Nachzündrate läßt sich aus der Formel (11) erkennen, daß C_n mit zunehmender Temperatur abnimmt. Die physikalische Ursache dafür ist, daß bei hoher Temperatur die Haftstellen so schnell entleert werden, daß während der Entleerungszeit P_l noch klein ist. Denselben Effekt kann man auch durch eine Vergrößerung von RC in Beziehung (11) erreichen, was experimentell hier gefunden werden konnte. Daher kann man nun zwei wichtige Parameter des Strahlenschadens mit Hilfe von Gl. (11) ermitteln: die Dichte der Haftstellen (über N_t) und ihre energetische Lage E_t (über w). Um die energetische Lage der Haftstellenniveaus ermitteln zu können, muß w in Abhängigkeit von der Temperatur T gemessen werden. Dazu kann man folgenden Weg einschlagen: Zunächst wird bei jeder Temperatur ein festes ΔU eingestellt[9]. Wenn durch jeweilige Änderung des Schaltungsparameters C ein festes C_n eingestellt wird, so gilt

$$w\,R\,C = \text{const}\,.$$

Trägt man nun RC als $f(T)$ auf, so erhält man $w(T)$ und damit aus der Neigung der Kurve (in der logarithmischen Darstellung über $1/T$ aufgetragen) gemäß Gl. (4) die energetische Lage der Haftstellen. Es werden zur Zeit Experimente unternommen, um mittels dieser Methode die Haftstellen in bestrahlten und unbestrahlten Si- und GaAs-Dioden[10] zu ermitteln.

Herrn Professor Dr. M. Knoll danken wir für fördernde Unterstützung, dem Bundesministerium für wissenschaftliche Forschung für finanzielle Hilfe.

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[9] Um eine eventuelle Änderung von R_{iMP} mit der Temperatur aufzufangen, kann mit dem variablen R_L ein festes U_p eingestellt werden.

[10] G. Keil u. I. Ruge, J. Appl. Phys., erscheint demnächst.

Investigations on the Rare Earth Terpyridyl System

1. Preparation and Spectroscopic Studies of the Terpyridyl Complexes of Lighter Lanthanides

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Rare earth-mono-terpyridyl complexes of the type $\mathrm{M(Terp)Cl_3 \cdot}\,n\,\mathrm{H_2O}$ ($\mathrm{M=Ce-Gd}$, Terp = terpyridyl and $n = 1-2.5$) have been prepared and their ultraviolet, visible and infrared spectra have been investigated. Probable assignments of the excited levels of the tripositive rare earths to the observed bands are given. The $\mathrm{f \rightarrow f}$ transitions of the rare earths show red shift in the methanolic solution of the chelates with respect to the aquo ions. Definite indications of $\mathrm{4f \rightarrow 5d}$ transition of the Ce(III) and electron transfer band from the highest filled M.O. of the ligand to the partly filled 4f shell of Eu(III) and possibility of the same in case of Pr(III), Nd(III) and Sm(III) have been obtained. The infrared studies of the solid chelates strongly suggest the coordinated nature of the terpyridyl molecule. Some infrared bands of the chelates show shift towards higher wavenumber and lowering of intensities compared to the free ligand. Of particular interest is the pyridine ring breathing vibration of terpyridyl at 988 $\mathrm{cm^{-1}}$ which shows a shift of $\sim 25\ \mathrm{cm^{-1}}$ in the chelates. The out-of-plane inphase C—H deformation band at 830 $\mathrm{cm^{-1}}$ of terpyridyl shows considerable decrease of intensity in the chelates.

Rare earths belonging to class (a) of Ahrland, Chatt, and Davies[1] classification show rather greater affinity towards ligands containing oxygen atoms than for example nitrogen atoms as coordination centers, and not until recently have the complexes with ligands containing nitrogens as donors[2-4] been demonstrated. In aqueous solution the strongly hydrated rare earth ions [$\mathrm{M(OH_2)}_x^{3+}$ where x is larger than six] have a tendency to precipitate as highly insoluble hydroxides on addition of amines or nitrogen containing ligands. Following the original suggestion of Grinberg[5], that the less basic

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[5] A. A. Grinberg, An Introduction to the Chemistry of Complex Compound (Engl. Transl.), Pergamon Press, Oxford 1962, pp. 325—327.

ligands may help the formation of rare earth-nitrogen bonds, KONONENKO and POLUEKTOV [2] were the first to demonstrate the formation of 1,10-phenanthroline complexes of some rare earths even in aqueous solution, proving that in the competition between the aquated rare earth ion and the chelated species, the chelation took place in preference to the formation of hydroxo-complexes. One might of course assume that the removal of the aqueous phase by an anhydrous organic medium may help the formation of complexes, and actually the isolation of both hydrated and anhydrous phenanthroline-complexes [3] from absolute ethanol has established this view point.

