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Fluorescence Thermochromism and Symmetry of Copper(I) Complexes

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In previous papers [1–3] we reported on the preparation and luminescence properties of different copper(I) compounds. From fluorescence of copper (I) perchlorate complexes whose structures [4, 5] show that they are monomeric, *i.e.* $Cu(Py)_4ClO_4$, it becomes evident that this property can be attributed to $3d^{10} \dashrightarrow 3d^9\pi^*$ transitions of Cu^+ centres.

Among series of copper(I) halide complexes with cyclic nitrogen bases (L), $Cu(L)_nX$ (n = 1, 2, 3) some monosolvates reversibly alter their fluorescence colour with temperature (Fluorescence Thermochromism) [6]. For elucidation of this phenomenon we have recorded emission and excitation spectra at different temperatures between 293 K and 77 K of several compounds and compared these results with structure data from the literature. The structure of monosolvates (L = piperidine [7], morpholine [8], pyridine [9]) consists of $Cu_4L_4J_4$ clusters with short copper–copper distances ranging from 2.59 to 2.72 Å.

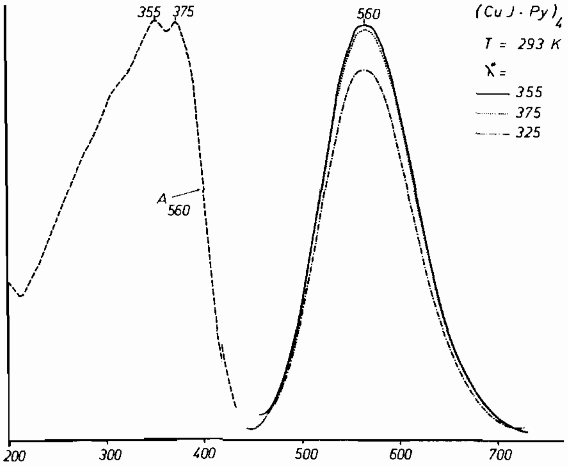

Fig. 1. Emission and excitation spectra of $Cu_4(Py)_4J_4$ at 293 K.

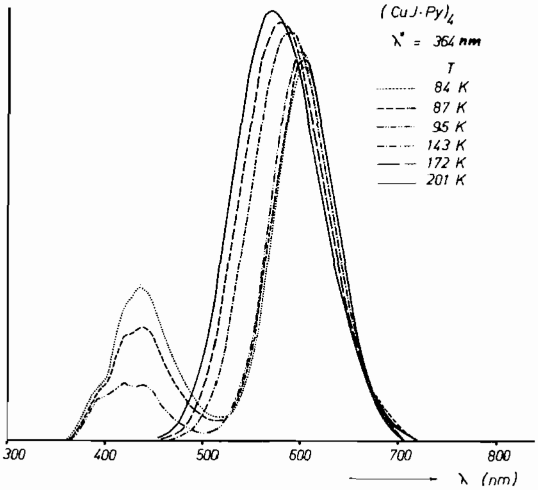

Fig. 2. Emission spectrum of $Cu_4(Py)_4J_4$ at different temperatures excited with 364 nm.

In Fig. 1 the emission and excitation spectra of pyridine copper(I) iodide at 293 K are shown. The shape of the fluorescence band is independent of the exciting wavelength. On lowering the temperature the emission peak gradually shifts to longer wavelengths (see Fig. 2). At about 100 K a new band situated on the high energy side of the spectrum appears, increasing in intensity on further cooling whilst the first one diminishes. A temperature dependent equilibrium between the two emissions results as shown by the isosbestic point in the spectra. At 77 K the two emissions have different excitation spectra suggesting that the emissions result from copper ions with different environments following to lower symmetries of the $Cu_4(Py)_4J_4$ cluster. A similar behavior is found in the spectra of other thermochromic compounds, *i.e.* 3-ethylpyridine copper(I) iodide. This compound, however, did not show any change in structure when cooled to 77 K as Guinier X-ray photographs are identical [10].

In the spectra of piperidine copper(I) iodide and morpholine copper(I) iodide only a red shift of the fluorescence band takes place. In all the three cases the long wave excitation peaks disappear at 77 K. As shown in the Table the extent of the red shift of the emission peak with temperature depends more on the symmetry of the cluster than on copper–copper distances. The higher the symmetry of the cluster, the less the red shift. These observations make it probable that at low temperature higher excited states are preferentially populated. According to a similar red shift with temperature observed by H. Yersin and G. Gliemann [11] in the emission spectra of $Mg[Pt(CN)_4] \cdot 7H_2O$ we presume that also here because of short metal distances, an increase of electronic interactions between adjacent copper ions in the excited state with lowering temperature is the reason for the obvious red shift of the emission band.

TABLE. Structure and Fluorescence Data of Some $Cu_4(L)_4J_4$ Compounds.

Ligand L	Crystal System and Space Group	Characteristic Symmetry of the Cluster	Copper–Copper Distances (Å)	Emission and Excitation Peaks (nm)				Red Shift of Emission (nm)
				T = 293 K		T = 77 K		
				λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	
Piperidine	Tetragonal $P4_2/m$	$\bar{4}$	2.63/2.67	570	350/375/387	585	350	15
Morpholine	Monoclinic B2/b	2	2.59–2.71	625	355/377/392	660	355/375	35
Pyridine	Orthorhombic $P2_12_12_1$	1	2.62–2.72	560	355/375	610 440	317 270/295/364	50

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