Investigations on the influence of the coordination formation between dibenzo and benzo derivatives of 18-crown-6 and 15-crown-5 crown ethers with Pr (III) and Nd (III) ions in solution

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ABSTRACT

In this communication we report the influence of the coordination formation between the dibenzo and benzo derivatives of the crown ethers. The electronic absorption spectra of the derivatives of 18-crown-6 and 15-crown-5 with Pr (III) and Nd (III) ions have been recorded and studied in 1:1,1:2,1:3 and 1:6 metal -ligand ratios in visible range i.e.340-760 nm in solution. The energy and intensity of *f-f* transitions in these spectra have been quantified and explained in terms the various energy and intensity parameter such as Racah (E^k), Slator-Condon (F_k) Lande (V_{4f}), Oscillator Strength (P) and Judd-Ofelt parameter ($T_{\hat{e}}$) etc. These were computed using partial and regression statistical method. The bonding parameter (b½) and nephalauxetic ratio (b) have also been evaluated. The metal and ligand interaction have been discussed on the basis of these parameters. These parameters suggest the covalent nature of metal and ligand bond.

Key words: Crown ether, energy and intensity parameters.

INTRODUCTION

The crown ethers are now well-known molecules. They are characterized by repeating ($CH_2\ CH_2O$) units. The simplest examples are unfettered by substituents and can be fully described as ($CH_2\ CH_2O$)$_n$. The most common simple macrocycle is 18-crown-6-ether, which has the formula ($CH_2\ CH_2O$)$_6$.[1] Crown ethers, macrocyclic and macropolycyclic molecules show a high complexation selectivity which makes them adequats ligands for the investigation of the coordinative properties of the lanthanoid ions. Recently[2-6], attention has been focused on lanthanoid & crown ether complexes since they can be used for the lanthanoid ion separation, for stabilizing Ln (II) oxidation states and for studying high coordination numbers of the lanthanoid ions. A search through literature[7-13] reveal that very little work has been done on the electronic spectra of metal ions, Pr(III) and Nd(III) complexes with

macrocyclic ligand (crown ethers) namely, 18-Crown-6($6CE_1$), Benzo-18 crown -6($6CE_2$), Dibenzo 18- crown -6($6CE_3$), 15-Crown -5($5CE_1$), Benzo 15-crown-5($5CE_2$), Dibenzo 15-Crown-5($5CE_3$). The electronic spectra of the complexes in different metal-ligand stoichiometry (1:1, 1:2, 1:3, 1:6) have been recorded and various energy and intensity parameters have been computed. In this communication we report the investigations on the influence of the coordination formation between Pr(III) and Nd(III) ions and the crown ethers 15-Crown -5 , 18-Crown -6 & their derivatives.

EXPERIMENTAL

The crown ether ligands have been dissolved in 1:3 mixture of CH3OH and/or CH_3CN solution. The sample solutions for recording electronic spectra of Pr(III) and Nd(III) metal ions in the ligand environment having different metal ligand (M:L) stoichiometry i.e. (1:1, 1:2, 1:3 and

1:6) have been prepared. All the spectra were recorded in solution in the range of 340-760 nm on a Beckman DU 600 spectrophotometer.

The absorbance measurement of the solutions of different stoichiometry shows maximum absorbance for 1:1 metal-ligand ratio hence; all the different parameters were calculated for this metal-ligand stoichiometry.

All chemicals and reagents (Across) used were of AnalaR or AR grade. The lanthanide acetates were obtained from Indian Rare Earth Ltd., Udhyogmandalam, India.

RESULTS AND DISCUSSION

The spectra thus obtained were analyzed and various energy, intensity and bonding parameters were computed in order to explained the structure and bonding in the complexes as per theory propounded by Judd-Oflet[14-17].

Energy parameters

The energy level structure of $4f^N$ configurations arise as a result of coulombic and spin-orbit interactions, which are expressed as inter electronic repulsion parameters, namely, Slator-Condon(F_k), Racah(E^k) and Lande parameters ($z4f$) respectively: These parameter can be evaluated by solving Taylor series expansion equations. The Table 1&2 shows the variation in magnitude of these energy parameters

$$Ej(F_k, \zeta_{4f}) = E_{0j}(F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial F_{4f}} \Delta \zeta_{4f}$$

Where E_{oj}= the zero order energy of level j.

$$F_k = f_k^0 + \Delta F_k$$
$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f}$$
$$\Delta F_k << F_k^0, \Delta \zeta_{4f} << \zeta_{4f}^0$$

The difference between the observed E_j values and zero-order ones, DE_j, can be expressed as

$$\Delta E_j = \sum_{K=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f}$$

The magnitude of parameters F_2, F_4, F_6 and z_{4f} were computed using regression analysis and refined by the least squares techniques.