Emboldened by our previous work on bis-dipyridyl complexes of rare earths [4] we moved to the higher homologue of dipyridyl, i. e. 2,2′,2″-terpyridyl for several reasons: (a) It was interesting to know whether or not we can generalize our previous method [4] of preparation, (b) if the $=\mathrm{N}\diagup^{\mathrm{C}-\mathrm{C}}\diagdown\mathrm{N}=$ group has anything to do with the stability of the complexes, then the availability of

$$\mathrm{N-C-C-N-C-C-N}$$

grouping which may coordinate three positions at a time may be still more favourable and (c) above all to study the spectroscopic behaviour of these new types of complexes. These complexes being soluble in methanol facilitate the investigation of the absorption spectra.

Systematic studies of the absorption and fluorescence spectra [6] of rare earth-terpyridyl systems are underway and in the present paper we report the isolation of the solid terpyridyl complexes of cerium through gadolinium (except promethium) and the studies on the ultraviolet, visible and infrared absorption spectra with their special features.

Experimental

Preparation of the complexes

The mono-terpyridyl-rare earth(III) complexes were isolated from absolute ethanol (commercially available) medium as solids by adding 2,2′,2″-terpyridyl (abbreviated hereafter as Terp and obtained from Fluka A.G., Switzerland) dissolved in a minimum volume of ethanol to a warm solution of hydrated rare earth (Ce – Gd) chlorides also in ethanol, in a mole ratio of 1 : 1 and refluxing the mixture for about ten minutes. After the reaction was over the mixture was cooled and the solids separated were washed with small portions of hot ethanol and dried in a vacuum desiccator for a few days.

The attempts to prepare the bis-terpyridyl complexes by adding two equivalents of the ligand per mole of rare earth chloride resulted in the mono-complex except in case of Eu(III). It is really remarkable that only Eu(III) formed the bis-complex directly.

The results of microanalysis are: Calculated for $\mathrm{Ce(C_{15}H_{11}N_3)Cl_3 \cdot H_2O}$: C, 36.19; H, 2.63; Cl, 21.37; N, 8.44. Found: C, 35.76; H, 2.63; Cl, 22.0; N, 8.29. Calcd. for [7] $\mathrm{Pr(C_{15}H_{11}N_3)Cl_3 \cdot 2\,H_2O}$: $\mathrm{H_20}$, 6.97; anhydrous sample requires C, 37.48; H, 2.31; Cl, 22.13; N, 8.74. Found $\mathrm{H_2O}$, 6.10; C, 36.03; H, 3.0; Cl, 18.2; N, 7.73. Calcd. for [7] $\mathrm{Nd(C_{15}H_{11}N_3)Cl_3 \cdot 1.5\,H_2O}$: $\mathrm{H_2O}$, 5.29; anhydrous sample requires C, 37.22; H, 2.29; Cl, 21.98; N, 8.68. Found: $\mathrm{H_2O}$, 5.62; C, 35.08; H, 2.98; Cl, 18.31; N, 7.06. Calcd. for [7] $\mathrm{Sm(C_{15}H_{11}N_3)Cl_3 \cdot 2.5\,H_2O}$: $\mathrm{H_2O}$, 8.11; anhydrous sample requires C, 36.76; H, 2.26; Cl, 21.70; N, 8.57. Found: $\mathrm{H_2O}$, 7.95; C, 36.58; H, 2.76; Cl, 20.60; N, 8.17. Calcd. for $\mathrm{Eu(C_{15}H_{11}N_3)Cl_3 \cdot H_2O}$: C, 35.35; H, 2.57; Cl, 20.87; N, 8.25. Found: C, 35.44; H, 3.1; Cl, 20.87; N, 8.11. Calcd. for $\mathrm{Eu(C_{30}H_{22}N_6)Cl_3 \cdot 4\,H_2O}$: C, 45.21; H, 3.79; Cl, 13.34; N, 10.54. Found: C, 45.54; H, 3.95; Cl, 13.17; N, 10.72. $\mathrm{Gd(C_{15}H_{11}N_3)Cl_3 \cdot 2\,H_2O}$: C, 33.83; H, 2.84; Cl, 19.97; N, 7.89. Found: C, 34.38; H, 3.04; Cl, 19.12; N, 7.40.

The rare earth terpyridyl complexes are quite stable in dry air. The noteworthy aspect is the marked change of colour for certain complexes with respect to the salts used:

Thus $\mathrm{Ce(Terp)Cl_3 \cdot H_2O}$ is sulfur yellow, $\mathrm{Nd(Terp)Cl_3 \cdot 1.5\,H_2O}$ is ash yellow, $\mathrm{Sm(Terp)Cl_3 \cdot 2.5\,H_2O}$ is yellow, $\mathrm{Eu(Terp)Cl_3 \cdot H_2O}$ is yellow, $\mathrm{Eu(Terp)_2Cl_3 \cdot 4\,H_2O}$ is light straw yellow and $\mathrm{Gd(Terp)Cl_3 \cdot 2\,H_2O}$ is slight yellow. $\mathrm{Pr(Terp)Cl_3 \cdot 2\,H_2O}$ preserved the light green colour of the Pr(III) ion. These complexes are soluble in methanol and a concentration of 5×10^{-2} M is easily reached.

