Observation of multiple MLCT emissions for a Cu'N₄ chromophore in rigid matrices

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[CuL₂]ClO₄ (I), where L is a 1:2 condensate of ethylenediamine and benzophenone, displays four MLCT emissions with maxima λₑᵥₑ₅ = 617, 583, 549 and 494 nm in poly(methyl methacrylate) matrix at room temperature. Three of these emissions are observed for I in methanol glass at 77 K with λₑᵥₑ₅ = 473, 440 and 412 nm. The origins of these emissions are investigated by Extended Huckel calculations on [CuL₂]⁺ at the crystallographically determined geometry.

First observation of a photoluminescent CuN₄ chromophore was reported by Buckner and McMillin in 1978. The relevant copper(I) species was [Cu(dmp)]⁺ where dmp is 2,9-dimethyl-1,10-phenanthroline. Subsequently, photochemistry of copper(I)-bisphenanthrolines have been studied extensively by McMillin, Karpishin, Armaroli and others in order to understand the stereoelectronic factors governing the properties of the excited state(s). It has also been found that very few N-donor ligands other than phenanthrolines can yield photoluminescent CuN₄ chromophores. The CuN₄ cores in copper(I)-bisphenanthrolines usually display only one emission band upon excitation within the MLCT envelope. Very rarely, two ill-resolved bands have been observed; that too, at low temperatures. The origin of two bands in such cases is still not clearly understood, though, in principle, two bands are possibly expected – one from a higher lying MLCT excited state and another from a lower lying MLCT excited state. Herein we report observation of multiple emission bands for a CuN₄ chromophore assembled using an N,N-donor ligand which is not a kin of 1,10-phenanthroline.

Experimental

PMMA powder (average Mₙ = 120,000) was purchased from Aldrich and was used as received. Complex I was synthesized as reported elsewhere. Emission spectra were recorded in air by using a Hitachi F-4500 spectrophotometer. Extended Huckel calculations were performed by HyperChem package purchased from Hypercube Inc., Canada.

Incorporation of I in PMMA

PMMA (80 mg) was dissolved in 1 ml of chloroform. In this colourless solution, was dissolved 5 mg of I. The resulting reddish yellow solution was thinly and evenly spread over a glass slide and dried in air to obtain a transparent film. The film, picked up by a sharp blade, was cut and shaped to a rectangle (1.2 cm×5 cm). The thickness of the film varied between 0.0045-0.0060 cm with an average of 0.0050 cm.

Results and discussion

Earlier we have reported that [CuL₂]ClO₄ (I), where L is a 1:2 condensate of ethylenediamine and benzophenone, is weakly emissive in dichloromethane and methanol at room temperature. Since many of the applications of photoluminescent inorganic complexes require the complexes attached to solid supports or incorporated in solid matrices, we have now studied the emission behaviour of I in rigid media. Two types of rigid media have been chosen: poly (methyl methacrylate) [abbreviated as PMMA] matrix and methanol glass.

It is found that when I is embedded in a PMMA film, it displays four overlapping but somewhat distinct emission bands (Fig. 1) upon excitation at 360 nm (within the MLCT envelope) at room temperature. The emission maxima (λₑᵥₑ₅) of these bands, as found by Gaussian analysis (see Fig. 1), are 617 (peak I), 583 (peak II), 549 (peak III) and 494 (peak IV) nm. Identical excitation spectrum was obtained by monitoring the four different emission maxima, which has a profile very similar to the absorption spectrum of the film (Fig. 2). This means that the observed emission is due to the copper(I) complex I and not any other species. The reproducibility of our observations has been checked by embedding I in PMMA several times.
Fig. 1—Emission spectrum of 1 in a PMMA film at room temperature. Excitation wavelength $\lambda_{ex}$, 360 nm. Absorbance at 360 nm, 1.81. Results of the Gaussian analysis are as follows. Peak I: $\lambda_{em}$, 617 ± 0.4 nm; half-width ($w$), 50 ± 0.5 nm; $A$, 1689 ± 25. Peak II: $\lambda_{em}$, 583 ± 0.3 nm; $w$, 25 ± 0.7 nm; $A$, 476 ± 40. Peak III: $\lambda_{em}$, 549 ± 0.3 nm; $w$, 40 ± 0.9 nm; $A$, 1510 ± 35. Peak IV: $\lambda_{em}$, 494 ± 0.4 nm; $w$, 32 ± 0.7 nm; $A$, 365 ± 11.

Fig. 2—The absorption spectrum of 1 in PMMA matrix. The inset shows a typical excitation spectrum of the film.
The emission behaviour of 1 in the PMMA matrix is in sharp contrast with the room temperature solution behaviour of the photoluminescence of 1 where only one very broad band is observed. Earlier Parker and Crosby have studied the emission behaviour of \([\text{Cu(bcn)}_2]\text{ClO}_4\) \((\text{bcn} = 2,9\text{-dimethyl-4,7-diphenyl-1,10-phenanthroline (batho-cuproine)})\) in PMMA and found that its emission profile over a range of temperature \((300-4.2\) K) is essentially similar to that in dichloromethane solution at room temperature. Very recently Karpishin and co-workers have found that the heteroleptic \([\text{Cu(dbp)(dmp)}]\text{PF}_6\) \((\text{dbp} = 2,9\text{-di-tert-butyl-1,10-phenanthroline})\) shows a featureless broad single emission band in the solid at room temperature as in dichloromethane solution. Thus the resolution of a single emission band into four bands in going from solution to solid state is very novel in the photophysics of \(\text{Cu}^1\text{N}_1\) chromophores.

