

Fluorescent zinc–terpyridine complex containing coordinated peroxy counter ion in aqueous medium

S KAPOOR and M S SASTRY*

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085,
India

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Abstract. We describe a mixed ligand–zinc (d^{10}) complex containing coordinated peroxy ion and 2,2',2''-terpyridine and exhibiting fluorescence in the visible region (473 nm) on excitation at 390 nm in aqueous medium at room temperature. We also discuss the unusual phenomenon of enhancement of this fluorescence intensity on addition of some transition metal ions ($3d^5$, $3d^{10}$, $4d^0$ and $3d^9$ electronic configurations).

Keywords. Zinc peroxy complex; terpyridine complexes; fluorescence enhancement.

1. Introduction

Transition metal complexes capable of interacting with DNA or its parent bases and nucleotides etc., have great potential applications in elucidating metal ion toxicity and carcinogenicity¹. Polypyridine ligands like 1,10-phenanthroline, 2,2',2''-terpyridine and their metal chelates are potential intercalating agents and have been studied extensively for their biological activity². Several investigations have been reported on the DNA nuclease activity of copper phenanthroline, and its use as a DNA sequencing probe for structure determination³. Zinc is an essential element for normal function of most organisms and is the main constituent in a number of metallo-enzyme proteins⁴. 2,2',2''-Terpyridine, its protonated derivatives and several inorganic/organic complexes are the subject of many investigations on their luminescence behaviour by a number of workers⁵. Surprisingly very meagre information is available in the literature on the luminescence behaviour of corresponding transition metal complexes⁶. The photo-physical/chemical studies of transition metal terpyridine complexes would be very interesting because of the potential ability of these complexes to undergo electron or energy transfer processes with other molecules. Recently, we reported⁷ the synthesis and characterisation of the title compound. In this communication, we discuss some novel and very interesting results on the fluorescence enhancement of the title compound, in aqueous medium, on addition of various transition metal ions that are known fluorescent quenchers.

*For correspondence

2. Experimental

All chemicals used were either of analytical reagent grade or the equivalent. CuSO_4 , ZnSO_4 , MnCl_2 , ammonium sulphate, ammonium molybdate were obtained from BDH and used as received. Nano pure water was used for making the solutions. Steady state fluorescence measurements were done using a Hitachi F-4010 spectrofluorimeter. Fluorescence lifetime measurements were carried out on a single-photon counting spectrophotometer model 199 (Edinburgh Instruments, UK). The excitation source was a gated hydrogen discharge lamp with a repetition rate of 30 kHz and FWHM ~ 1 ns. The nonlinear iterative least square fit method was used for analysing the observed fluorescence decay function $F(t)$ by the procedure known as iterative reconvolution⁸. Life-times were determined by taking into account the minimum reduced χ^2 values and the distribution of the weighted residuals.

The transition metal–mixed ligand complexes, viz. $[\text{Zn}(\text{L})(\text{O}_2)]\cdot\text{H}_2\text{O}$ and [1% Cu, 99% $\text{Zn}(\text{L})(\text{O}_2)]\cdot\text{H}_2\text{O}$, are designated compounds **1** and **2** respectively, L = 2,2',2''-terpyridine. The compounds were prepared by the reported method⁷. Aqueous solutions containing 1.0×10^{-4} mol dm^{-3} of the above compounds were used as such unless otherwise stated. Both absorption and emission studies were carried out in aerated aqueous solutions at ambient 295 K. It was observed that fluorescence yields were not affected in the presence of air.