Measurement of the spectra

The ultraviolet, visible and near infrared spectra of freshly prepared methanolic solutions of all complexes and terpyridyl were recorded with a Cary 14 recording spectrophotometer using methanol as blank. In some cases the difference spectra were obtained by careful compensation of the ligand absorption using methanolic solution of terpyridyl as reference. The solid state infrared spectra between 4000 $\mathrm{cm^{-1}}$ to 700 $\mathrm{cm^{-1}}$ were obtained with a Perkin Elmer 221

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[6] Part II and III. Part II on the fluorescence spectra of Eu(III) and Tb(III) terpyridyl chelates were presented at the Conference of Luminscence, University of Hull, England, September 1964. – Z. Naturforschg. **20 a**, 164 [1965].

[7] To check, some results were obtained on anhydrous samples after determining the water content.

Heptane			Carbon tetrachloride			Dioxane			Methanol		
mμ	cm^{-1}	$\varepsilon \times 10^{-2}$	mμ	cm^{-1}	$\varepsilon \times 10^{-2}$	mμ	cm^{-1}	$\varepsilon \times 10^{-2}$	mμ	cm^{-1}	$\varepsilon \times 10^{-2}$
234.7	42610	225				235.8	42410	240	232.3	43040	225
246 sh	40650					249 sh	40160		246 sh	40650	
251 sh	39840										
276.5	36170	205	278.2	35950	221	277.3	36060	227	277 sh	36100	
									281.2	35560	207
300 sh	33333		302 sh	33110		301 sh	33222		301 sh	33222	
312 sh	32050		313 sh	31950		314 sh	31840		334 sh	29940	
382 sh	26180		386 sh	25900		382 sh	26150		397 sh	25160	~ 0.13
406.5	24600	~ 0.1	406.5	24600	~ 0.1	405 sh	24690				

Table 1. Absorption Spectrum of Terpyridyl in different Solvents.

Terpyridyl	Rare earth-mono-terpyridyl complexes					
	Ce (III)	Pr (III)	Nd (III)	Sm (III)	Eu (III)	Gd (III)
43.04		43.05	43.14	42.94	42.77 [a]	42.72
40.65 (sh)		40.00 (sh)				
36.10 (sh) $\pi \to \pi^*$		36.18	36.14	36.09	35.99 [a]	35.93
35.56		35.39	35.35	35.10	34.93 [a]	35.27
33.21 (sh)		33.16 (sh)	33.33 (sh)	33.33 (sh)	33.21 (sh [a])	
		31.84 (sh)	31.64 (sh)			
29.94 (?)		29.96	29.96	29.93	29.88 [a]	29.88
			26.17			
			25.98 ct (?)	25.99 ct (?)		
25.16 (sh)		25.87 (sh) ct (?)	25.76			
	24.93 ct		23.32 $^2P_{1/2}$	24.78 ^6P	25.41 [a] $^5L_7$	~ 24.89
	(4f → 5d)	22.37 $^3P_2$	23.26		25.34	(Ligand absorp.)
		22.19 (sh)	21.66 $^4G_{11/2}$	21.65	25.39 [b]	
		21.17 $^3P_1$	21.25 $^2D_{3/2}$	21.57	24.46 [b] ct	
			20.99 $^4G_{9/2}$		24.35 [a]	
		20.68 (sh)		20.94		
			19.49 $^2G_{9/2}$		21.55 [a]	
		20.61 $^3P_0$			21.52 [a, b] $^5D_2$	
		20.51 (sh)	19.15 (sh)	10.52 $^6F_{11/2}$		
			19.06 $^4G_{7/2}$			
			19.03 (sh)	9.19 $^6F_{9/2}$		
		16.81 $^1D_2$	18.99 $^2K_{13/2}$	9.03 (sh)		
			18.95 (sh)			
			17.37 (sh)			
			17.26 (sh)			
			17.19 $^2G_{7/2}$			
			17.13 $^4G_{5/2}$			
			16.85 (sh)			
			16.62 (sh) $^2H_{11/2}$			
			14.68 $^4F_{9/2}$			
			13.56 (sh)			
			13.49 $^4S_{3/2}$			
			13.37 $^4F_{7/2}$			
			13.29 (sh)			
			12.46 $^4F_{5/2}$			
			12.43 $^2H_{9/2}$			
			11.50 $^4F_{3/2}$			
			11.45 (sh)			

Table 2. Observed bands of terpyridyl and its complexes in methanol with probable assignments (wavenumber unit is kK. 1 kK = 1000 cm^{-1}, sh = shoulder, ct = charge transfer band).

[a] The bands are observed in case of $Eu(Terp)_2Cl_3 \cdot 4\,H_2O$. [b] The bands are observed in case of $Eu(Terp)Cl_3 \cdot H_2O$.

spectrophotometer using KBr pellet technique. Halide exchange may occur during pelleting. The unit of wavenumber for ultraviolet, visible and near infrared regions is kK (kiloKayser) = 1000 cm^{-1} and for the infrared region the usual cm^{-1}.

