Asian Journal of Chemistry Vol. 5, No. 4 (1993), 857–873

Characterization of Some Schiff-Base Complexes of Nd (III) in Terms of Electronic Spectral Parameters

P.R. BHATTI*, K.P. SONI, P.C. TATER, G.K. JOSHI and S.N. SWAMI
Department of Chemistry
Government Dungar College
Bikaner-334 001, India

Fifteen schiff bases derived from veratraldehyde, ethyl vanilline, 2,5 dimethoxy benzaldehyde, methyl acetocetate and ethyl acetoacetate with o^-, m^- and p^- phenylene diamines have been synthesized involving condensation reactions. The fifteen complexes of Nd(III) with the above ligands having general formula out of $[M(L_1)(H_2O)_4(Cl)]$ and $[M(L_2)(H_2O)_4(Cl)_3]$ have been characterized on the basis of IR and various electronic spectral parameters *viz.* Slater Condon, Lande's and Judd-Ofelt. The study provides useful information about interelectronic repulsion and spin orbit interactions involved in metal ligand bond.

INTRODUCTION

Since after the publication of Judd-Ofelt theory[1–3] for the lanthanide intensities in the year 1962 a great deal of work has been reported on the measurement of f $\leftrightarrow$ f transitions of free and aquo ions of lanthanide in different chemical environment by several workers[1–7]. The Schiff base complexes of lanthanide (III) ions exhibit absorption spectra characterized by bands in visible region, but these spectra have not been studied extensively[4–7] in terms of various electronic spectral parameters. The present investigation was undertaken with a view to make a comparative study of various energy and intensity parameters resulting from different energy levels of Nd (III) Schiff base complexes having both nitrogen and oxygen donor ligands.

The values of the various electronic spectral parameters like Judd-Ofelt (T_λ), Slater Condon (F_K), Racah (E^K), Lande (ζ_{4f}), Oscillator strength (P), Nephelauxetic ratio (β) and bonding ($b^{1/2}$); which give useful informations regarding spin orbit interactions, interelectronic repulsions, nephelauxetic effect and bonding in the complexes have been calculated by using partial and multiple regression method involving theories given by Slater-Condon-Lande and Judd-Ofelt.

The analytical and infrared spectral studies of the present Nd (III)-Schiff base complexes were also undertaken to support inferences derived regarding the molecular structure, chemical bonding and complexation.

EXPERIMENTAL

Ethyl vanilline (Et.V), veratraldehyde (V), , 2,5-dimethoxy benzaldehyde (2,5 DMB), methyl acetoacetate (MeAA), ethyl acetoacetate (EtAA), o^-, m^- and p^- phenylenediamines (OPD, MPD, PPD) of AR grade and $NdCl_36H_2O$ (Rare Earth Division, Udyog Mandal) of 99.99% purity were used. The amines were purified by the method as described in vogel[10]. Schiff bases of phenylenediamines with various aldehydes and β–keto esters have been synthesized involving condensation reactions in ethanolic solution in 1 : 2 molar ratio[5].