There is red shift and there slight decrease in values of Slator-Condon(F_k) and Racah(E^k) and Lande parameters (z_{4f}) which indicate covalancy in metal ligand bond.

For all the complexes of both the metal ions the order of Slator-Condon parameter is found
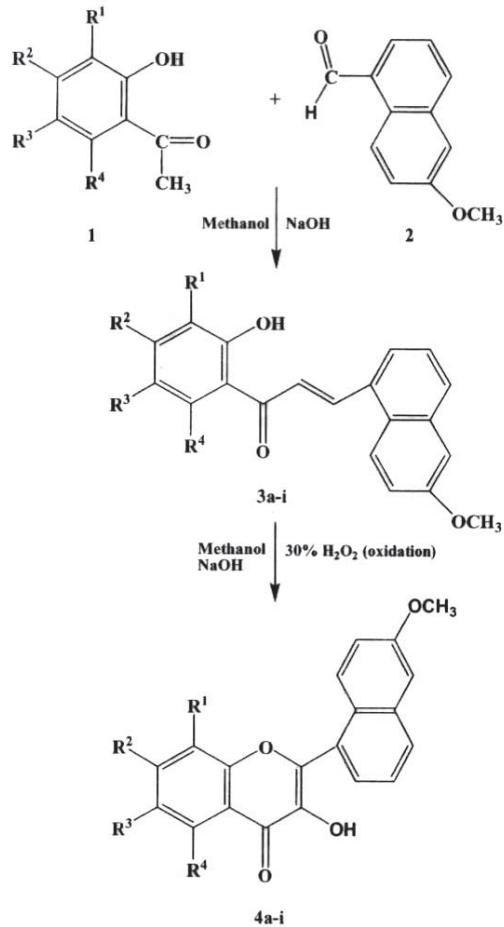
Scheme 1

Table 1 : Oscillator strength and judd-ofelt parameters of pr(iii) ions with different ligands in 1:1 metal-ligand stoichiometry

Ligand	Oscillator strength and energy	Energy Levels				+σr.m.s	Judd-Ofelt Parameter			
		$^1D_2$	^3P_o	$3P_1$	$^3P_2$		$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	$T_4/T6$
$6CE_1$	$P_{exp} \times 10^6$	7.0547	9.9570	10.7513	39.5699	0.26×10^{-6}	-100.0	2.8800	12.2000	0.2368
	$P_{cal} \times 10^6$	7.0500	10.300	10.4000	39.6000					
	E_{exp} (cm^{-1})	16983.70	20729.68	21285.65	22573.36	108.543				
	E_{cal} (cm^{-1})	17121.38	20725.02	21232.99	22414.07					
$6CE_2$	$P_{exp} \times 10^6$	5.3639	6.6181	7.0418	30.7456	0.11×10^{-6}	-82.00	1.8900	9.5500	0.1978
	$P_{cal} \times 10^6$	5.3600	6.7800	6.8800	30.7000					
	E_{exp} (cm^{-1})	16995.24	20772.75	21331.06	22573.36	107.03				
	E_{cal} (cm^{-1})	17136.05	20769.51	21259.33	22429.01					
$6CE_3$	$P_{exp} \times 10^6$	4.1395	2.8619	3.6466	16.6893	0.27×10^{-6}	-16.00	0.9050	5.2100	0.1736
	$P_{cal} \times 10^6$	4.1400	3.2500	3.2600	16.7000					
	E_{exp} (cm^{-1})	16966.41	20695.36	21303.79	22482.01	98.133				
	E_{cal} (cm^{-1})	17099.88	20695.31	21200.78	22381.55					
5CE1	Pexp × 106	3.8455	2.1464	3.6466	14.1457	0.52X10-6	-6.400	0.8060	4.4100	0.1813
	Pcal × 106	3.8500	2.8700	2.9100	14.1000					
	Eexp (cm-1)	17001.02	20798.67	21321.96	22573.36	105.431				
	Ecal (cm-1)	17136.54	20794.56	21264.45	22422.46					
5CE2	Pexp × 106	3.2255	2.0868	2.8922	13.2250	0.28 X10-6	-14.00	0.6930	4.1400	0.1673
	Pcal × 106	3.2300	2.4800	2.4900	13.2000					
	Eexp (cm-1)	16966.41	20772.75	21303.79	22451.73	94.886				
	Ecal (cm-1)	17095.36	20772.28	21208.98	22349.77					

