

ON THE LUMINESCENCE OF BIS (TRIPHENYLPHOSPHINE) PHENANTHROLINE COPPER (I)

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The luminescence spectra and decay times of the emission of the $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$ ion have been measured down to liquid helium temperature. The long decay time at low temperatures is interpreted in terms of the triplet level of the charge-transfer state.

1. Introduction

Recently some copper(I) complexes have been shown to luminesce in solution [1,2]. In view of the fact that the ligands involved have low-lying, unoccupied π^* levels the emission was ascribed tentatively to metal-to-ligand charge-transfer transitions (CTTL). Metal-centred transitions could, however, not be eliminated convincingly. Since some of the complexes involved show efficient luminescence at room temperature in the solid state, we extended the previous work to solid-state luminescence studies down to liquid helium temperature. The first results are reported in this letter. They relate to the $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$ ion.

2. Experimental

Samples were prepared and characterized by the methods described previously [1,2]. The optical measurements were carried out at room temperature, liquid nitrogen and liquid helium temperature as described before [3].

3. Results

The complex $[\text{Cu}(\text{PPh}_3)_2(\text{phen})][\text{BF}_4]$ has a yellow body colour. At room temperature it shows an intense greenish emission. Upon cooling to lower temperatures the intensity of the emission does not change, but the colour becomes yellowish. In fig. 1

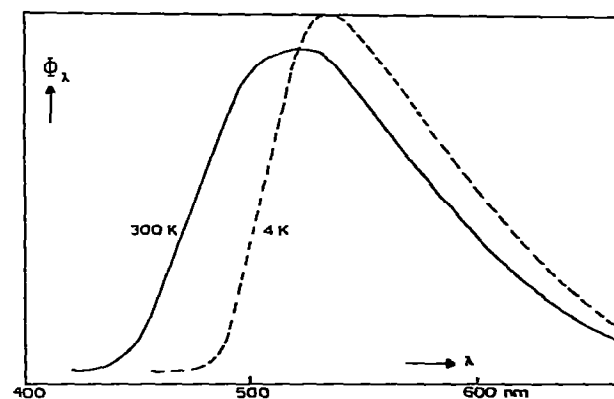


Fig. 1. Spectral energy distribution of the emission of the $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$ ion at 4.2 and 300 K under long wavelength ultraviolet excitation. Φ_λ gives the radiant power per constant wavelength interval in arbitrary units. The figures are not to scale; their maxima have been drawn in such a way that clarity is optimized.

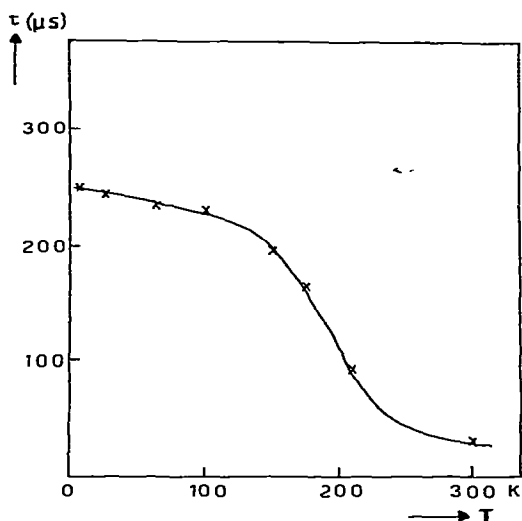


Fig 2 Decay time of the luminescence of the $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$ ion as a function of temperature. All times correspond to exponentials. Excitation is in the maximum of the excitation band. Note that the luminescence intensity is independent of temperature in the temperature region concerned.

we present the room temperature as well as the liquid helium temperature emission spectrum. It is clear that the room temperature spectrum contains an additional component at shorter wavelength.

The excitation spectrum of this emission has a maximum at about 400 nm at all temperatures. It extends far into the ultraviolet region. The room temperature excitation spectrum is broader than that at liquid helium temperature.

