu(NN)(PR_3)_2^+$ systems than for the corresponding $Ag(NN)_2^+$ systems because the ^{3}d–π^* states occur at much higher energies in the silver systems.[6]

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-8414267.

Registry No. $Cu(dmp)(P(p\text{-Cl-Ph})_3)_2^+$, 105061-79-8; $Cu(dmp)(PPh_3)_2^+$, 78809-58-2; $Cu(dmp)(P(p\text{-Me-Ph})_3)_2$, 105061-77-6.

---

(14) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956.

(15) Brenin, J. S.; Rosebrook, D. D.; Hirt, R. C. *J. Phys. Chem.* **1963**, *67*, 2651–2655.

(16) Perkampus, H.-H.; Knop, A.; Knop, J. V. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1968**, *23A*, 840–848.

(17) Kirchhoff, J. R.; McMillin, D. R.; Robinson, W. R.; Powell, D. R.; McKenzie, A. T.; Chen, S. *Inorg. Chem.* **1985**, *24*, 3928–3933.

(18) A reviewer has pointed out that the bands in Figure 2 may equally reasonably be interpreted in terms of a ^{3}d–π^* state that is much as 1000 cm^{-1} *below* the $^3\pi$–π^* state. Although we agree that eq 1 provides only an approximation to the zero–zero energy, the changes in the energies of the $^3\pi$–π^* states, albeit slight, are at least consistent with the proposal that the ^{3}d–π^* states are the higher energy states.

(19) Cremers, T. L.; Crosby, G. A. *Chem. Phys. Lett.* **1980**, *73*, 541–544.

(20) Giorgano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888–2897.

Contribution from the University Chemical Laboratory,
Cambridge CB2 1EW, U.K.,
and Department of Physical Sciences,
Trent Polytechnic, Nottingham NG11 8NS, U.K.

Electronic Spectra of High-Nuclearity Cluster Carbonyls

Simon R. Drake,[†] Brian F. G. Johnson,[†] J. Lewis,*[†]
and R. Guy Woolley[‡]

Received October 22, 1986

The study of the physicochemical properties of high-nuclearity clusters consisting of several metal atoms is of considerable interest. Fundamental questions concerning the changes in physical and chemical properties as the number of metal atoms increases need to be resolved. In this paper we report studies of the electronic spectra of several high-nuclearity osmium cluster carbonyls. These are compounds in which polyhedral arrangements of metal atoms are surrounded by a shell or sheath of CO ligands.[1] Solution visible/UV spectra for a set of high-nuclearity osmium carbonyls are shown in Figures 1–4, and a schematic energy level diagram for such clusters, adapted from ref 1, is shown in Figure 5.

Some physical properties of $Os_6(CO)_{18}$ were reported earlier,[2] and the solution spectra of the clusters $[Pt_3(CO)_6]_n^{2-}$ (n = 2–6) (Figure 6) have been discussed by Chang and Woolley.[3] It is convenient to begin by reviewing these findings before discussing the spectra shown in Figures 1–4.

Gas-phase photoemission studies of $Os_6(CO)_{18}$ show that the ionization threshold (≈8 eV) occurs in the metal cluster d band, which extends down to about 12 eV; as usual in these systems, the carbonyl "5σ" and "1π" features overlap and peak at ≈14.5 eV (±1.5 eV).[4] Transmission and optical spectroscopy suggest that this compound is a semiconductor with a band gap of ≈1 eV, in agreement with the resistivity measurements. The first strong electronic transitions peak at ≈2.7 eV (±0.2 eV) in both crystals and solution.[2] The platinum cluster carbonyl dianions $[Pt_3(CO)_6]_n^{2-}$ (see Figure 6, for example) all show strong optical absorptions in the visible range. All of them are colored with the energy of the first intense absorption maximum in the visible, decreasing steadily as the cluster size increases (from 3.3 eV for n = 1 to 1.6 eV for n = 6). Early calculations by Chang and Woolley[3] have been improved by Bullett,[5] who also extended them to the Pt_9 species (n = 3). Bullett's results give a significant improvement to the description of the levels at the HOMO–LUMO gap and suggest that the HOMO of the dianion is an in-phase combination of carbonyl 2π^* levels split off from the main group of 2π^* levels, which remain empty, as suggested by Lauher.[6] This unusual feature arises from the particular geometry of these platinum carbonyls, which is based on the stacking of nearly planar layers of $Pt_3(CO)_6$ moieties (Figure 6). The normal energy level pattern for cluster carbonyls is shown schematically in Figure 5; the metal cluster d levels lie in the gap between the M–CO bonding

---

[†] University Chemical Laboratory.

[‡] Trent Polytechnic.