Table 2 : Ligand Oscillator strength and energy Energy Levels ±sr.m.s Judd-Ofelt Parameter

		$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4F_{9/2}$	$^4G_{5/2}$	$^4G_{7/2}$	$^2G_{9/2}$	$^4G_{9/2}$	$^4G_{11/2}$	$^2P_{1/2}$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	T_4/T_6
6CE₁	$P_{exp} \times 10^6$	0.2132	1.3675	0.8211	0.0796	1.8063	0.4816	0.2268	0.1021	0.0958	0.0782	0.14×10^{-6} 0.06122	0.1105	0.1740	0.6353
	$P_{cal} \times 10^6$	0.4025	1.1883	1.0486	0.1140	1.8554	0.5815	0.0788	0.3017	0.04301	0.0982				
	E_{exp} (cm-1)	11518.08	12501.56	13388.67	14718.87	17319.02	19153.42	19550.34	21331.06	21635.66	23169.60	62.944			
	E_{cal} (cm-1)	11468.88	12494.03	13320.89	14781.50	17284.66	19280.55	19626.48	21272.49	21590.65	23174.88				
6CE₂	$P_{exp} \times 10^6$	0.2132	1.4377	0.8211	0.10875	1.7999	0.4305	0.2106	0.1095	0.09535	0.07746	0.16×10^{-6} 0.0588	0.1153	0.1802	0.6399
	$P_{cal} \times 10^6$	0.4190	1.2331	1.0865	0.1181	1.8565	0.5999	0.0817	0.31311	0.04463	0.1024				
	E_{exp} (cm-1)	11562.03	12512.51	1309.86	14727.54	17388.28	19182.81	19550.34	21331.06	21743.86	23201.86	83.764			
	E_{cal} (cm-1)	11513.40	12544.58	13373.92	14817.29	17351.18	19304.61	19667.29	21261.40	21670.00	23208.16				
6CE₃	$P_{exp} \times 10^6$	0.2132	1.2204	0.7517	0.1087	1.6903	0.7064	0.2286	0.1096	0.09536	0.08249	0.13×10^{-6} 0.0522	0.1119	0.1483	0.7544
	$P_{cal} \times 10^6$	0.3899	1.0649	0.9037	0.09967	1.7071	0.5489	0.07217	0.2802	0.03869	0.0993				
	E_{exp} (cm-1)	11562.03	12501.56	13509.86	14723.20	17394.33	19182.81	19550.34	21331.05	21743.85	23164.23	85.69			
	E_{cal} (cm-1)	11511.30	12543.14	13370.68	14812.12	17351.69	19306.12	19668.61	21261.02	21667.06	23171.06				
5CE1	$P_{exp} \times 10^6$	0.2132	1.1444	0.7517	0.10875	1.5804	0.7064	0.24571	0.12368	0.1106	0.07782	0.12×10^{-6} 0.0489	0.1011	0.1421	0.7118
	$P_{cal} \times 106$	0.3574	1.0021	0.8622	0.09460	1.5767	0.5065	0.06740	0.2604	0.0364	0.08982				
	E_{exp} (cm-1)	11535.36	12496.88	13435.44	14725.37	17367.14	19149.75	19561.82	21317.42	21630.98	23180.34	68.617			
	E_{cal} (cm-1)	11488.29	12510.88	13336.81	14785.90	17314.70	19287.07	19635.56	21256.33	21609.82	23187.84				
5CE2	$P_{exp} \times 10^6$	0.1917	1.2907	0.6824	0.1087	1.4649	0.7064	0.2106	0.1096	0.09536	0.07746	0.15×10^{-6} 0.0323	0.1269	0.1460	0.8690
	$P_{cal} \times 106$	0.4281	1.0973	0.8988	0.1002	1.5028	0.5708	0.0754	0.2958	0.0400	0.1127				
	E_{exp} (cm-1)	11562.03	12501.56	13506.21	14729.71	17394.33	19179.13	19659.81	21258.56	21644.03	23170.49	81.448			
	E_{cal} (cm-1)	11508.70	12533.65	13358.48	14798.42	17349.47	19306.00	19659.81	21258.56	21644.03	23158.87				
5CE3	$P_{exp} \times 106$	0.2343	1.2907	0.8189	0.1048	1.3499	0.7064	0.2457	0.1166	0.0996	0.08796	0.13×10^{-6} 0.02765	0.1170	0.1597	0.7328
	$P_{cal} \times 106$	0.4105	1.1356	0.9704	0.1064	1.3671	0.5503	0.0762	0.2943	0.0412	0.1039				
	E_{exp} (cm-1)	11518.08	12503.13	13401.23	14701.56	17349.06	19135.09	19550.34	21340.16	21616.95	23169.60	72.448			
	E_{cal} (cm-1)	11473.90	12492.67	13316.64	14773.18	17294.91	19288.20	19626.78	21272.93	21579.87	23174.74				