TABLE 1
ANALYTICAL DATA OF METAL COMPLEXES

Empirical formulae of the compound	Colour	Elemental analysis found (Calc) %				
		M	C	H	N	Cl
$Nd(C_{16}H_{18}N_2O_4)Cl\cdot4H_2O$	Wine red	25.98	34.46	4.60	5.00	6.38
[Nd–MeAA–OPD]		(26.05)	(34.67)	(4.69)	(5.06)	(6.41)
$Nd(C_{16}H_{18}N_2O_4)Cl\cdot4H_2O$	Dark Purple	25.90	34.70	4.53	5.00	6.27
[Nd–MeAA–PPD]		(26.05)	(34.67)	(4.69)	(5.06)	(6.41)
$Nd(C_{16}H_{18}N_2O_4)Cl\cdot4H_2O$	Dark reddish	25.92	34.72	4.64	5.02	6.32
[Nd–MeAA–MPD]		(26.05)	(34.67)	(4.69)	(5.06)	(6.41)
$Nd(C_{18}H_{22}N_2O_4)Cl\cdot4H_2O$	Light red	24.72	37.10	5.08	4.70	6.02
[Nd–EtAA–OPD]		(24.79)	(37.13)	(5.16)	(4.81)	(6.10)
$Nd(C_{18}H_{22}N_2O_4)Cl\cdot4H_2O$	Purple	24.70	37.00	5.10	4.68	6.00
[Nd–EtAA–PPD]		(24.79)	(37.13)	(5.16)	(4.81)	(6.10)
$Nd(C_{18}H_{22}N_2O_4)Cl\cdot4H_2O$	Reddish black	24.74	37.18	5.12	4.74	6.04
[Nd–EtAA–MPD]		(24.79)	(37.13)	(5.16)	(4.81)	(6.10)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Red brown	19.76	39.50	4.28	3.80	14.40
[Nd–V–OPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.65)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Orange	19.80	39.68	4.30	3.74	14.36
[Nd–V–PPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.65)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Dark orange	19.72	39.75	4.35	3.72	14.50
[Nd–V–MPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.65)
$Nd(C_{24}H_{24}N_2O_4)Cl\cdot4H_2O$	Buff	22.00	43.90	4.60	4.16	5.30
[Nd–EtV–OPD]		(22.06)	(44.05)	(4.59)	(4.28)	(5.43)
$Nd(C_{24}H_{24}N_2O_4)Cl\cdot4H_2O$	Reddish	21.92	43.88	4.50	4.20	5.36
[Nd–EtV–PPD]		(22.06)	(44.05)	(4.59)	(4.28)	(5.43)
$Nd(C_{24}H_{24}N_2O_4)Cl\cdot4H_2O$	Brown red	22.02	43.86	4.48	4.12	5.32
[Nd–EtV–MPD]		(22.06)	(44.05)	(4.59)	(4.28)	(5.43)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Violet tinge	19.50	39.50	4.32	3.80	14.45
[Nd–2,5 DMB–OPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.65)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Purple	19.38	39.68	4.28	3.70	14.40
[Nd–2,5 DMB–PPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.64)
$Nd(C_{24}H_{24}N_2O_4)Cl_3\cdot4H_2O$	Dark red	19.46	39.56	4.26	3.72	14.38
[Nd–2,5 DMB–MPD]		(19.85)	(39.63)	(4.40)	(3.85)	(14.65)

TABLE 2
COMPUTED VALUES OF OSCILLATOR STRENGTH OF THE BANDS OBSERVED FOR THE VARIOUS Nd (III) COMPLEXES.

Compd.	Nd–MeAA–OPD		Nd–EtAA–OPD		Nd–V–OPD		Nd–Et–V–OPD		Nd 2,5 DMB–OPD	
Level	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
$^2P_{1/2}$	2.380	0.780	3.420	0.716	1.19	0.996	1.36	0.555	4.39	0.908
$^4G_{11/2}$	1.440	0.194	3.900	0.230	2.71	0.212	2.05	0.133	1.11	0.187
$^4G_{9/2}$	2.670	1.640	4.680	1.750	2.46	1.960	2.41	1.170	1.46	1.710
$^2G_{9/2}$	1.710	0.400	1.560	0.445	2.10	0.459	1.85	0.283	2.72	0.405
$^4G_{7/2}$	2.440	3.550	3.500	3.570	5.49	4.570	2.91	2.880	3.58	3.960
$^4G_{5/2}$	9.850	11.100	9.360	10.500	16.60	18.200	13.20	13.600	13.50	14.200
$^4F_{9/2}$	0.263	0.436	0.543	0.559	1.15	0.438	2.35	0.295	3.19	0.374
$^4F_{7/2}$	3.260	3.570	4.810	4.880	2.66	3.360	2.87	2.350	2.90	2.830
$^4F_{5/2}$	3.380	5.260	4.300	6.230	3.68	5.650	2.03	3.580	3.42	4.970
$^4F_{3/2}$	2.120	2.670	1.820	2.630	1.82	3.260	2.21	1.880	3.10	2.960
	r.m.s. dev. ± 1.17		r.m.s. dev. ± 1.90		r.m.s. dev. ± 1.40		r.m.s. dev. ± 1.25		r.m.s. dev. ± 1.71	

TABLE 3

COMPUTED VALUES OF OSCILLATOR STRENGTH OF THE BANDS OBSERVED FOR THE VARIOUS Nd (III) COMPLEXES.