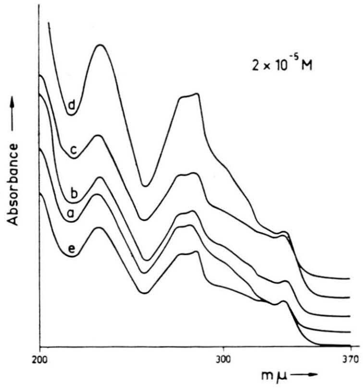

Fig. 1. Ultraviolet spectra of some rare earth terpyridyl complexes in methanol. a) Pr(Terp)$Cl_3 \cdot 2\ H_2O$, b) Nd(Terp)$Cl_3 \cdot 1.5\ H_2O$, c) Sm(Terp)$Cl_3 \cdot 2.5\ H_2O$, d) Eu(Terp)$_2Cl_3 \cdot 4\ H_2O$, and e) Gd(Terp)$Cl_3 \cdot 2\ H_2O$. For better representation the curves are placed one after another and the absorption scale has no meaning.

Results

The ultraviolet and visible spectra of terpyridyl (Terp) in different solvents have been investigated and the positions of the bands are tabulated in Table 1. The spectra of methanolic solutions of the mono terpyridyl rare earth chloride hydrate complexes are presented in Figs. 1 and 2 and the results with probable assignments are given in Table 2. We have tried to extract the electron transfer bands in case of

[Ce(Terp)]$^{3+}$, [Eu(Terp)]$^{3+}$ and [Eu(Terp)$_2$]$^{3+}$ by obtaining difference spectra with careful com-

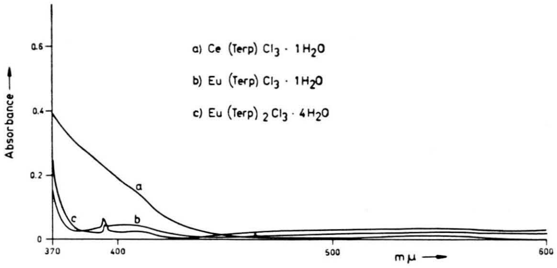

Fig. 3. Difference spectra of a) Ce(Terp)$Cl_3 \cdot H_2O$, b) Eu(Terp)$Cl_3 \cdot H_2O$, and d) Eu(Terp)$_2Cl_3 \cdot 4\ H_2O$.

