Investigations on the Rare Earth Terpyridyl System

III. Photoluminescence of Sm^{3+}, Dy^{3+} and Tm^{3+} Terpyridyl Chelates

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The room temperature luminescence spectra of the monoterpyridyl chelates of trivalent samarium, dysprosium and thulium have been studied in solid state by exciting with monochromatic radiation of 3200 Å. The spectra of these chelates show intra f → f fluorescent transitions of the chelated rare earth ions as well as the molecular band fluorescence. The "bottleneck" nature of the energy transfer from the nitrogen containing heterocyclic ligands to the coordinated rare earth ions is proposed. The fluorescence data of mono-terpyridyl chelates have been compared with those of bis-dipyridyl one.

The phosphorescence spectrum of terpyridyl has also been investigated. The lowest triplet state of the free ligand is found at 22 940 cm^{-1} above the ground level. The phosphorescence lifetime of terpyridyl is about 2 sec.

In part II of this series [1] we have discussed the indirect excitation of the 4f electronic levels of Eu^{3+} and Tb^{3+} ions in terpyridyl chelates via intramolecular energy transfer (IMET) process from the ligand to the coordinated rare earth ions. This communication extends the studies to the other rare earth ions Sm^{3+}, Dy^{3+} and Tm^{3+} coordinated to terpyridyl ligand. Previously, weak visible fluorescence has been observed from these ions in several chelates [2–7].

Results and Discussion

The results of fluorescence measurements of the solid chelates at room temperature are presented in Table 1. It is evident from the table that beside the intra f → f fluorescent transitions of the rare earth ions, some molecular emission bands are present. Eu^{3+} and Tb^{3+} chelates however showed [1] bright line emission only which are compatible with previous results of Crosby et al. [3, 5] on β-diketonate chelates.

Fluorescence Spectra of the Chelates

Sm^{3+} Chelate: The resonance level of Sm^{3+} ion ($4f^5$) lies [8] approximately 17 800 cm^{-1} above the ground state ($^6H_{5/2}$). This level has been identified [9] as $^4G_{5/2}$. The fluorescent transition $^4G_{5/2} \rightarrow {}^6H_{5/2}$ at 17 810 cm^{-1} has been observed in the mono-terpyridyl chelate. This value may be compared to that

Emission Band mμ	cm^{-1}	Assignment
$Sm(Terp)Cl_3 \cdot 2.5H_2O$		
467.5	21390	
490	20408	Sm^{3+} ion fluorescence ?
514.5	19436	organic fluorescence
543.5	18400	
561.5	17810	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
580	17241	
598	16722	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
601 Sh	16638	
630 ?	15873	
$Dy(Terp)(NO_3)_3 \cdot 2H_2O$		
479	20876	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
498	20080	organic fluorescence
511.5	19550	
517.5 Sh	19323	
526 Sh	19011	
542.5	18433	
574	17421	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
602.5 ?	16597	
697.5	14336	$^4F_{9/2} \rightarrow {}^6H_{11/2}$
$Tm(Terp)(NO_3)_3 \cdot H_2O$		
472.5 Sh	21164	$^1G_4 \rightarrow {}^3H_6$
480	20833	
512.5	19512	organic fluorescence
530 Sh	18868	
578	17300	
728.5	13726	$^1G_4 \rightarrow {}^3H_5$
750	13333	
776	12886	$^3F_4 \rightarrow {}^3H_6$

Table 1. Details of the Emission Spectra of Sm^{3+}-, Dy^{3+}- and Tm^{3+}-Terpyridyl Chelates at Room Temperature.

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[1] S. P. Sinha, Z. Naturforschg. **20 a**, 164 [1965].

[2] N. Filipescu, M. R. Kagan, N. McAvoy, and F. A. Serafin, Nature (London) **196**, 467 [1962].

[3] R. E. Whan and G. A. Crosby, J. Mol. Spectr. **8**, 315 [1962].

[4] G. A. Crosby and R. E. Whan, J. Chem. Phys. **36**, 863 [1962].

[5] G. A. Crosby, R. E. Whan, and J. J. Freeman, J. Phys. Chem. **66**, 2493 [1963].

[6] J. J. Freeman and G. A. Crosby, J. Phys. Chem. **67**, 2717 [1963].

[7] S. P. Sinha, C. K. Jørgensen, and R. Pappalardo, Z. Naturforschg. **19 a**, 434 [1964].