Compd	Nd–MeAA–MPD		Nd–EtAA–MPD		Nd–V–MPD		Nd–Et–V–MPD		Nd 2,5 DMB–MPD	
Level	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
$^2P_{1/2}$	2.34	1.250	1.67	0.771	2.750	0.399	2.11	0.350	1.650	0.654
$^4G_{11/2}$	5.44	0.346	1.53	0.260	2.540	0.356	2.33	0.379	2.890	0.282
$^4G_{9/2}$	3.36	2.810	2.09	1.990	2.630	2.270	1.95	2.310	3.770	2.080
$^2G_{9/2}$	2.90	0.699	3.60	0.506	9.060	0.630	5.17	0.654	7.010	0.541
$^4G_{7/2}$	4.99	6.080	2.63	4.350	1.090	4.990	1.86	4.700	1.350	4.840
$^4G_{5/2}$	18.80	21.00	16.30	17.900	28.400	30.400	22.90	25.600	25.200	26.700
$^4F_{9/2}$	1.14	0.811	1.01	0.650	0.621	1.070	7.09	1.160	.783	0.765
$^4F_{7/2}$	7.39	6.870	5.95	5.690	10.400	10.200	10.60	11.100	7.110	6.880
$^4F_{5/2}$	5.14	9.390	4.12	7.070	6.270	9.980	6.89	10.600	4.760	7.790
$^4F_{3/2}$	4.34	4.400	2.97	2.880	2.530	2.290	1.27	2.260	3.000	2.670
	r.m.s. dev. ± 0.69		r.m.s. dev. ± 0.49		r.m.s. dev. ± 1.17		r.m.s. dev. ± 2.42		r.m.s. dev. ± 3.350	

TABLE 4

COMPUTED VALUES OF OSCILLATOR STRENGTH OF THE BANDS OBSERVED FOR THE VARIOUS Nd (III) COMPLEXES.

Compd	Nd–MeAA–PPD		Nd–EtAA–PPD		Nd–V–PPD		Nd–Et–V–PPD		Nd 2,5 DMB–PPD	
Level	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
$^2P_{1/2}$	2.23	1.340	2.21	1.380	1.180	0.671	2.75	0.659	0.20	0.489
$^4G_{11/2}$	2.21	0.229	2.21	0.278	1.860	0.164	1.74	0.187	1.44	0.145
$^4G_{9/2}$	2.47	2.650	2.46	2.590	1.850	1.420	1.62	1.520	1.69	1.210
$^2G_{9/2}$	2.80	0.634	3.01	0.608	1.740	0.345	2.52	0.375	5.30	0.300
$^4G_{7/2}$	5.18	6.050	5.69	6.090	3.180	3.310	3.50	3.340	2.41	3.080
$^4G_{5/2}$	19.90	22.100	21.00	23.100	12.500	13.800	11.80	12.700	17.20	17.700
$^4F_{9/2}$	1.76	0.630	1.41	0.556	0.556	0.363	1.64	0.441	1.24	0.358
$^4F_{7/2}$	3.89	4.930	3.37	4.140	2.290	2.950	4.12	3.720	3.44	3.000
$^4F_{5/2}$	5.28	7.950	4.55	7.370	2.920	4.420	3.06	5.050	2.39	3.950
$^4F_{3/2}$	3.05	4.440	3.25	4.470	1.210	2.280	2.36	2.330	2.11	1.750
	r.m.s. dev. ± 1.62		r.m.s. dev. ± 1.60		r.m.s. dev. ± 1.04		r.m.s. dev. ± 1.33		r.m.s. dev. ± 1.85	

TABLE 5

COMPUTED VALUES OF ENERGIES (cm^{-1}) OF THE BANDS FOR THE VARIOUS Nd (III) COMPLEXES.

Compd	Nd–MeAA–OPD		Nd–EtAA–OPD		Nd–V–OPD		Nd–Et–V–OPD		Nd 2,5 DMB–OPD	
Level	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^2P_{1/2}$	23137	23139	23127	23109	23148	23138	23121	23114	23127	23117
$^4G_{11/2}$	21390	21359	21636	21410	21505	21383	21413	21334	21459	21327
$^4G_{9/2}$	21035	21062	21079	21095	21075	21078	20991	21006	21053	21051
$^2G_{9/2}$	19524	19456	19570	19478	19531	19643	19493	19425	19512	19435
$^4G_{7/2}$	19194	19154	19164	19154	19121	19148	19139	19120	19099	19137
$^4G_{5/2}$	17235	17226	17227	17203	17316	17207	17235	17216	17241	17202
$^4F_{9/2}$	14654	14621	14616	14657	14620	14641	14590	14597	14570	14603
$^4F_{7/2}$	13154	13205	13149	13224	13193	13213	13158	13193	13141	13184
$^4F_{5/2}$	12308	12397	12285	12408	12285	12400	12312	12387	12293	12378
$^4F_{3/2}$	11448	11429	11421	11416	12393	11418	11418	11422	11429	11412
	r.m.s. dev. ± 44.81		r.m.s. dev. ± 91.3		r.m.s. dev. ± 68.8		r.m.s. dev. ± 43.5		r.m.s. dev. ± 60.96	

TABLE 6

COMPUTED VALUES OF ENERGIES (cm^{-1}) OF THE BANDS FOR THE VARIOUS Nd (III) COMPLEXES.