3. Results and discussion

The absorption spectrum of **1** is shown in the insert of figure 1. The sharp increase in absorbance below 340 nm is ascribed to intraligand absorptions and the band observed in the 365–400 nm region to the interligand (peroxo)–terpyridine *c-t* band^{7,9}. When 1.0×10^{-4} mol dm^{-3} aqueous solution of **1** is subjected to excitation at 390 nm it exhibits a broad fluorescence peak in the visible region (400–600 nm) with maximum at 473 nm (figure 1). By comparing the emission and absorption spectra of **1** with that of known pure terpyridine^{5a,b}, it is clear that on complexation with Zn(II) ions the position of the emission peak changes substantially. This suggests that the red shift of about 80 nm may be due to the effect of Zn(II) (d^{10} electron core) on the transition band. The fluorescence lifetime of **1**, analysed using a single component decay is 6.5 ns ($\chi^2 = 1.169$). Also, on excitation of **1** (2.0×10^{-5} mol dm^{-3}) at the intraligand absorption band region (330 nm), a well-structured fluorescence peak is observed, without much Stoke's shift. The spectrum obtained is similar to that reported for free terpyridine ligand^{5a-c}. Thus, the observation of the structured fluorescence peak is due to intraligand absorption of the terpyridine ring and another broad fluorescence emission peak in the visible region is due to interligand absorption band transition from peroxo oxygen filled- p_p orbitals to low-lying vacant p^* orbitals of the N atom of terpyridine ligand through the Zn(II) ion⁹.

Not much is known about the fluorescence behaviour of Zn terpyridine complexes with counter ions like halides, nitrate, sulphate etc.^{10,6b}. However, on comparison with the fluorescence behaviour in the UV region of related bipyridine and phenanthroline Zn(II) chelates of halides, nitrates etc.¹¹, it appears that the presence of coordinated peroxo ion along with terpyridine in the mixed chelate has an effect on fluorescence behaviour, since on excitation at 390 nm **1** exhibits fluorescence in the visible region. This may be due to the strong terdentate chelating behaviour of terpyridine containing hard donor nitrogen and chelating bidentate peroxo oxygen ligand atoms on hard acid

Zn(II) ions (ZnN_3O_2 chromophore), compared to the bidentate chelating behaviour of bipyridine/phenanthroline ligand atoms and unidentate halides/nitrate ligands (ZnN_4X_2 chromophore).

To understand the influence of different transition metal ions on the fluorescence behaviour of **1**, both excitation and emission spectra of aqueous solution ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) of **1** were taken after addition of different concentrations of various metal ion solutions. The metal ion solutions used were of MnCl_2 ($3d^5$), CuSO_4 ($3d^9$), ammonium molybdate ($4d^0$), ZnSO_4 ($3d^{10}$) and $(\text{NH}_4)_2\text{SO}_4$. In each case an increase in intensity of the fluorescence peak at 473 nm was observed. It is important to mention that there was no significant change in the optical absorbance value at the excitation wavelength on addition of the different metal ion solutions. Also, the shape of the emission and excitation spectrum of **1**, both in the presence and absence of the other transition metal ions remained similar. Relative increases in the fluorescence of **1** at different metal ion concentrations are shown in table 1. However, no significant change was observed in the fluorescence life-time. Also, a 1% copper(II) doped zinc peroxo terpyridine, **2**, was synthesized⁷ to study the fluorescence behaviour of the doped compound, and interestingly the compound also showed enhancement of fluorescence intensity, similar to that when Cu(II) ion is added to **1**. The result is shown in figure 1.

The luminescence quantum yield of **1** increased on addition of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ammonium molybdate from 0.05 to 0.08. It was independent of excitation wavelength in the range 380 to 400 nm. Below 380 nm the absorbance of the compound shows a steep

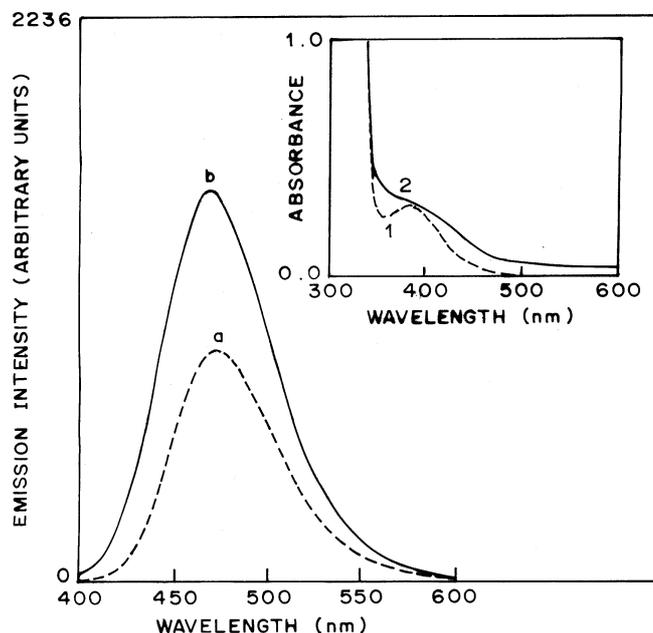


Figure 1. Emission spectrum of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ zinc peroxo terpyridine (a) and 1% Cu(II) doped zinc peroxo terpyridine (b) in aqueous solution. Excitation wavelength 390 nm. Insert: Absorption spectrum of (1) zinc peroxo terpyridine, and (2) 1% Cu(II) doped zinc peroxo terpyridine.