[8] H. Lammermann, Z. Phys. **150**, 551 [1958].

[9] M. S. Magno and G. H. Dieke, J. Chem. Phys. **37**, 2354 [1962]; see also reference [12].

of the bis-dipyridyl chelate[7] at 17 790 cm^{-1}. The $^6H_{7/2}$ level of Sm^{3+} ion is roughly 1100 cm^{-1} above the ground level and the transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 16 722 cm^{-1} (Table 1) places the $^6H_{7/2}$ level about 1088 cm^{-1} above the ground level in good agreement with the values of MAGNO and DIEKE[9]. The same transition in the bis-dipyridyl chelate occurs at 16 690 cm^{-1}. These values indicate a very slight red shift for the dipyridyl chelate compared to the terpyridyl one. This red shift in case of bis-dipyridyl chelate is possibly due to the effect of four nitrogen atoms in the coordination sphere of samarium in contrast to the chelate ring formed by the three nitrogen atoms in mono-terpyridyl complex.

It is debatable whether the observed band (Table 1) around 20 000 cm^{-1} is due to a samarium fluorescent transition, but it seems possible that the band group near 19 000 cm^{-1} for these chelates is due to molecular band fluorescence from the organic moiety. From the studies of absorption and fluorescence spectra of $SmCl_3$ MAGNO and DIEKE[9] have assigned the lines at 20 000, 18 857 and 17 800 cm^{-1} to $^4G_{7/2}$, $^4F_{3/2}$ and $^4G_{5/2}$ levels respectively. Several fluorescent lines at 645 mμ (15 504 cm^{-1}), 598 mμ (16 722 cm^{-1}) and 562 mμ (17 794 cm^{-1}) both at room temperature and 77 °K in case of samarium-tris-(4,4,4-trifluoro-1,2-thienyl-1,3-butanedione) have been reported[2]. In the present case observations around 650 mμ became complicated (as explained in the experimental section) and the transition at 630 mμ (15 873 cm^{-1}) may contain fluorescence originating from the chelated samarium beside the main contribution from the excitation source.

Dy^{3+} Chelate: The ground state ($^6H_{15/2}$) of Dy^{3+} ion ($4f^9$) belongs to the inverted ^6H multiplet. From the absorption and fluorescence spectra of dysprosium ion DIEKE and SINGH[10] have assigned the line at 20 958 cm^{-1} as the resonance line and belonging to $^6F_{11/2}$ level. However, JØRGENSEN[11] has considered the band group between 23 400 and 21 100 cm^{-1} as due to ^4M. The argument of DIEKE and SINGH is that the transition observed by them is not so weak as one may expect from a quartet to sextet transition. The calculations of WYBOURNE[12] show 62% quartet character for the 20 963 cm^{-1} line and that it belongs to ^4F (not M) having $J = 9/2$. We also tend to believe that the observed transition at 20 876 cm^{-1} (Table 1) for mono-terpyridyl chelate is due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$. The other two bands at 17 420 and 14 336 cm^{-1} may be assigned to the transitions terminating at $^6H_{13/2}$ and $^6H_{11/2}$ respectively. The $^6H_{11/2}$ transition although quite weak appears in the mono-terpyridyl chelate, whereas absent in bis-dipyridyl complex, probably due to change in transition possibility.

Tm^{3+} Chelate: According to CROSBY and WHAN[4] trivalent thulium ($4f^{12}$) has two resonance levels, $^1G_4$ and $^3F_4$, from where fluorescent transitions can take place. They have also demonstrated selective excitation of the Tm^{3+} levels via IMET process in tris-benzoylacetonate and in tris-dibenzoylmethide chelates. From Table 1 it will be seen that the mono-terpyridyl chelate shows fluorescent transitions from both resonance levels. However, the fluorescence from $^3F_4$ level is very weak. No visible fluorescence has been observed from the bis-dipyridyl chelate.