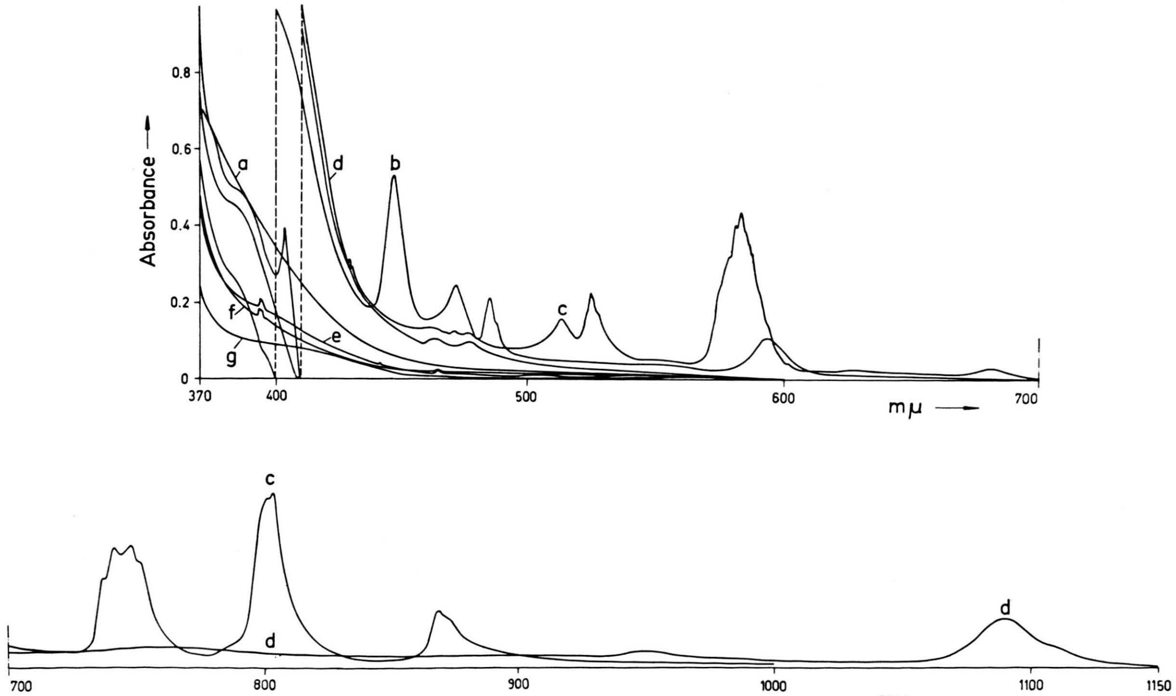

Fig. 2. Visible and near infrared spectra of the rare earth terpyridyl complexes in methanol. a) Ce(Terp)$Cl_3 \cdot H_2O$, b) Pr(Terp)$Cl_3 \cdot 2\ H_2O$, c) Nd(Terp)$Cl_3 \cdot 1.5\ H_2O$, d) Sm(Terp)$Cl_3 \cdot 2.5\ H_2O$, e) Eu(Terp)$Cl_3 \cdot H_2O$, f) Eu(Terp)$_2Cl_3 \cdot 4\ H_2O$, and g) Gd(Terp)$Cl_3 \cdot 2\ H_2O$.

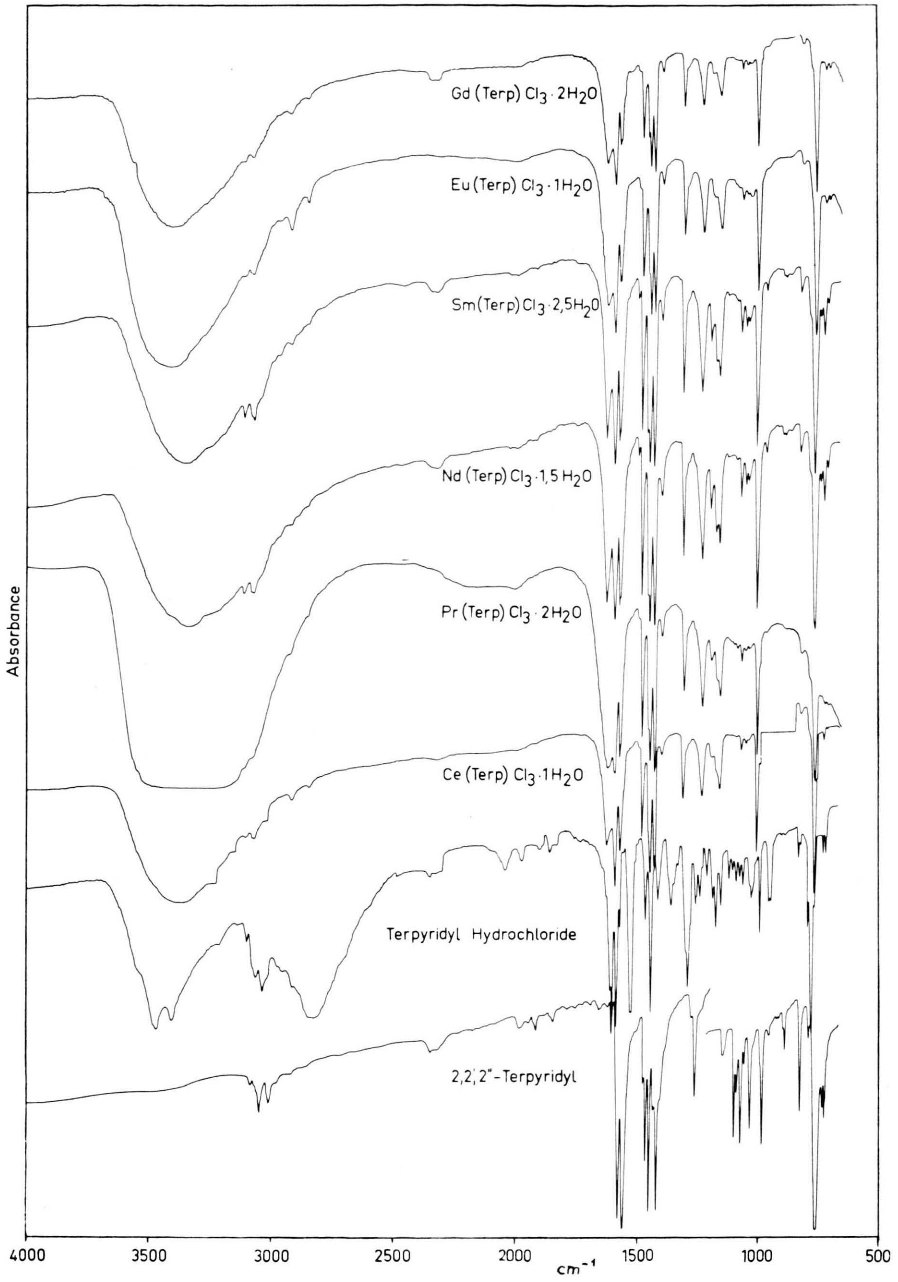

Fig. 4. Infrared spectra of terpyridyl, terpyridyl hydrochloride and the rare earth terpyridyl complexes in solid state.

pensation of terpyridyl absorption and these are presented in Fig. 3.