Determination of quantum yield (\(\Phi\)) in a rigid medium is difficult. We have made no attempt to measure the quantum yield of the total emission observed for 1 in the PMMA film. However, the areas \((\text{A})\) under the bands I-IV in Fig.1, as obtained from Gaussian analysis, show that \(\Phi_1 > \Phi_II > \Phi_{III} >> \Phi_{IV}\).

Fig. 3—Calculated contour diagrams of (b) HOMO, (c) LUMO, (d) LUMO+1, (e) LUMO+2 and (f) LUMO+3 in the model (a) of the cation [Cu-2]. For the clarification of the nature of the model (a), see text. Selected bond distances in (a) taken from ref. 13: Cu-N1 2.077, Cu-N3 2.065, Cu-N8 2.014, Cu-N11 2.183 Å. Relative energies (in eV) of the MO's: (b) set to 0, (c) 2.56, (d) 2.60, (e) 2.64 and (f) 2.71.
where the Roman numeral subscripts refer to the respective bands/peaks.

In order to understand the origin of four emission bands for I in PMMA film, we have performed Extended Hückel calculations on the cation [CuL₂]⁺ at the crystallographically determined geometry¹³ which does not have any symmetry. For clarity of presentation and convenience, we have replaced the phenyl groups by H atoms to generate model (a) in Fig. 3. The calculated contour diagrams of the HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and three next energetically higher MO’s, LUMO+1, LUMO+2 and LUMO+3, are shown in Fig. 3. The HOMO, as expected, is mainly localised on the metal. The four unoccupied MO’s, LUMO to LUMO+3, are found to be quite diffuse having large contributions of the π⁻ orbitals of the imino fragments. Still, it can be said that the LUMO is somewhat localised on the C1=N2 fragment and LUMO+2 on C7=N8 while LUMO+1 and LUMO+3 are much more delocalised. Thus electronic transition from the HOMO to any of the four unoccupied MO’s in Fig. 3 can result in an MLCT transition. We reckon that the lowest energy emission, band I, is from an MLCT excited state arising out of HOMO → LUMO transition; band II is an HOMO → LUMO+1 CT emission, band III HOMO → LUMO+2 CT emission and band IV HOMO → LUMO+3 CT emission. Since LUMO+1 and LUMO+3 are more diffuse than LUMO and LUMO+2 (Fig. 3), the transition moment integral involving LUMO+1 or LUMO+3 is likely to be smaller than that involving LUMO or LUMO+2. Accordingly, the probability of the formation (which in turn we correlate to the lifetime) of the HOMO → LUMO+1 CT excited state or the HOMO → LUMO+3 CT excited state is smaller than that of the HOMO → LUMO CT excited state or the HOMO → LUMO+2 CT excited state. As a consequence, ΦII and ΦIV are indeed expected to be less than ΦI and ΦIII.

Fig. 4—Emission spectrum of I in methanol glass at 77 K, λex, 350 nm. Absorbance at 350 nm at room temperature, 0.54.

Fig. 5—The absorption spectrum of I in methanol. The inset shows a typical excitation spectrum of I in methanol glass at 77 K.
An unconventional observation in the photophysics of copper(I)-bisphenanthroline is that the intensity of the MLCT emission decreases with the temperature leading to very weak or no emission at 77 K in most cases. We have found that our complex I displays three emission bands in methanol glass at 77 K (Fig. 4). The \( \lambda_{em} \)'s of these bands are 473 (peak I), 440 (peak II) and 412 (peak III) nm. The origin of the respective bands are same as in the PMMA matrix, i.e. band I is a HOMO \( \rightarrow \) LUMO CT emission, band II HOMO \( \rightarrow \) LUMO+1 CT emission and band III HOMO \( \rightarrow \) LUMO+2 CT emission. The other band, peak IV, observed in Fig. 1 due to HOMO \( \rightarrow \) LUMO+3 CT, is expected to occur at a wavelength shorter than 412 nm. Since the excitation wavelength in Fig. 4 is 350 nm, we could not observe it in methanol glass at 77 K. Again identical excitation spectrum was obtained by monitoring three different emission maxima (Fig. 5).

A comparison of Fig. 1 and Fig. 4 shows that the individual bands undergo a blue shift in going from PMMA matrix at room temperature to methanol glass at 77 K. This is due to the fact that the flattening distortion of the Jahn-Teller sensitive copper(II) center generated in the photoexcited state is more restricted in the methanol glass than in the PMMA film. Since we do not know whether the complex I dissolves in PMMA, it will be appropriate to assume that in the PMMA matrix the molecules of I form aggregates leaving some room for the cation to relax in the excited state. This is evident from the excitation spectra also. The counterpart of the 400 nm MLCT band in the absorption spectra appears at 362 nm in the excitation spectrum of I in PMMA film and at 275 nm in the excitation spectrum of I in methanol glass. This phenomenon leads to another significant difference in the emission behaviour of I in the PMMA film and in the methanol glass — in the energy (E) separation between two consecutive peaks. In PMMA film, from Fig. 1 we find that \( E_{II-E_{III}} = 946 \) and \( E_{II-E_{III}} = 1062 \) cm\(^{-1}\); these values in Fig. 4 are 1585 and 1545 cm\(^{-1}\) respectively. Thus the flattening distortion of the copper(II) center in the excited state tends to result in overlapping of the various MLCT states in \([CuL_2]\)^+. Since this distortion is expected to be maximum in a fluid solution, we observe only one emission in the methanol or dichloromethane solution of I at room temperature in the form of a very broad band. It is noteworthy that the areas of the bands I-III in Fig. 4 are more or less same. Consequently it is unlikely that the observed multiple emissions of I in rigid matrices are due to vibronic coupling(s).

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References