Comments on the Phosphorescence Spectrum of Terpyridyl

The maxima of the phosphorescence bands of terpyridyl in 3-methyl pentane at 77 °K are listed in Table 2. The phosphorescence spectrum is also taken in alcoholic (3 : 1 ethanol-methanol) solvent, where the same peaks are observed. The peaks in alcoholic solvent are not so sharp as in 3-methyl pentane (the sharpening of the structure is a property of this solvent) and a very slight blue shift

Wave-length Å	Wave-number cm^{-1}	Δ cm^{-1}	Assignment
4359	22940	0	$0 \rightarrow 0$
4400	22727	213	
4482	22310	630	655[a]
4537	22040	900	830
4611	21684	1256	1262
4669	21417	1523	1560
4746	21070	1870	1262+655
4820	20746	2194	1262+830 or 1560+655
4886	20466	2474	
4961 ?	20356	2584	
5060	19762	3178	2×1560
5152	19410	3530	
5236	19098	3842	
5300	18868	4072	

[a] Measured with a Perkin Elmer 337 grating spectrophotometer in KBr pellet. The vibrational spectrum is given in ref. [13].

Table 2. Details of the Phosphorescence Spectrum of 2,2′,2″-terpyridyl in 3-methyl pentane at 77 °K.

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[10] G. H. DIEKE and S. SINGH, J. Opt. Soc. Amer. **46**, 495 [1956].

[11] C. K. JØRGENSEN, Acta Chem. Scand. **11**, 1981 [1957].

[12] B. G. WYBOURNE, J. Chem. Phys. **36**, 2301 [1962].

is observed for the higher wavelength bands in alcoholic solvent compared to the hydrocarbon one.

The shortest wavelength phosphorescence band is assumed to be the 0 → 0 transition. This places the lowest triplet level at 22 940 cm^{-1} above the ground state. Table 2 gives the vibrational spacings of terpyridyl and they are compared with the previously observed [13] vibrational spectrum of the ligand. The phosphorescence lifetime for terpyridyl is approximately 2 sec.

A red shift of $\sim 230\ \text{cm}^{-1}$ (22 940 cm^{-1} to 22 710 cm^{-1}) for the 0 → 0 transition band of terpyridyl has been observed by adding three drops of concentrated H_2SO_4 to the original alcoholic solution of terpyridyl. The exact nature of the protonated species is unknown but from the absorption spectrum it appears [14] that mostly the doubly protonated species $[\text{Terp}\ H_2]^{2+}$ is present [15].

The data of part II and the present study place the so called CROSBY's *triplet state energy level* for terpyridyl chelates at $\sim 21\,200\ \text{cm}^{-1}$. The value for dipyridyl chelates [7] is $\sim 20\,800\ \text{cm}^{-1}$. The luminescence yield for the complexes studied here is low and the emissions originating from the triplet state of the complexes and that from the 4f electronic levels of Sm^{3+}, Dy^{3+} and Tm^{3+} ions are present. Although no detailed temperature dependence studies have been carried out, the preliminary results and comparison with the similar dipyridyl chelates suggest the "bottleneck" nature of the energy transfer from the nitrogen containing heterocyclic ligands to the resonance level of the rare earth ions.

Experimental

The chelates were prepared by the usual method as has been described previously [13].

Fluorescence and Phosphorescence measurements: The solid chelates have been finely ground and enough sample has been placed to fill the 0.2 mm groove of a sandwich cell (106-QS). An Aminco-Bowman spectrophotofluorometer has been used to record the emission spectra of the solid chelates at room temperature. Excitation radiation was obtained from the Xenon lamp of the instrument and 3200 Å monochromatic light was chosen for excitation of the chelates. Two entrance slits of 1 mm were used for excitation monochrometer. Various arrangements of recorder sensitivity and the rotary turret for slit control for the photomultiplier tube were used and they were so adjusted as to record the weak lines when needed. The maximum phototube response was in the region of 6500 Å and the second order contribution from the excitation radiation around 6400 Å strongly hindered observations of fluorescence lines in this region (for example the transition to $^3H_4$ of Tm^{3+} around 15 000 cm^{-1}).

The phosphorescence spectra of terpyridyl under various environments at 77 °K were kindly measured by Dr. J. S. BRINEN of the Central Research Division of American Cyanamid Company. The experimental procedure will be reported soon [16].

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[13] S. P. SINHA, Z. Naturforschg. **20 a,** 552 [1965].

[14] R. B. MARTIN and J. A. LISSFELT, J. Amer. Chem. Soc. **78,** 938 [1956].

[15] The molar extinction coefficient (ε) is 1.9×10^4 at 289 mμ agreeing well with the ε value of the diprotonated species reported in ref. [14]. The characteristic splitting of this band is also observed.

[16] J. S. BRINEN, F. HALVERSON and J. R. LETO, to be published.