Because of the relatively small changes in the ultraviolet spectrum of the ligand on complex formation we have examined the vibrational spectra of terpyridyl and its rare earth complexes in the region 4000 – 700 cm^{-1}. Fig. 4 represents the corresponding infrared spectra and possible assignments of the bands are given in Table 3. A comparison of the spectrum of terpyridyl with those of its complexes shows that considerable changes have occured due to complex formation, although the spectra of the complexes are very similar to one another. A new band around 1310 cm^{-1} appeared in the spectra of all

Terpyridyl	(Terp)H_3^{3+}	Rare earth-mono-terpyridyl complexes						
		Ce (III)	Pr (III)	Nd (III)	Sm (III)	Eu (III)	Gd (III)	assignments
	3478	~ 3385	~ 3350 vb	~ 3345	~ 3355	~ 3408	~ 3405	O−H stretching of H_2O
	3410							
3082	3108							C−H stretching of pyridine ring
3045	3068	~ 3080	?	~ 3115	~ 3115			
3010	3040			~ 3075	~ 3075	~ 3078	~ 3080	
	~2830							N−H stretching
	2045							
1985								
1910	1978							
1850	1865							
	1620	1640	1635	1637	1635	1638	1635	H−O−H bending
1610	1612							
1580	1592	1602	1600	1600	1600	1606	1600	terpyridyl bands (C=C and C=N)
1560	1575	1585	1582	1583	1582	1586	1580	
	1535							pyridinium ion
	1530							
1478		1500 sh (?)	1500 sh (?)	~ 1504	~ 1504	1500 sh(?)	1500 sh(?)	terpyridyl band (C=C and C=N)
1468	1470	1492	1490	1490	1490	1490	1487	
1452	1450	1460	1455	1458	1457	1458	1455	
1435		1442	1440	1440	1440	1440	1438	
1422	1420	1410	1407	1407	1406	1408	1405	
	1365	1325	1317	1320	1318	1320	1316	ring vibration and ortho substituted pyridine vibration
1280	1300	1245	1240	1240	1242	1242	1240	
1262	1265							
	1250							
	1220							
	1198	1210 sh	1205	1207	1207	1198 sh	1200 sh	
	1180	1175	1180 sh	1185	1185 sh			
1150	1162		1167	1170	1170	1168	1166	ring vibration and C−H deformation
	1130							
	1115							
1092	1100							
1078	1088	1085 w	1080 w	1080	1080	1080 w	1080 w	
1060	1070			1060	1060			
1038	1038			1050	1050			
988	1000	1020	1015	1015	1016	1018	1015	pyridine ring breathing
	960			975 (?)	975			
	952							
890								three adjacent ring hydrogen
830	840	840 w	835 w	835	835	830	830	
792	800							two groups of four adjacent ring hydrogen
760	788	780	775	775	775	776	775	
735	740	740	735 w	735	736	738 w	735 w	
728	728							

vb = very broad, sh = shoulder, w = weak

Table 3. Infrared frequencies of terpyridyl and its rare earth complexes in cm^{-1}.

complexes. The band groups in the region between 1100 and 1030 cm^{-1} show decrease in intensities compared to the ligand, and the ring breathing vibration at 990 cm^{-1} of terpyridyl is shifted towards higher wavenumber in the rare earth complexes.

Discussion

The solvent effect on the absorption spectrum of terpyridyl is apparent from Table 1. The 42.6 kK band of terpyridyl in heptane shows a blue shift (43.0 kK) in methanol. A splitting of 36.1 kK band is observed in methanol solution. These bands are attributed to the $\pi \rightarrow \pi^*$ transition in terpyridyl. Slight change in position for 43 kK band is noticable (Table 2) during complex formation although greater splittings of the 36.10 kK band have been observed for rare earth complexes. In the near ultraviolet region prominent shoulders at about 26 kK and 24.6 kK (peak in case of heptane solution) are observed for terpyridyl in heptane, carbon tetrachloride and dioxane solutions whereas in methanol solution only one shoulder at 25.16 kK shows up (Table 1).

The 4 f^n Transitions

Due to the presence of the incomplete 4 f shells, rare earths show bands originating from the internal transition of the 4 f electrons and particularly Pr(III), Nd(III) and Sm(III) are rich in bands in the visible and near infrared region. Due to complexation these bands show slight red shift, the nephelauxetic effect [8]. In this study particular attention has been directed to the transitions of Pr(III) and Nd(III) complexes. Very minute solvent effect has been reported [9] for $PrCl_3$ by replacing methanol for water and it was concluded that the LANDÉ factor is fairly constant and very close to the theoretical value, whereas the spectrum of U(IV), having 5 f^2 configuration shows marked dependance on the ligands. The visible spectrum of $[Pr(Terp)]^{3+}$ in methanol exhibited red shift with respect to aquo ion for the band groups $^3P_2$, $^3P_1$ and $^3P_0$ with some splitting, but $^1D_2$ band at 16.8 kK remained virtually unaffected.