Compd	Nd–MeAA–PPD		Nd–EtAA–PPD		Nd–V–PPD		Nd–Et–V–PPD		Nd 2,5 DMB–PPD	
Level	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^2P_{1/2}$	23148	23144	23148	23145	23121	23115	23137	23134	23126	23120
$^4G_{11/2}$	21441	21343	21436	21334	21468	21354	21505	21373	21454	21346
$^4G_{9/2}$	21088	21086	21075	21074	21097	21102	21106	21111	21088	21090
$^2G_{9/2}$	19512	19438	19493	19431	19539	19452	19508	19467	19516	19439
$^4G_{7/2}$	19077	19130	19084	19126	19102	19144	19150	19158	19084	19127
$^4G_{5/2}$	17230	17162	17227	17164	17235	17170	17238	17190	17218	17153
$^4F_{9/2}$	14616	14627	14609	14619	14624	14632	14631	14642	14616	14629
$^4F_{7/2}$	13158	13186	13154	13182	13137	13190	13167	13203	13149	13185
$^4F_{5/2}$	12255	12372	12252	12369	12262	12377	12270	12390	12258	12370
$^4F_{3/2}$	11421	11391	11422	11392	11418	11394	11435	11407	11406	11385
	r.m.s. dev. ± 61.7		r.m.s. dev. ± 59.7		r.m.s. dev. ± 65.9		r.m.s. dev. ± 62.0		r.m.s. dev. ± 61.9	

TABLE 7

COMPUTED VALUES OF ENERGIES (cm^{-1}) OF THE BANDS FOR THE VARIOUS Nd (III) COMPLEXES.

Compd	Nd–MeAA–MPD		Nd–EtAA–MPD		Nd–V–MPD		Nd–Et–V–MPD		Nd 2,5 DMB–MPD	
Level	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^2P_{1/2}$	23127	23122	23137	23132	23148	23140	23121	23116	23120	23114
$^4G_{11/2}$	21413	21334	21505	21353	21482	21361	21459	21348	21436	21326
$^4G_{9/2}$	21053	21060	21088	21084	21079	21083	21075	21080	21061	21063
$^2G_{9/2}$	19531	19444	19512	19451	19524	19449	19501	19444	19508	19430
$^4G_{7/2}$	19120	19148	19102	19147	19113	19138	19120	19136	19091	19128
$^4G_{5/2}$	17266	17214	17241	17192	17218	17181	17224	17177	17235	17175
$^4F_{9/2}$	14599	14606	14599	14626	14611	14633	14612	14624	14590	14608
$^4F_{7/2}$	13172	13189	13158	13195	13151	13198	13150	13190	13144	13179
$^4F_{5/2}$	12262	12384	12257	12384	12297	12384	12282	12378	12267	12370
$^4F_{3/2}$	11439	11419	11450	11408	11418	11403	11413	11398	11410	11397
	r.m.s. dev. ± 57.5		r.m.s. dev. ± 71.6		r.m.s. dev. ± 57.3		r.m.s. dev. ± 54.0		r.m.s. dev. ± 59.6	

The complexes have been synthesized[9] by refluxing for about 6 hrs a mixture of ethanolic solution of $NdCl_36H_2O$ and the schiff-base ligands. The ligands were prepared from ethyl vanilline, veratraldehyde, 2,5-dimethoxy benzaldehyde, ethyl acetoacetate, methyl acetoacetate and various phenylenediamines in the molar ratio 1 : 1. All the complexes were found to be soluble in DMSO.

The solution spectra of the present complexes have been recorded by using standard spectrophotometer in region 350–900 nm. the various electronic spectral parameters were calculated by using partial and multiple regression method. These have been given in the Tables 2–9.