The temperature dependence of the luminescence decay time is given in fig. 2. At low temperatures it becomes very long (some 250 μs) in comparison with the room temperature value (30 μs). This decrease cannot be ascribed to the occurrence of nonradiative transitions in view of the constant and high intensity of the luminescence. Due to the fact that our excitation source was a xenon lamp, components in the decay curve with time constants of 1 μs or less could not be observed. Pulsed excitation with a N_2 -laser pumped dye laser will be performed in the near future.

4. Discussion

From the temperature dependence of the emission spectrum and the decay time we conclude that the radiative processes have to be described with at least a three-level system. The lower excited level yields the yellow emission which corresponds to a highly-forbidden transition in view of the long decay time at liquid helium temperature. The higher excited level yields the green emission.

Assuming the nonradiative transitions between the two excited levels to be fast in comparison with the radiative transitions, the temperature dependence of the decay time is given by

$$\frac{1}{\tau} = \frac{1}{\tau_2} \frac{\exp(\Delta E/kT)}{1 + \exp(\Delta E/kT)} + \frac{1}{\tau_3} \frac{1}{1 + \exp(\Delta E/kT)},$$

where ΔE is the energy difference between the two excited levels, and τ_2 and τ_3 are the reciprocals of the transition probabilities from the lower and the higher excited levels to the ground level, respectively [4]. It is possible to fit the curve in fig. 2 to this formula with ΔE about 1000 cm^{-1} , τ_2 about 230 μs and τ_3 about 0.2 μs . The fit is not perfect which might be due to a temperature dependence of τ_2 and τ_3 or to a more complicated level scheme. The present results give, nevertheless, a reliable first-order approximation of the complete energy level scheme involved. If the room temperature emission is regarded as a mixture of the component seen at low temperatures and a shorter wavelength component the energy difference between the two maxima amounts to about 900 cm^{-1} , in good agreement with the decay time measurements.

The present results confirm the idea of a CTTL transition. If the excited state would be $3d^9\pi^*$ we expect a singlet and a triplet level. This fits the energy level diagram given above. Felix et al. [5] have recently reported the CTTL transitions of Fe^{2+} , Ru^{2+} and Os^{2+} in $\text{Zn}(\text{bipy})_3\text{Br}_2 \cdot 6\text{H}_2\text{O}$ and the energy difference between the triplet and singlet levels is of the same order of magnitude as observed here.

Let us, however, consider the possibility of a $3d-4s$ transition on the Cu^+ ion. A semi-empirical molecular orbital calculation has been given for Cu^+ in some alkali halides where the Cu^+ ion is "on centre" [6]. The $3d^9 4s$ state yields the following state: ${}^3T_2 < {}^1T_2 < {}^2E < {}^1E$. The energy difference between the singlet

and triplet levels is of the same order of magnitude as the ΔE value mentioned above. The fact that the orbital triplets lie below the orbital doublets for octahedral coordination of Cu^+ in the alkali halides is due to the fact that $J(t_{2g}, a_{1g})$ is much larger than $J(e_g, a_{1g})$, where J represents a Coulomb integral.

In the present complex with tetrahedral coordination for the Cu^+ ion the orbital doublet is expected to be the lower level. If this is the case the two excited states in our model are 3E and 1E . Transitions from both levels are symmetry forbidden. Although in the complex involved the symmetry of the Cu^+ ion is definitely lower than tetrahedral, the value of τ_3 seems much too short to relate to the 1E level. We feel, therefore, that our experimental results confirm the proposal of a CTTL transition in the case of the present Cu^+ complex.

Finally we compare our results with recent measurements on $\text{Cu}_4(\text{Py})_4\text{I}_4$ [7,8], because these seem to bear some relation to ours. Below 100 K there is a blue emission ascribed in ref. [8] to the pyridine ligand. We did not observe a comparable emission band (see, however, ref. [2]). From room temperature down to low temperature there is also a yellow emission band showing a red-shift for decreasing temperature. This parallels our observations. In ref. [7] this is ascribed to an increase of electronic interactions between adjacent copper ions in the excited state with lowering temperature. Decay times reported in

ref. [8] are nearly temperature independent and do not reach the long values reported here. This suggests that the energy level scheme for the tetrameric clusters in refs. [7,8] is essentially different from the one proposed here.

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