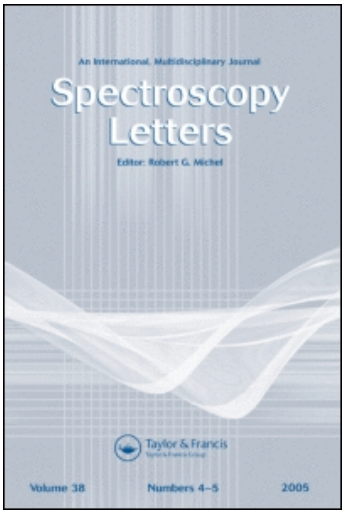

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COMMENTS ON LUMINESCENCE FROM LOWEST MLCT EXCITED STATE OF MIXED AMINE CARBONYL COMPLEXES OF 6B METAL GROUP

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Dear Sir:

During the last fifteen years several works related to the photochemistry and photophysics of $M(CO)_{6-n}(L)_n$, where the lowest excited state is generated by a metal ligand charge transfer (MLCT) process have been published in several journals (1-9). A single molecular description of the emission properties in terms of a luminescent triplet MLCT excited state is frequently invocated (1-9). However, two aspects not considered in all these published works have called our attention. First, radiative lifetimes determined from the singlet MLCT absorption spectra respect to those obtained from emission parameters as the experimental lifetimes and emission quantum yields are different in several orders of magnitude. Second, the heavy atom effect on going from the Mo to the W complexes is absent on luminescent properties of these assumed emitting triplet excited states.

The analysis of the radiative decay constant (k_r) expected for these organometallic species is an aspect generally absent in all these luminescent studies (1-9). Although several authors (10) have introduced different modifications in the original equation developed by Einstein (11), relating the probability absorption to the spontaneus emission, we will make use of this simple expression modified by Lewis and Kasha (12) (eq./1/).
Thus,

$$k_r = (1/\tau) = 2.88 \cdot 10^{-9} \nu_o^2 \; n^2 \int \epsilon(\nu) \, d\nu \qquad / 1 /$$

where ν_o is the wavenumber maxima of the absorption band, n is the refractive index of the solvent and ϵ is the molar absorption coefficient.

TABLE I

Spectral absorption data and luminescence parameters of some organometallic compounds

Compounds	Absorption			Emission			
	band maxima	ϵ	k_r (a)	band maxima	τ_{br}	ϕ	k_r
	kK	10^{-3}	$10^{-7}s^{-1}$	kK	μs	10^{2}	$10^{-3}s^{-1}$
$Mo(CO)_4$(5-X-1,10-phen) (b)							
X:							
H	21.74	3.55	3.3	15.66	11.6	9	7.8
Me	21.28	4.56	4.1	15.55	13.2	8	6.1
Cl	20.79	3.53	3.0	14.40	13.3	4	3.0
$W(CO)_4$(5-X-1,10-phen) (b)							
X:							
H	20.83	5.02	4.3	15.30	11.6	5	4.3
Me	20.62	3.39	2.8	14.90	12.5	4	3.2
Cl	19.96	5.39	4.2	14.40	7.9	2	2.5

$W(CO)_5$(4-X-pyridine)	(c)						
X:							
acetyl	24.88	9.81	12	15.90	0.258	0.016	0.62
benzoyl	24.81	9.53	11	16.42	0.235	0.023	0.98
cyano	24.75	8.04	9.7	15.54	0.269	0.013	0.48
formyl	24.88	7.28	8.9	15.38	0.139	0.010	0.72
$BrW(CO)_2$(TMEDA)(CPh)	(d)						
	22.22	0.40	3.9	15.87	0.180	0.053	2.9

a. Determined from eq./1/, where $\int \epsilon(\nu)d\nu \approx \epsilon_{max.} \Delta\nu_{1/2}$

b. Ref. 2. Emission data determined at 77 K.

c. Ref. 1. Emission data determined at RT.

d. Ref. 17. Emission data determined at RT.

Table I shows a set of reported experimental spectroscopic data for several organometallic compounds. In the same Table are presented the radiative constants (k_r) determined by means of eq./1/. These k_r values are found in the range of $1 \cdot 10^7$ to $12 \cdot 10^7$ (s^{-1}) for the singlet MLCT absorption band. We have used an estimated mean band wide of 3.5 kK. On the other hand, we have include the k_r values obtained from emission data according to eq. /2/,

$$k_r = \phi / \tau_{br} \qquad / 2 /$$

where experimental quantum yields (ϕ) at RT and 77 K and experimental lifetimes (τ_{br}) are collected in Table I. Thus, we can see that both sets of results are completly different being the k_r determined from emission data lower in four order of magnitude than the k_r estimated from the singlet MLCT absorption band.

In addition, an abnormal large Stoke's shift observed in these spectral data clearly permite to reject the singlet MLCT excited state as the emitting source of the luminescence.

It has been claimed by several authors the presence of some triplet MLCT absorption bands in these kind of complexes (2, 13). And frequently the luminescent excited state has been invocated as triplet MLCT nature (1-9). However, we can observe from Table I a constancy of the lifetime measurements for Mo and W species under the same conditions (2, 8, 9). Therefore, the luminescent excited state merge independently of the nature of the metal center and so, the MLCT excited states can not be adscrived as the emitting states.