A blue shift has been observed for $^2P_{1/2}$ band of Nd(III) in case of $[Nd(Terp)]^{3+}$ complex (23.32 kK) compared to $NdCl_3$ in methanol (23.27 kK), but both of them showed red shift with respect to aquo ion (23.40 kK). It is worth noting that the $^2P_{1/2}$ band shows some structures, even in case of $NdCl_3$ in methanol; this was previously observed [10] in the reflection spectra of Nd-bis-dipyridyl chloride and Nd-bis-(4,4'-dimethyl-2,2'-dipyridyl) chloride although no splitting is expected due to KRAMERS degeneracy [11]. The conspicuous splitting of $^4F_{7/2}$ band (13 kK) into four distinct components, arising from the crystal field (n = no. of sublevels $= J + \frac{1}{2}$ for odd electrons) suggests a low symmetry for the complex species. The same type of splitting was not observed in the case of $NdCl_3 \cdot 6\,H_2O$ in methanol.

The band groups in the near infrared and visible region show red shift for the complex with respect to the aquo ion [10].

The ^6P level of Sm(III) appears as a sharp peak at 24.78 kK in the spectrum of $[Sm(Terp)]^{3+}$ complex. The other band groups in the visible and in the near infrared do not show any particular trend.

The $^5L_7$ band [12] of Eu(III) can be seen as a small but sharp peak at 25·4 kK above the electron transfer band in the Eu(III)-mono-terpyridyl complex and as a structured peak (25.41 and 25.34 kK) in the Eu(III)-bis-terpyridyl complex (Figs. 2 and 3). The other transition of $^5D_2$ level, though very weak, is recognizable in both spectra.

The Electron Transfer Bands

The electron transfer bands in rare earths are not very common as these elements have very little tendency to be oxidized to +4 state or reduced to +2 state and were not reported until 1962 when JØRGENSEN [13] identified the moderately strong, very broad absorption bands of ethanolic solutions of lanthanide bromides and dialkyldithiocarbamate complexes (rather unstable) as electron transfer bands. The sulfur yellow colour of $[Ce(Terp)]^{3+}$ suggests a 4 f → 5 d transition in Ce(III). The methanolic solution of $[Ce(Terp)]^{3+}$ showed continuous strong absorption from 22 kK towards the ultraviolet. But fortunately in the difference spectrum (Fig. 3) of $[Ce(Terp)]^{3+}$ a broad band ~24.93 kK

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(401 mμ) having ε value approximately 17.5 showed up, which we assign to the 4 f$\rightarrow$5 d transition of Ce(III). Ce(III) has no strong absorption in this region. The above ε value agrees well when one substracts the ε value of terpyridyl ligand ($\sim$12) from the actual ε value of the cerium complex ($\sim$30) as obtained from the absorption spectrum in Fig. 2 at the wavelength in question.

In the case of Gd(III) chelate (where no electron transfer band is expected) the ε values are roughly the same as for the free ligand and a difference spectrum hardly shows any absorption in the near ultraviolet and visible region indicating that the extinction coefficients for terpyridyl when acting as a ligand and when dissolved in methanol are the same.

Extremely interesting is the situation of the narrow $^5L_7$ peak of Eu(III) at 25.39 kK ($\varepsilon \approx 3$) above the electron transfer band (24.46 kK $\varepsilon \approx 3$, $\delta(-) \approx 0.93$ kK) which was observed in the difference spectra of $[Eu(Terp)]^{3+}$. Jørgensen [13] reports the intensification of the $^5L_7$ band in the dialkyldithiocarbamate complex ($\varepsilon \approx 5$) compared to the aquo ion ($\varepsilon = 2.36$). The present case does not indicate any dramatic hypersensitiveness of this band [14], although a very slight increase of ε value was noted in case of $[Eu(Terp)]^{3+}$ with respect to the aquo ion. The difference spectrum of $[Eu(Terp)_2]^{3+}$ complex shows a small hump around 24.35 kK superposed on the $^5L_7$ band of Eu(III) which is split into two components (Fig. 3 c).

The appearance of shoulders in the near ultraviolet region in the case of Pr (25.87 kK), Nd (26.17,25·98 and 25.76 kK) and Sm (25.99 kK) may also be due to the electron transfer from the highest filled MO of the ligand to the partly filled 4 f shells, but no definite conclusion can be drawn at present.

The Infrared Spectra (4000 – 700 cm^{-1})

The main bands of terpyridyl with their probable assignments are given in Table 3. Taking the spectrum of the ligand as reference we shall now proceed to interpret the spectra of the complexes recorded. The spectrum of terpyridylium hydrochloride

$$(C_{15}H_{11}N_3 \cdot 3\,HCl \cdot 4\,H_2O = \text{Terp } H_3^{3+}),$$

prepared by the method of Morgan and Burstall [15] was also examined. The quarternization of the nitrogens in terpyridyl will result in more infrared active bands as is evident from the spectrum (Fig. 4). The C – H stretching frequencies of terpyridyl rings are shifted towards higher wavenumbers in case of Terp H_3^{3+}. The N – H stretching frequency in Terp H_3^{3+} occurs near 2830 cm^{-1} indicating strong hydrogen bonding in the salt [16]. The bands at $\sim$3478, 3410 and $\sim$1620 cm^{-1} in Terp H_3^{3+} are due to the antisymmetric, symmetric O – H stretching mode and H – O – H bending mode of water. The broad $\sim$3350 cm^{-1} band for the rare earth terpyridyl complexes is assigned to the O – H stretching which seems to vary from compound to compound due to the presence of varying amounts of water of crystallization. The bending mode of water is shifted towards higher frequencies ($\sim$1635 cm^{-1}) in the complexes.

