Luminescence Spectra of Group 6 Metal Carbonyls and Substituted Carbonyls in Frozen Gas Matrices at 12 K

By Terence M. McHugh, Ramaier Narayanaswamy, Antony J. Rest,* and Kingsley Salisbury*
(*Department of Chemistry, The University, Southampton* SO9 5NH)

Summary Luminescence spectra have been obtained for $[M(CO)_6]$ (M = Cr, Mo, or W) and $[M(CO)_5L]$ [M = Mo or W, L = pyridine (py); M = W, L = 3-bromopyridine (3-Br-py)] complexes in argon and methane matrices at 12 K for the first time.

Although dissociative decay leading to ejection of CO or L has been well documented as a major deactivation pathway for excited electronic states of transition metal carbonyls and substituted carbonyls (Scheme), information about other pathways, *e.g.* radiative and non-radiative decay processes, for such complexes is sparse.[1] For example, only substituted metal carbonyl complexes, *viz.* [M(CO)$_4$(bipy)] (M = Cr, Mo, or W; bipy = bipyridyl),[2] [W(CO)$_5$L] (L = simple donors, *e.g.* amines, ethers, or ketones),[3,4] and [ClRe(CO)$_3$L] (L = 1,10-phenanthroline-X, where X = H, 5-Me, or 5-Cl)[5] have been shown to luminesce and most of the experiments have to be carried out using hydrocarbon glasses at 77 K. Now that the quantum yield of photosubstitution of CO by pyridine (py) in [Cr(CO)$_6$] has been established as 0·67 ± 0·2 rather than 1·0,[6] *i.e.* radiative and non-radiative deactivation processes must be occurring, a routine means of investigating photophysical deactivation processes is required if progress is to be made in understanding details of the photochemistry of metal carbonyls. Matrix isolation studies have proved very successful in characterising species formed in dissociative processes, *e.g.* [M(CO)$_n$] and [M(CO)$_{n-1}$L] in the Scheme.[7] We present here preliminary results of an investigation of the luminescence spectra of metal carbonyl complexes in gas matrices at 12 K.†

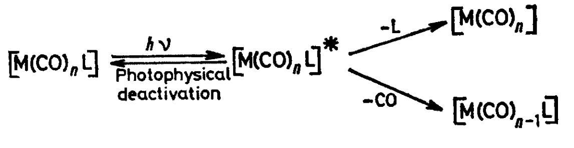

Table. Positions of emission maxima [λ_{em}(max)/nm] for [M(CO)$_6$] and [M(CO)$_5$L] complexes in gas matrices and glasses with intensities[a] in parentheses.

Complex	Matrix (12 K) Argon	Matrix (12 K) Methane	Glass (77 K)
[Cr(CO)$_6$]	347 (w)	349 (w)	b
[Mo(CO)$_6$]	353 (m)	345 (m)	b
[W(CO)$_6$]	360 (s)	342 (s)	b
[Mo(CO)$_5$(py)]	c	522 (w)	d,e
[W(CO)$_5$(py)]	424 (w) 523 (s)	420 (w) 525 (s)	510[d], 523[e]
[W(CO)$_5$(3-Br-py)]	c	544 (s)	529[e]

[a] Relative emission intensities (w = weak, m = medium, and s = strong) were obtained by laying down the matrix sample until the absorption bands to be excited had comparable absorbances (0·5—0·6 o.d. units). However, this data must be interpreted with care because the complexes have different volatilities, *i.e.* the matrix samples were of different thickness corresponding to the different complex : host matrix ratios. [b] No detectable emission (ref. 1). [c] Data not yet available. [d] Data from ref. 3 for methylcyclohexane glass. [e] Data from ref. 3 for ether–pentane–alcohol glass.

Representative matrix isolation‡ emission spectra of [M(CO)$_5$L] and [M(CO)$_6$] complexes are shown in the Figure (a and b) which include the corresponding absorption spectra. Emission data are presented in the Table. In order to be certain that the luminescence was due to the metal complexes, the following precautions were taken and checks were made.