Table 3 : Racah, slator-condon and average bonding parameters of Pr(III) and Nd(III) ions with different ligands in 1:1 metal-ligand stoiciometry

Ligand	Metal(III) ion	Racah parameters(E^k)(cm^{-1})			Slator-Condon parameters (F^k) (cm^{-1})			Lande parameter (z_{4f})	Nephelaux-etic ratio (b)	Bonding parameter ($b^{1/2}$)
		E_1	E_2	E_3	F_2	F_4	F_6			
6CE$_1$	Pr	4556.83	23.84	460.72	310.37	42.85	4.69	696.91	0.964	0.1349
	Nd	5051.26	23.23	493.41	328.58	52.01	5.22	868.60	0.992	0.0624
6CE$_2$	Pr	4569.61	23.90	462.01	311.24	42.97	4.70	688.18	0.966	0.1297
	Nd	5048.51	23.73	495.17	330.67	51.23	5.22	873.24	0.999	0.0271
6CE$_3$	Pr	4551.10	23.81	460.14	309.98	42.79	4.68	695.68	0.962	0.1371
	Nd	5036.13	23.52	495.26	329.70	51.42	5.18	872.22	0.996	0.0469
5CE$_1$	Pr	4578.69	23.95	462.93	311.86	43.05	4.71	678.58	0.968	0.1260
	Nd	5041.45	23.39	495.39	329.41	51.72	5.18	867.65	0.995	0.0514
5CE$_2$	Pr	4580.42	23.96	463.10	311.98	43.07	4.71	662.54	0.969	0.1253
	Nd	5054.84	23.11	493.92	328.38	52.30	5.21	864.14	0.992	0.0648
5CE$_3$	Pr	4582.50	23.97	463.31	312.12	43.09	4.72	662.26	0.969	0.1244
	Nd	5053.08	23.41	494.35	329.50	51.77	5.22	867.31	0.995	0.0500

to be $F_2 > F_4 > F_6$ and values are summarized in Table 3.

On complexation, contraction or expansion of wave function occurs, which is reflected by changes in values of F_k and z_{4f} parameters with respect to the corresponding free ion values. This phenomenon is known as nephelauxetic effect and can be expressed by the nephelauxetic ratio[18].

$$\beta \frac{F_k^c}{F_k^f}$$

Where $_c$ and f refer to the complex and free ion respectively.

The values of nephelauxetic ratio for all the metal complexes were found less than one. The values of this parameter were summarized in Table 3. This indicates the metal-ligand interaction is not merely ionic but there is mixing of metal and ligand orbitals, and hence covalent nature of metal- ligand bond may be concluded.

The bonding parameter ($b^{½}$) is also related to nephelauxetic ratio (b) by the relation

$$b\tfrac{1}{2} = [\tfrac{1}{2} - (1 - \beta)]^{\gamma_1}$$

The values of energies (E) for peaks of various *f-f* transitions of all the metal- ligand complexes are summarized in Table 1 and 2.

The change in values of all these parameters in all the complexes and also in the various metal and ligand (M-L) ratios (1:1, 1:2, 1:3 and 1:6) is not much appreciable. Further, this

Table 4: Physical data of compounds 3a-i

Compounds	R¹	R2	R3	R4	mp(°C)	Yield (%)
3a	H	H	H	H	156	94
3b	Cl	H	Cl	H	220	92
3c	H	H	Cl	H	194	95
3d	Cl	H	H	H	165	93
3e	H	H	Br	H	185	90
3f	CH_3	H	CH_3	H	149	90
3g	CH_3	H	H	H	156	94
3h	H	H	CH_3	H	133	92
3i	H	CH3	Cl	H	191	94