The region between 1600 and 1200 cm^{-1} is most interesting. Two groups of very intense bands arise between 1600 and 1400 cm^{-1} for terpyridyl which are the characteristic bands for pyridine, substituted pyridine [17] and the higher analogues [4] and are due to the C = C and C = N vibration. The band group at 1600 cm^{-1} particularly shows shift towards higher frequencies: 12 – 15 cm^{-1} for Terp H_3^{3+} and $\sim$20 cm^{-1} for rare earth complexes. An intense band at 1535 cm^{-1} (doublet) which appears in the spectrum of Terp H_3^{3+} is thought to be due to "immonium" band [18].

In some rare earth complexes a small sharp peak appears at 1500 cm^{-1}. The second group of three bands also seems to be sensitive to the nature of the cation and shows some shift and splitting. A small band around 1400 cm^{-1} seems to be characteristic of the complexes studied here and is not present in case of terpyridyl and Terp H_3^{3+}.

A strong relatively broad band was observed at 1360 cm^{-1} for Terp H_3^{3+} and as sharp peak at $\sim$1320 cm^{-1} for the rare earth terpyridyl complexes. Between 1300 and 1200 cm^{-1} terpyridyl is characterized by only one sharp peak at 1262 cm^{-1}. In the complexes this peak shifts towards higher frequency with appearance of smaller peaks on the

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[14] The real hypersensitive band of Eu(III) is $^5D_2$ at 21.5 kK. C. K. Jørgensen and B. R. Judd, Mol. Phys. **8**, 281 [1964].

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smaller wavenumber side, and suggests that this may arise from some kind of ring vibration which includes the N atom of the ring or may be either an overtone or combination band which is more probable. In case of ortho substituted pyridine, bands around this region are observed.

The region of 1200 to 700 cm^{-1} is rather more complicated and definite assignments of all bands are difficult. The 1150 cm^{-1} band of terpyridyl is shifted towards higher wavenumber for both Terp H_3^{3+} and the complexes and shows structure. The group of bands between 1100 and 1000 cm^{-1} is usually considered to be due to ring vibrations and C – H deformations. On protonation and complex formation in the present case these bands show remarkable change of intensities. The 988 cm^{-1} band of terpyridyl is assigned definitely to the pyridine ring vibration and is shifted to ~1000 cm^{-1} in Terp H_3^{3+} and to ~1015 for the rare earth complexes, thus indicating the formation of complexes and stronger perturbation in the rare earth complexes than in the Terp H_3^{3+} salt. This also indicates that no pyridyl ring is free, otherwise one may have expected another peak near 990 cm^{-1} due to the breathing vibration of the uncoordinated pyridine ring. The 960 cm^{-1} band of Terp H_3^{3+} may have the same origin as that of 1535 cm^{-1} band, i. e. the immonium ion band. SPINNER [19] has assigned a band near 910 cm^{-1} to the $N^+ - H$ out-of-plane bending in pyridinium chloride. The 830 cm^{-1} and 760 cm^{-1} bands are probably due to the one group of three and two groups of four adjacent hydrogens of the rings of terpyridyl and on protonation and on complex formation the intensity of 830 cm^{-1} bands reduces significantly. The bands in this region originate from the out-of-plane in-phase C – H deformation. The considerable lowering of intensity of the 830 cm^{-1} band of terpyridyl due to protonation and complex formation suggests an out-of-plane out-of-phase motion [20] of the ring hydrogens. This indication may be very helpful for assigning the structure of the structure of the complexes, but further interpretation must wait for more data.

From the above infrared investigation it is evident that the terpyridyl molecule is coordinated definitely with the rare earths; all of the three nitrogens are coordinated in the solid state and the nature of the coordinated species of different rare earths is very similar to one another (except the nature of the bonding of water molecules). It is rather difficult to draw any definite conclusion on the structure or the nature of the coordinated species although some evidence [21] has been obtained that they differ much with respect to the 3 d-transition terpyridyl complexes.

It seems that the aromaticity of the ligands containing nitrogens has something to do in forming complexes with rare earths. When attempts were made to prepare complexes containing the – N – C – C – N-grouping where both nitrogen atoms are outside the aromating ring (for example

$$C_6H_5 - CH = N - CH_2 - CH_2 - N = CH - C_6H_5),$$

precipitation of the hydroxides of rare earths resulted. It is also possible that the steric condition of some ligands like dipyridyl and phenanthroline are more favourable for forming complexes.

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