TABLE 8

COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS (F_x and $\%^rF_2$) FOR Nd (III) COMPLEXES

Sl. No.	Parameters Nd–Complexes	F_2	F_4	F_6	F_4/F_2	F_6/F_2	$\%^rF_2$
1.	Nd–OPD–MeAA	329.59	52.24	5.30	0.158489	0.0160890	0.4741
2.	Nd–OPD–EtAA	328.83	51.79	5.27	0.157492	0.0160390	0.7041
3.	Nd–OPD–V	329.57	51.88	5.31	0.157435	0.0161140	0.4769
4.	Nd–OPD–Et.V	329.99	51.87	5.31	0.157188	0.0160880	0.3505
5.	Nd–OPD–2,5 DMB	328.90	52.42	5.29	0.159368	0.0160740	0.6816
6.	Nd–PPD–MeAA	329.08	52.11	5.34	0.158338	0.0162350	0.6263
7.	Nd–PPD–EtAA	329.26	52.10	5.35	0.158249	0.0162410	0.5739
8.	Nd–PPD–V	328.09	52.35	5.30	0.159553	0.0161403	0.9246
9.	Nd–PPD–Et.V	328.57	52.33	5.29	0.159274	0.0161280	0.7828
10.	Nd–PPD–2,5 DMB	328.48	52.10	5.32	0.158618	0.0161960	0.8092
11.	Nd–MPD–MeAA	328.91	52.53	5.29	0.159702	0.0160880	0.6780
12.	Nd–MPD–EtAA	328.86	52.31	5.31	0.159049	0.0161380	0.6917
13.	Nd–MPD–V	329.24	52.02	5.33	0.158000	0.0161770	0.5801
14.	Nd–MPD–Et.V	328.56	52.21	5.30	0.158894	0.0161380	0.7859
15.	Nd–MPD–2,5 DMB	328.60	52.32	5.31	0.159230	0.0161520	0.7736
	*Free ion Nd^{3+}	331.16*	50.71*	5.15*			
	Average**	328.96	52.17	5.31	0.158592	0.0161358	0.6609

The analytical data suggest the following molecular formulae for the present Nd (III) complexes.

(i) Nd $(L_1)(H_2O)_4(Cl)$

where L_1 = MeAA–OPD, MeAA–PPD, MeAA–MPD, EtAA–OPD, EtAA–PPD, EtAA–MPD, Et.V–OPD, Et.V–PPD, Et.V–MPD

(L_1 = Tetradentate bifunctional ligand)

(ii) Nd $(L_2)(H_2O)_4(Cl)_3$

(L_2 = bidentate ligand)

The following equations involving the Slater-Condon Lande's and Judd Ofelt theories to compute energy and intensity parameters resulting from f ↔ f transitions have been employed in the present Nd (III) complexes.

TABLE 9
COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS (E^k AND ζ_{4f}) FOR Nd (III) COMPLEXES.

S. N.	Parametrs Nd(III)–Complexes	E^1 (in cm^{-1})	E^2 (in cm^{-1})	E^3 (in cm^{-1})	ζ_{4f} (in cm^{-1})	$\%r_{\zeta_{4f}}$	β	$b^{1/2}$
1.	Nd–OPD–MeAA	5083.83	23.33	492.93	835.07	5.53	0.9940	0.055
2.	Nd–OPD–EtAA	5059.98	23.38	491.64	849.54	3.90	0.9917	0.064
3.	Nd–OPD–V	5076.58	23.45	491.97	843.68	4.56	0.9940	0.055
4.	Nd–OPD–Et.V	5078.99	23.51	492.70	832.66	5.81	0.9953	0.049
5.	Nd–OPD–2,5 DMB	5081.93	23.19	492.30	832.88	5.78	0.9919	0.063
6.	Nd–PPD–MeAA	5085.42	23.35	490.62	843.66	4.56	0.9925	0.061
7.	Nd–PPD–EtAA	5087.78	23.37	490.77	841.54	4.80	0.9930	0.059
8.	Nd–PPD–V	5073.47	23.12	490.89	843.86	4.54	0.9895	0.072
9.	Nd–PPD–Et.V	5077.48	23.19	491.53	843.63	4.57	0.9909	0.067
10.	Nd–PPD–2,5 DMB	5075.63	23.27	490.29	845.82	4.32	0.9907	0.068
11.	Nd–MPD–MeAA	5083.56	23.15	492.73	831.74	5.91	0.9920	0.063
12.	Nd–MPD–EtAA	5080.99	23.23	491.74	839.64	5.02	0.9919	0.064
13.	Nd–MPD–V	5080.78	23.38	491.21	843.70	4.56	0.9930	0.059
14.	Nd–MPD–Et.V	5074.92	23.23	491.17	841.83	4.77	0.9910	0.067
15.	Nd–MPD–2,5 DMB	5079.32	23.20	491.31	837.58	5.25	0.9910	0.067
	*Free ion Nd^{2+}	5024.00	23.90	497.00	884.00	4.92	0.9922	0.062
	Average**	5073.72	23.29	491.50	840.46			