Table 5: Physical data of compounds 4a-i

Compounds	R¹	R2	R3	R4	mp(°C)	Yield (%)
4a	H	H	H	H	232	92
4b	Cl	H	Cl	H	262	95
4c	H	H	Cl	H	186	94
4d	Cl	H	H	H	226	90
4e	H	H	Br	H	228	93
4f	CH_3	H	CH_3	H	242	92
4g	CH_3	H	H	H	192	95
4h	H	H	CH_3	H	232	94
4i	H	CH_3	Cl	H	218	95

Table 6: Characterization data of compounds 4a-i

Comp.	IR cm^{-1}	1H NMR δppm
4a	3270 (-OH), 1642(-C=O), 1494(C=C), 1266 (-C-O)	8.74 (s, 1H, benzene), 8.28 (m,2H, benzene), 7.88 (t, 2H, naphthalene), 7.44 (t, naphthalene), 7.68 (d, 1H, benzene), 7.44 (t, 1H, napthalene), 7.21 (m 2H, naphthalene), 3.96 (s, 3H, OCH$_3$)
4b	3177 (-OH), 1609(-C=O), 1476(C=C), 1272 (-C-O)	8.74(s, 1H, benzene), 8.26 (d, 1H, naphthalene), 7.99 (d, 1H, naphthalene), 7.96(d, 1H, naphthalene), 7.90 (t, 2H, naphthalene), 7.26 (s, 1H, benzene), 7.16 (dd, 1H, napthalene), 3.89 (s, 3H, OCH$_3$)
4c	3294 (-OH),1675(-C=O), 1499(C=C), 1380 (-C-O)	8.80(s, 1H, naphthalene), 8.25 (m, 1H, benzene), 7.95 (t, 2H, naphthalene), 7.89 (t, 2H, naphthalene), 7.82 (d, 1H, naphthalene), 7.26 (s, 1H, benzene), 7.16 (m 2H, naphthalene), 3.90 (s, 3H, OCH$_3$)
4d	3241 (-OH),1642 (-C=O), 1467(C=C), 1165 (-C-O)	8.85 (s, 1H, naphthalene), 8.40 (d, 1H, benzene), 8.19 (d, 1H, benzene), 7.89 (t, 1H, benzene), 7.80 (t, 2H, naphthalene), 7.80 (s, 1H, benzene), 7.36 (t, 1H, naphthalene), 7.20 (m, naphthalene) 3.97 (s, 3H, OCH$_3$)
4e	3290 (-OH),1645 (-C=O), 1477(C=C), 1170 (-C-O)	8.73(s, 1H, benzene), 8.27 (m, 1H, benzene), 8.18 (d, 1H, naphthalene), 7.94 (d, 2H, naphthalene), 7.81 (d, 1H, naphthalene), 7.39 (d, 1H, benzene), 7.22 (dd, 2H, naphthalene), 3.90 (s, 3H, OCH$_3$)
4f	3275 (-OH),1659 (-C=O), 1479(C=C), 1166 (-C-O)	8.76(s, 1H, benzene), 8.27 (m, 1H, maphthalene), 7.97 (d, 1H, naphthalene), 7.95 (d, 1H, naphthalene), 7.27 (s, 1H, benzene), 7.17 (dd, 1H, naphthalene), 2.68 (s, 6H, CH$_3$), 3.90 (s, 3H, OCH$_3$)
4g	3220 (-OH),1654(-C=O), 1475(C=C), 1163 (-C-O)	8.76(s, 1H, naphthalene), 8.30 (d, 1H, benzene), 8.17 (d, 1H, benzene), 7.86 (t, 2H, naphthalene), 7.55 (d, 1H, benzene), 7.35 (t, 1H, naphthalene), 7.20 (m 2H, naphthalene), 2.67 (s, 3H, CH$_3$) 3.95 (s, 3H, OCH$_3$)
4h	3287 (-OH),1728(-C=O), 1442(C=C), 1220 (-C-O)	8.75(s, 1H, naphthalene), 8.30 (d, 1H, benzene), 8.16 (d, 1H, benzene), 7.85 (t, 2H, naphthalene), 7.55 (d, 1H, benzene), 7.34 (t, 1H, naphthalene), 7.20 (m 2H, naphthalene), 2.65 (s, 3H, CH$_3$) 3.96 (s, 3H, OCH$_3$)
4i	3280 (-OH),1690(-C=O), 1485(C=C), 1180 (-C-O)	8.74(s, 1H, naphthalene), 8.28 (s, 1H, benzene), 8.18 (s, 1H, benzene), 7.84 (t, 2H, naphthalene), 7.36 (t, 1H, benzene), 7.22 (t, 1H, naphthalene), 7.22 (m, 2H, naphthalene), 2.64 (s, 3H, CH$_3$) 3.90 (s, 3H, OCH$_3$)

shows that ligands have little effect on the spectral pattern thereby indicating largely outer sphere (high spin) complexation[19] and also metal ligand interaction is not merely ionic.