Recently, we have studied the luminescence of some tungsten(0)-carbyne complexes ($XW(CO)_2(TMEDA)(CPh)$, (X = Br, I)) and we have detected the triplet MLCT absorption band at low energy of the singlet MLCT absorption band (14). This band is dependent on the nature of the X ligand, increasing their molar absorption coefficient from Br to I. But this internal heavy atom effect not change the luminescent properties of these complexes (14).

If we consider a good overlap between the singlet ground state and the triplet MLCT excited state, the intersystem crossing will increase in the tungsten(0) complexes respect to the molibdenum complexes. This assumption can be corroborated with the luminescence quantum yield diminution observed in Table I. Thus, new transient species generated in excited state from these MLCT excited states must originate the emitting state, where the concentration reached for all these new transient species will decrease on going to Mo to W complexes in according to the intersystem crossing expected, without a change in the lifetime nature. Considering that the luminescence observed in these emitting Mo and W complexes are not dependent on the metal center, as can be infered from the lifetimes measurements, the electronic nature of this species

must envolve ligand structure only. By following, the interconversion efficiency (ϕ_p) from a MLCT excited state to a luminescent species could be estimated according to

$$\phi = \phi_p \cdot k_{br} \cdot \tau_{br} \qquad / 3 /$$

where k_{br} and τ_{br} are the radiative constant and the experimental lifetime of the true emitting species, respectively. Table I presents the apparent radiative constant k_r determined from ϕ / τ_{br} which indeed correspond to ($k_{br} \cdot \phi_p$). For radiative lifetimes slightly longer than the experimental lifetimes we will found ϕ_p values lower than 10% and therefore the MLCT excited states can be considered as efficient radiativeless channels. Nowadays, it is well known that a polarized emission spectra contribute quite well to determine the excited state nature of the emitting species respect to the electronic state involved in the excitation of their absorption band (15, 16). At this respect, recently we have showed a complete depolarization of the luminescence of some tungsten(0)-carbyne complexes at 77 K in glass rigid matrix of 2-methyltetrahidrofuran after excitation with polarized light (13). Obviously, these experiments suggested us to consider new species as the luminescent source instead the first excited state of MLCT nature of our metal carbyne complexes observed from the absorption spectra. Therefore, in the future these experiments should be solicited in order to stablish the origin of the luminescence.

Based on the experimental lifetime magnitude order and the heavy atom effect independence, a biradical excited state centered on the ligand derived from the MLCT process can be assumed as the emitting source. This biradical model generated after MLCT process in these mixed amine carbonyl complexes of 6B metal group can explain well different results spread out in several works (1-9, 17) as: (a) complexes having low-energy MLCT transitions have been shown to be relatively unreactive photochemically following excitation directly into this state; (b) the overwhelming M-N lability in the excited state compared to M-C lability in photosubstitution process; (c) the before mentioned behavior respect to the depolarization of the emission observed under light polarized excitation for some complexes of similar MLCT excited states; (d) the non expected long lifetimes emission found in all these organometallic compounds and (e) the heavy atom effect independence of the emission lifetime.

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References

1. A.J. Lees and A.W. Adamson, J.Am.Chem.Soc, 104 (1982) 3804-3812.
2. M.S. Wrighton and D.L. Morse, J.Organomet.Chem., 97 (1975) 405-420.
3. M.S. Wrighton, H.B. Abrahamson and D.L. Morse, J.Am.Chem.Soc., 98 (1976) 4105-4109.
4. H.B. Abrahamson and M.S. Wrighton, Inorg.Chem., 17 (1978) 3385-3388.
5. D.M. Manuta and A.J. Lees, ibid., 22 (1983) 572-573.
6. S. Chun, E.E. Getty and A.J. Lees, ibid., 23 (1984) 2155-2160.
7. R.M. Kolodziej and A.J. Lees, Organometallics, 5 (1986) 450-455.
8. D.M. Manuta and A.J. Lees, Inorg.Chem., 25 (1986) 1354-1359.
9. A.J. Lees, Chem.Rev., 87 (1987) 711-743. And references there in.
10. S.J. Strickler and R.A. Berg, J.Chem.Phys., 17 (1962) 814-822.
11. A. Einstein, Physik Z., 18 (1917) 121.
12. G.N. Lewis and M. Kasha, J.Phys.Chem., 67 (1945) 994-1003.
13. R.G.E. Morales, D.S. McClure and A. Mayr, Procc. XIII International Conference on Organometallic Chemistry (Turin), 1 (1988) 404.
14. R.G.E. Morales, D.S. McClure and A. Mayr, to be published.
15. P.P. Feofilov, "The Physical Basis of Polarized Emission", Consultant Bureau, N.Y., 1961.
16. J. Lakowicz, "Principles of Fluorescence Spectroscopy", Plenum Press, N.Y., 1983.
17. A.B. Bocarsly, R.E. Cameron, H.D. Rubin, G.A. McDermott, C.R. Wolff and A. Mayr, Inorg.Chem., 24 (1985) 3976-3978.

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