Communications

Photophysics of Metal Carbonyl Complexes. Multiple Emissions from Diimine–Tetracarbonyl Complexes of Group 6B Metals in Room-Temperature Solution[1]

Sir:

Currently there is considerable interest in the photochemistry of transition-metal carbonyls having metal to ligand charge-transfer (MLCT) excited states.[2-5] Group 6B metal carbonyls having low-energy MLCT transitions have been shown to be relatively unreactive photochemically following excitation directly into this state.[2,3] Recently, it has been established that several complexes of this type undergo radiative decay in fluid solution and that the MLCT excited state is the emitting one.[6] As a consequence we are investigating complexes of the form $M(CO)_4L$, where M = Cr, Mo, or W and L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), in which the lowest energy excited states are clearly MLCT.[7] The MLCT states are so well separated from the higher energy states in the diimine complexes that they offer an opportunity to study the photophysical and photochemical properties of the MLCT excited states exclusively. We report here our preliminary observations that these complexes are emissive in room-temperature solution and that they each appear to have two emitting MLCT excited states. Multiple emissions have not previously been recognized to be a feature of group 6B metal carbonyl complexes in room-temperature solution.

The $M(CO)_4L$ complexes (M = Cr, Mo, W; L = bpy, phen) were prepared by photolysis of $M(CO)_6$ in N_2-purged isooctane containing excess L.[8] Purification was achieved by repeated washings of the product with isooctane. Spectroscopic grade solvents were distilled several times to ensure removal of emitting or quenching impurities. Carbonyl-containing impurities in the solvents were removed according to literature procedures.[9]

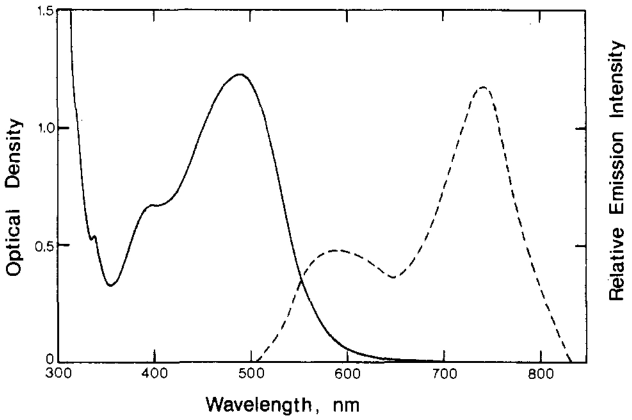

Figure 1. Electronic absorption (—) and emission (- - -) of 2×10^{-4} M $Mo(CO)_4phen$ in benzene at 298 K. The emission spectrum is corrected for variations in instrumental response as a function of wavelength, and the excitation wavelength is 400 nm.

Table I. Electronic Absorption and Emission Spectral Features of $M(CO)_4L$ Complexes in Solution at 298 K[a]

complex	solvent	absorption max, nm	corrected emission max,[b] nm
$Cr(CO)_4bpy$	methanol	333, 404 (sh), 494	607
	benzene	333, 400 (sh), 530	625, 778
$Mo(CO)_4bpy$	methanol	350 (sh), 392, 460	570
	benzene	354, 388 (sh), 492	586, 743
$W(CO)_4bpy$	methanol	354 (sh), 387 (sh), 474	563
	benzene	364, 387 (sh), 514	594, 746
$Cr(CO)_4phen$	methanol	327, 420 (sh), 488	608
	benzene	330, 420 (sh), 519	635, 747
$Mo(CO)_4phen$	methanol	336 (sh), 395 (sh), 460	563
	benzene	340 (sh), 396, 490	587, 740
$W(CO)_4phen$	methanol	336 (sh), 396 (sh), 472	560
	benzene	340, 396 (sh), 510	588, 746

[a] 8×10^{-5}–4×10^{-4} M deoxygenated solutions. [b] The excitation wavelength is 400 nm.

The electronic absorption spectrum for $Mo(CO)_4phen$ in benzene is shown in Figure 1. The absorption data obtained from all the complexes studied are summarized in Table I. For each complex the lowest energy absorption has been assigned to be a MLCT transition and shown to have an exceptionally large solvent dependence.[7] The absorptions in the 330–420-nm region have been assigned to ligand-field (LF) or metal to carbonyl charge-transfer transitions and in contrast show very little solvent dependence.[7] The MLCT absorption in isooctane is considerably red-shifted and shows the presence of two components (see Figure 2). Absorption spectra for these $M(CO)_4L$ complexes in EPA at 77 K have been reported to exhibit similar resolved features,[2b] and recently resonance Raman and magnetic circular dichroism measurements have indicated that the MLCT band comprises several different electronic transitions.[4a,10] There is thus a gathering of evidence that the $M(CO)_4L$ complexes have at least two low-energy MLCT excited states.