(a) Slater Condon Lande equation (Energy parameters)

It is give as follow.

$$E_j(F_k, \zeta_{4f}) = E_{oj}(F_k^o, \zeta_{4f}^o) + \sum_{k=2,4,6} \frac{\partial E}{\partial F_k} \Delta F_k + \frac{\partial E}{\partial \zeta_{4f}} k^{\Delta}\zeta_{4f}$$

Where E_{oj} is the zero order energy of the jth level. By substitute the observed energy value of E_j and zero order energy value of E_{oj} and the partial derivatives for the free ion the F_k (K = 2,4,6) and ζ_{4f} have been computed by using partial multiple and regression method[10] for the complexes and have been given in the Tables 5–7. The F_k parameters are also related with another set of energy parameter E^k known as Racah parameter (k = 2,4,6) which have been computed and given in the Table 8.

(b) Bonding Parameter

The nephelauxetic ratio (β) and the bonding parameter ($b^{1/2}$) along with the ratio of F_4/F_2 and F_6/F_2 which infer's some covalency due to complexation have also been given in the Table 8.

TABLE 10

INFRARED VIBRATION FREQUENCIES IN cm^{-1} ALONG WITH THEIR RELATIVE INTENSITIES AND PROBABLE ASSIGNMENTS FOR THE VARIOUS Nd (III) COMPLEXES.

Sl. No.	Assignments	Nd–(MeAA–OPD) 1	Nd–(EtAA–OPD) 2	Nd–(V–OPD) 3	Nd–(Et V–OPD) 4	Nd–(2,5 DMB–OPD) 5	(V–OPD) 6
1.	Lattice water	3390 br	3390 br	3400 br	3400 br	3395 br	—
2.	as –C=N	1625 vs	1620 s	1625 vs	1625 w	1640 vs	1615 s
3.	as C=O	1585 s	1590 m	—	—	—	—
4.	H–D–H bonding+ ring Vibration	1520 vw	1520 m	1520 vs	1520 vs	1515 s	—
5.	as C–O phenolic in Ethyl Vanilline stretching	—	—	—	1460 s	—	—
6.	–O–H deform	1240 m	1245 w	1245 s	1245 w	1245 w	1245 w
7.	C–H aromatic	—	—	1220 s	1220 s	1220 s	1220 s
8.	C–H bond + as (C–O—C)	1140 w	1130 w	1110 s	1110 s	1110 s	1110 m
9.	Co-ordinated H–O–H	810 m	820 m	820 vs	820 s	820 s	—
10.	As metal nitrogen	760 s	755 m	775 s	775 s	760 s	—

TABLE 11

COMPARATIVE STUDY OF THE RELATION ($P \propto b^2T_4$ or $b^2T_4/P_{obs} = K$) FOR HYPERSENSITIVE TRANSITION ($^4G_{5/2} \leftarrow {}^4I_{9/2}$) FOR THE VARIOUS Nd (III) COMPLEXES.