Table 1. Effect of various metal ion concentration on the fluorescence intensity of **1**

[M], mol dm ⁻³	<i>I/I</i> ₀ *				
	Zn ²⁺	Mn ²⁺	Ammonium molybdate	(NH ₄) ₂ SO ₄	Cu ²⁺
0.0	1.00	1.00	1.00	1.00	1.00
0.33 × 10 ⁻⁶	1.05	1.04	1.07	1.00	1.14
0.99 × 10 ⁻⁶	1.11	1.16	1.10	1.01	1.19
1.65 × 10 ⁻⁶	1.24	1.18	1.12	1.01	1.22
5.00 × 10 ⁻⁶			1.33		
1.00 × 10 ⁻⁵			1.35		
5.00 × 10 ⁻⁵			1.44		
1.00 × 10 ⁻⁴			1.69		

**I* and *I*₀ are fluorescence quantum yield in the presence and absence of added metal ion. Results are accurate within limits of ± 5%.

increase in optical density, hence it is not used for determining quantum yield. To the best of our knowledge, this is the first reported system in which fluorescence intensity enhancement (in the visible region) has been observed on addition of different transition metal ions (viz. ions of $3d^5$, $3d^{10}$, $3d^9$ and $4d^0$ electronic configuration) instead of expected quenching^{12,13}. Thus it is our considered view that although fluorescence enhancement (UV region) of organic systems like amides, cyptands etc. has been observed in the presence of some transition metal ions^{5d-f}, the fluorescence enhancement of an inorganic transition metal complex on addition of various transition metal ions in an aqueous medium and in the visible region was not reported earlier. It is also of interest to note the enhancement of fluorescence intensity of zinc complex, **1**, on addition of zinc (II) sulphate. To confirm whether the enhancement of fluorescence intensity on addition of ammonium molybdate is due to the presence of Mo(VI) or NH₄⁺ cation, (NH₄)₂SO₄ solution was added to **1** and no enhancement of intensity or quenching of fluorescence was observed, suggesting that the enhancement is due to Mo(VI) d^0 cation. It is known from specific conductivity measurements⁷ that **1** is not dissociated in aqueous solutions. The results obtained from the various experiments carried in this study viz. influence of various added metal ions on the fluorescence behaviour of **1**, even at concentrations in the region of 1.0×10^{-4} mol dm⁻³, corroborates the non-ionic nature of **1**. In case, **1** is dissociated in solution, the likely species being Zn²⁺, 2,2'2''-terpyridine, and OH⁻ ions or Zn(terp)²⁺, OH⁻ ions. Hence it is very unlikely to expect fluorescence emission at 473 nm and enhancement of fluorescence on addition of various transition metal ions because the fluorescence behaviour of pure terpyridine and related Zn(L)²⁺ complexes are known^{5,6,10}. Also, work done recently using pulse radiolysis confirms the non-dissociative behaviour of the complexes in aqueous buffered solutions¹⁴.

4. Conclusions

The results of our study significantly indicate the novel phenomena of enhancement of visible fluorescence on addition of some transition metal ions to the aqueous solution of zinc peroxo terpyridine, while the fluorescence emission of pure terpyridine solution or

the related $Zn(L)_x^{2+}X$ ($X = \text{halides, NO}_3^-$ etc.; $L = \text{phenanthroline, terpyridine}$) complex species is reported to be quenched^{5,6,10} by the addition of the corresponding metal ions. From the different molar concentrations of added metal ions and from the life time of visible fluorescence emission, it appears that fluorescence enhancement may be due to the ground state interaction (electrostatic) of the Zn complex with the added metal ions.

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