The emission spectrum obtained from a deoxygenated,[11] filtered[12] solution of $Mo(CO)_4phen$ in benzene is representative of the $M(CO)_4L$ complexes and is shown in Figure 1. The

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(2) (a) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105–4109. (b) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405–420. (c) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385–3388.

(3) (a) Dahlgren, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 1448–1454. (b) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1979**, *18*, 597–602.

(4) (a) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015–3021. (b) Balk, R. W.; Boxhoorn, G.; Snoeck, T. L.; Schoemaker, G. C.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1524–1530. (c) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Ibid.* **1981**, 1124–1133.

(5) Frazier, C. C.; Kisch, H. *Inorg. Chem.* **1978**, *17*, 2736–2744.

(6) (a) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6874–6876. (b) Lees, A. J. *Ibid.* **1982**, *104*, 2038–2039. (c) Lees, A. J.; Adamson, A. W. *Ibid.* **1982**, *104*, 3804–3812. (d) Chun, S.; Lees, A. J. *Inorg. Chim. Acta* **1982**, *65*, L167–L169.

(7) (a) Saito, H.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 359–364. (b) Saito, H.; Fujita, J.; Saito, K. *Ibid.* **1968**, *41*, 863–874.

(8) (a) Bock, H.; tom Dieck, H. *Angew Chem.* **1966**, *78*, 549–550. (b) Bock, H.; tom Dieck, H. *Chem. Ber.* **1967**, *100*, 228–246. (c) Brunner, H.; Herrmann, W. A. *Ibid.* **1972**, *105*, 770–783.

(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: New York, 1980.

(10) (a) Staal, L. H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *26*, 255–262. (b) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Ibid.* **1978**, *28*, 133–143. (c) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Chem. Commun.* **1978**, 1016–1017. (d) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1979**, *34*, 267–274. (e) Staal, L. H.; Terpstra, A.; Stufkens, D. J. *Ibid.* **1979**, *34*, 97–101.

(11) The $M(CO)_4L$ solutions were purged with N_2 for 20 min prior to taking measurements to avoid quenching effects by dissolved oxygen.

(12) The solutions were filtered through 0.22-μm Millipore filters to avoid effects of particulate matter in the absorption and emission experiments.

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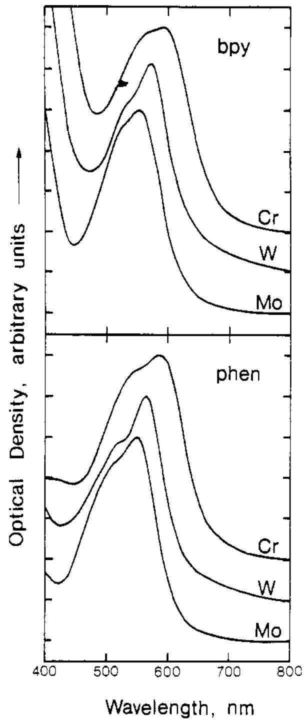

Figure 2. Lowest energy features in the electronic absorption spectra of M(CO)$_4$L complexes (M = Cr, Mo, W; L = bpy, phen) in isooctane at 298 K.