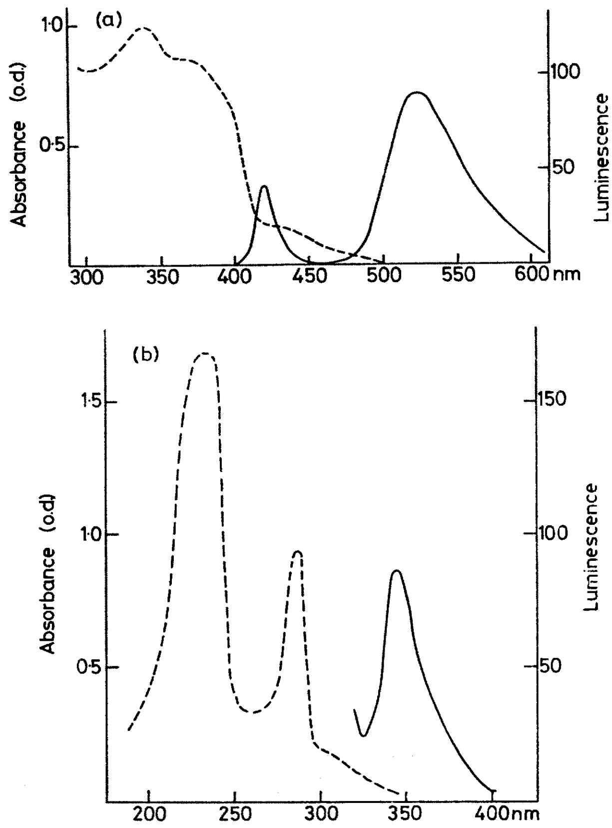

Figure. Combined absorption (- - - -) and emission (——) spectra for (a) [W(CO)$_5$(py)] and (b) [Mo(CO)$_6$] isolated at high dilution in CH$_4$ matrices at 12 K. The ordinate scale for emission spectra is a relative scale and does not correspond to the optical density scale of the absorption spectra.

(a) Exposure of matrix samples to the exciting radiation, which could cause photolysis,[8] was kept to a minimum by blocking off radiation between running spectra with different exciting wavelengths and the extent of any photolysis was monitored by running i.r. spectra before and after the luminescence measurements.

(b) The fact that emissions arose from the [M(CO)$_5$L] or [M(CO)$_6$] complexes was established by running blank experiments on the matrix gases alone and by seeking to observe luminescence spectra of authentic samples of matrix photolysis products, *i.e.* [M(CO)$_5$] or py;[8] it is noteworthy that the emission maxima (Table) were almost independent of the matrix gas whereas [M(CO)$_5$ . . . . matrix] species (matrix = Ne, Ar, Kr, Xe, or CH$_4$) show shifts (*e.g.* M = Cr, 624—489 nm) in the absorption spectra.[9]

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† Earlier attempts to obtain luminescence spectra of matrix isolated [W(CO)$_5$L] complexes were unsuccessful (J. R. Sodeau, Ph.D. Thesis, University of Southampton, 1977). Improvements in the signal-to-noise ratio afforded by a new custom-designed spectrofluorimeter (A. J. Rest and K. Salisbury, unpublished work) overcame the sensitivity problem.

‡ The isolation of discrete molecules was ensured by making >1 : 2000 (complex: host matrix) gas mixtures manometrically for [M(CO)$_6$] complexes and by careful slow spray-on for the involatile [M(CO)$_5$L] complexes and by checking for good isolation by comparing the i.r. spectra with previous spectra (ref. 8).

(c) Occurrence of luminescence was confined to excitation wavelengths where [$M(CO)_5L$] and [$M(CO)_6$] were known to absorb, as determined from the matrix u.v.–visible absorption spectra [see Figure (a and b)].

The matrix isolation results are in good agreement with the low temperature glass studies for the [$W(CO)_5L$] complexes (Table) where the emission at *ca.* 530 nm has been attributed to phosphorescence ($^3E \rightarrow {}^1A_1$) using emission-lifetime studies.[3] Several new features have been observed for gas matrices.

(i) A second emission at 420 nm for [$W(CO)_5(py)$]; this is probably fluorescence ($^1E \rightarrow {}^1A_1$) but proof of this awaits development of apparatus suitable for short-lifetime measurements on weakly luminescing species.

(ii) A new weak emission for [$Mo(CO)_5(py)$] but not for [$Cr(CO)_5(py)$]; this can be accounted for by the 'heavy atom' effect based on spin-orbit coupling[10] (the differentiation between Cr and the other members of Group 6 in this work is more satisfactory than for the glass studies[3] where only the W complex luminesced but only Cr has a negligible spin-orbit coupling constant).

(iii) Failure to observe emission from [$W(CO)_5$] in gas matrices calls into question the previous report [λ_{em}(max) = 533 nm, methylcyclohexane glass at 77 K];[3] the conditions under which the luminescence was observed, namely softening of the glass to allow photoejected CO molecules to diffuse away, could lead to the highly reactive [$W(CO)_5$] species dimerising or scavenging solvent impurities {*cf.* the problems which were encountered in obtaining reproducible flash photolysis results for [$Cr(CO)_6$] in solution}.[11]

The potential of the matrix isolation technique can be judged from the new luminescence results for the [$M(CO)_6$] complexes (Table). Previously sensitisation was required to observe luminescence for [$Cr(CO)_6$] since nothing could be detected on direct excitation of [$Cr(CO)_6$] in argon.[12] It is probable that the new emissions at 340—360 nm for [$M(CO)_6$] complexes correspond to fluorescence, *i.e.* $^1T_{1g} \rightarrow {}^1A_{1g}$ or $^1T_{2g} \rightarrow {}^1A_{1g}$,[13] because of their positions relative to the absorption bands [Figure (a and b)] and the observation of a triplet-sensitised emission for [$Cr(CO)_6$] at 400 nm.[12] Further work is in progress to obtain lifetime data for short-lived emissions (10^{-9}—10^{-1} s), excitation spectra, and vibrational fine structure for emission spectra.

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