The decrease in the values of the Lande parameter (ζ_{4f}) is more than Slator-Condon (F_k) parameter indicating that the ligands affect the spin-orbit coupling more than the electrostatic repulsion.

Intensity parameter

The intensity of absorption bands were measured in terms of oscillator strength (P), calculated by performing a Gaussian curve analysis of the curve. The Oscillator strength (P) of a transition between the ground state $\langle f^N\Psi_j|$ to excited state $f^N\Psi_j\rangle$ of the lanthanide ion in solution is given by

$$P_{obs} = \sum_{\lambda=2,4,6} T_\lambda \bar{\nu}(f^N\psi j \| U^{(\lambda)} \| f^N\psi j > ^2 /(2J+1)$$

Table 7: Antibacterial screening results of the compounds 4a-i

Compound	Antibacterial activity (Inhibition zone in mm)			
	E. coli	*Salmonella typhi*	*Staphylococcus aures*	*Bacillius subtilis*
4a	6	18	-ve	15
4b	10	-ve	22	22
4c	7	-ve	27	20
4d	7.5	20	-ve	22
4e	11	24	35	24
4f	8	-ve	-ve	20
4g	7.5	-ve	-ve	18
4h	9	21	32	23
4i	-ve	-ve	-ve	-ve
Penicillin	12	26	40	27
DMSO	-ve	-ve	-ve	-ve

-ve no antibacterial activity

Table 8: Antibacterial screening results of the compounds 4a-i

Compound	Antibacterial activity (Inhibition zone in mm)		
	Aspergillus niger	*Aspergillus flavus*	*Fusarium moneliforme*
4a	-ve	-ve	+ve
4b	-ve	+ve	-ve
4c	-ve	-ve	+ve
4d	+ve	+ve	+ve
4e	-ve	-ve	-ve
4f	-ve	-ve	+ve
4g	+ve	-ve	+ve
4h	-ve	-ve	-ve
4i	+ve	+ve	+ve
Grysofulvin	-ve	-ve	-ve
control	+ve	+ve	+ve

Legends: +ve - Growth   No Antifungal activity
        -ve - No growth   Antifungal activity observed

Where the unit tensor operator $U^{(\lambda)}$ connects the initial and final states through three phenomenological parameters, T_λ (l = 2,4,6). These parameters are related to the radial part of $4f^N$ wave function, wave function of perturbing configuration and ligand field parameters that characterize them and the immediate environment around the metal ion. These parameters and oscillator strength of all the bands observed in Pr (III) and Nd (III)-metal ion complexes are given in Table 1 and 2.

The Judd-Ofelt parameter (T_2) is found negative in the present case as expected for Pr (III) metal-ion complexes and this may be due to overlapping of *f-d* orbital in the region of *f-f* transition. The presence of this tail enhances the intensity of $^3P_2$ in the visible region. The values of T_1 parameters are too low, thereby indicating outer sphere (high Spin) complexation[20]. But in Nd (III) metal ion, the T_2 Parameter has been considered to be an indication of the immediate coordination environment.

The ratio of Judd-Ofelt parameter T_4/T_6 of Pr (III) complexes and Nd (III) complexes has been found in the range 0.16-0.29 and 0.62-0.97 respectively, confirming that coordination is through the oxygen donor atoms.

The highest values of oscillator strength have been found for 1:1 metal-ligand stoichiometry complexes; so it can be inferred that 1:1 metal-ligand stoichiometry in the pH range of 7.5-8.5 in both the complexes; has more molecular stacking and molecular association, thereby indicating favourable stereo-environment around the metal ion for complexation.

Hence, at large it may be concluded that interaction of Pr (III) and Nd (III) ions with the crown ether has not been ionic but covalent and on the basis of oscillator strength the order of covalency may be given as: -

$$5CE_3 < 5CE_2 < 5CE_1 < 6CE_3 < 6CE_2 < 6CE_1$$
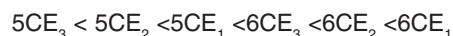
The complexation and covalency have been found related to spectral intensity (i.e., oscillator strength). The metal-ligand stoichiometry affects the oscillator strength. Higher the value of oscillator strength, higher will be the complexation and covalency. This is in agreement with earlier findings[21-24].

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