emission data obtained from all the complexes studied are summarized in Table I. The emission intensities of M(CO)$_4$L in methanol were very weak, and we were unable to observe maxima at wavelengths longer than 700 nm. These results imply that the emission efficiency of the diimine complexes is strongly dependent on solvent. Both emission bands are assigned as MLCT transitions; the higher energy one shows solvent shifts comparable to that observed in absorption, and the other band is too low in energy to be LF. Attempts to record emission data in isooctane were unsuccessful; this is attributed to either the sparing solubilities of these complexes in isooctane or, in view of the absorption solvent dependence, the possibility that emission in isooctane would likely be so red-shifted it would be difficult to detect experimentally. Further evidence for the MLCT assignment was obtained following a comparison with M(CO)$_4$en complexes, where M = Cr, Mo, or W and en = ethylenediamine. The M(CO)$_4$en complexes exhibit LF states at approximately the same energies as our diimine series but do not possess low-lying MLCT excited states.[7] Importantly, we did not observe emission from these complexes in room-temperature solution following excitation directly into the LF state at 400 nm. The observance of multiple emission indicates that interconversion between the emitting states is relatively slow compared to the radiative deactivation routes of the molecule and implies that the characters of these excited states are somewhat different. In this connection Staal et al. have recently reported evidence for both d $\rightarrow$ $\pi^*(a_2)$ and d $\rightarrow$ $\pi^*(b_2)$ charge-transfer absorptions in a series of M(CO)$_4$ diazabutadiene (M = Cr, Mo, W) complexes.[10e] Multiple emissions involving intraligand (IL) and MLCT states have been observed from several *fac*-[XRe(CO)$_3$phen] complexes.[13] However, our M(CO)$_4$L complexes appear to emit at too low energy to be associated with an unperturbed IL transition. We intend to learn more about the character of the excited states of M(CO)$_4$L through temperature dependence studies of the emission spectra and lifetimes. Emission has previously been observed for M(CO)$_4$L complexes (M = Mo, W; L = bpy, phen) in rigid glasses at 77 K.[2b] The low-temperature maxima (640-660-nm region) most likely correspond to the lowest energy maxima reported here, as recent observations of emission from related carbonyl complexes have been at lower energies in fluid solution than in rigid media.[2,6]

A particularly novel aspect of the emission data is that the chromium complexes constitute the only examples of a first-row transition metal carbonyl complex known to emit under fluid conditions. The absence of emission data from first-row metal carbonyl complexes has been attributed to the low spin-orbit coupling values of the central metal atom. In view of these results we prefer to associate the emission properties of the molecule with the presence of a low-lying MLCT excited state.

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Registry No. Cr(CO)$_4$bpy, 15668-63-0; Mo(CO)$_4$bpy, 15668-64-1; W(CO)$_4$bpy, 15668-66-3; Cr(CO)$_4$phen, 14168-63-9; Mo(CO)$_4$phen, 15740-78-0; W(CO)$_4$phen, 14729-20-5.

Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901

David M. Manuta
Alistair J. Lees*

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[13] Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415-7417.

Room-Temperature Isolation and Characterization of Group 6 Pentacarbonyls in Porous Vycor Glass

Sir:

In this paper, we describe the use of Corning's code 7930 porous Vycor glass, PVG, as a convenient alternative to low-temperature matrices[1-5] for isolation and characterization of group 6 pentacarbonyls. The adsorbed pentacarbonyls, designated M(CO)$_5$(ads) and generated by photolysis of the adsorbed hexacarbonyl, have spectroscopically quantitated lifetimes of $\geq$48 h in vacuo at room temperature.

Code 7930 PVG is a surface-hydroxylated, transparent,[6] porous glass containing $(1.2 \pm 0.3) \times 10^{18}$ pores/g,[7] with a pore diameter of 70 ± 21 Å.[8-14] Pieces of PVG (25 mm ×

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(1) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *J. Am. Chem. Soc.* **1962**, *84*, 3589.
(2) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *J. Am. Chem. Soc.* **1963**, *85*, 1013.
(3) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.
(4) Graham, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2939.
(5) Graham, M. A.; Rest, A. J.; Turner, J. J. *J. Organomet. Chem.* **1970**, *24*, C54.
(6) Relative to air, absorption spectra can be recorded to ca. 350 nm. Relative to an untreated piece of PVG, spectra have been recorded to ca. 240 nm on a Cary 14 spectrophotometer.
(7) Kennelly, T. Ph.D. Thesis, City University of New York, 1981.
(8) Elmer, T. H.; Nordberg, M. E. *J. Am. Ceram. Soc.* **1970**, *53*, 171.
(9) Sakairo, T. *Hyomen* **1971**, *9*, 115.
(10) Iler, R. K. "The Chemistry of Silica"; Wiley-Interscience: New York, 1979; p 551.
(11) Hockey, J. A. *Chem. Ind.* (*London*) **1965**, 57.
(12) Davydov, V. Y.; Kiselev, A. V.; Zhuravlev, L. T. *Trans. Faraday Soc.* **1964**, *60*, 2254; *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1964**, *38*, 1108.
(13) Kisselev, A. V. "The Structure and Properties of Porous Materials"; Everett, D. H., Stone, F. S., Eds.; Butterworths: London, 1958; p 195.

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