Sl. No.	Nd (III) Complex	$^4G_{5/2}$ $\bar{\nu}$	λ	$b^{1/2}$	b^2	P_{obs}	νb^2	T_4	b^2T_4	b^2T_4/P_{obs}
1	(a) Nd–OPD–MeAA	17235	580.21	0.055	9.15E–06	9.85E–06	0.0053	8.84E–10	5.13E–07	0.0521
	(b) Nd–OPD—EtAA	17227	580.48	0.064	1.68E–05	9.36E–06	0.0097	8.13E–10	4.72E–07	0.0504
	(c) Nd–OPD–V	17316	577.50	0.055	9.15E–06	1.66E–05	0.0053	1.13E–09	6.53E–07	0.0393
	(d) Nd–OPD–EtV	17235	580.21	0.049	5.76E–05	1.32E–05	0.0033	6.30E–10	3.66E–07	0.0277
	(e) Nd–OPD–2,5 DMB	17241	580.01	0.063	1.08E–05	1.35E–05	0.0091	1.03E–09	5.97E–07	0.0443
2	(a) Nd–PPD–MeAA	17230	580.38	0.061	1.38E–05	1.99E–05	0.0080	1.52E–09	8.82E–07	0.0443
	(b) Nd–PPD—EtAA	17227	580.48	0.059	1.21E–05	2.10E–05	0.0070	1.56E–09	9.06E–07	0.0431
	(c) Nd–PPD–V	17235	580.21	0.072	2.69E–05	1.25E–05	0.0156	7.62E–10	4.42E–07	0.0354
	(d) Nd–PPD–EtV	17238	580.11	0.067	2.02E–05	1.18E–05	0.0117	7.48E–10	4.34E–07	0.0368
	(e) Nd–PPD–2,5 DMB	17218	580.79	0.068	2.14E–05	1.72E–05	0.0124	5.55E–10	3.22E–07	0.0187
3	(a) Nd–MPD–MeAA	17266	579.17	0.063	1.58E–05	1.88E–05	0.0091	1.41E–09	8.17E–07	0.0434
	(b) Nd–MPD—EtAA	17241	580.01	0.064	1.68E–05	1.63E–05	0.0097	8.75E–10	5.08E–07	0.0311
	(c) Nd–MPD–V	17218	580.79	0.059	1.21E–05	2.84E–05	0.0070	4.50E–10	2.61E–07	0.0092
	(d) Nd–MPD–EtV	17224	580.59	0.067	2.02E–05	2.29E–05	0.0117	3.98E–10	2.31E–07	0.0101
	(e) Nd–MPD–2,5 DMB	17235	580.21	0.067	2.02E–05	2.52E–05	0.0117	7.42E–10	4.31E–07	0.0171

(c) Judd Ofelt equation (Intensity parameters)

The Judd Ofelt equation for experimentally observed oscillator strength is given as

$$P_{obs} = T_2 \times \nu[U^{(2)}]^2 + T_4\nu[U^{(4)}]^2 + T_6\nu[U^{(6)}]^2$$

The experimental oscillator strength is obtained from the equation given as

$$P_{obs} = 4.318 \times 10^{-9}\int \varepsilon_m \, d\nu$$

where ε_m is the molar extinction co-efficient corresponding to energy in wave number.

The value of $T_\lambda(= 2,4,6)$ parameter have been computed from the above equation where the values of reduced matrix elements have been taken from carnall *et al*[1]. The values of T_λ parameter's are considered to be characteristic of particular lanthanide complexes and by definition $T_\lambda > 0$ observed in Nd (III) complexes suggests that the Judd-Ofelt relation is applicable in the present form. The observed and computed value of oscillator strength along with T_λ value have been given in the Tables 2-4 and 12.

TABLE 12
COMPUTED VALUES OF T_λ PARAMETERS FOR THE VARIOUS Nd (III) COMPLEXES

S.No.	Parameters Nd^{3+} Complexes	$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6
1	a. Nd–MeAA–OPD	2.95	8.84	5.50	1.6
	b. Nd–MeAA–PPD	7.11	15.20	7.31	2.0
	c. Nd–MeAA–MPD	6.65	14.10	10.90	1.3
2	a. Nd—EtAA–OPD	2.80	8.13	7.92	1.0
	b. Nd—EtAA–PPD	7.58	15.60	5.85	2.7
	c. Nd—EtAA–MPD	7.19	8.75	9.30	1.0
3	a. Nd–V–OPD	6.35	11.30	4.86	2.3
	b. Nd–V–PPD	5.28	7.62	4.52	1.7
	c. Nd–V–MPD	16.90	4.50	17.70	0.3
4	a. Nd–Et. V–OPD	5.81	6.30	3.57	1.8
	b. Nd–Et. V–PPD	4.54	7.48	5.90	1.3
	c. Nd–Et. V–MPD	14.00	3.98	19.40	0.2
5	a. Nd–2.5 DMB–OPD	4.31	10.30	4.03	2.5
	b. Nd–2.5 DMB–PPD	8.72	5.55	4.80	1.2
	c. Nd–2.5 DMB–MPD	13.40	7.42	11.50	0.6

RESULTS AND DISCUSSIONS

In the present Nd (III) complexes the solution spectra yields ten bands *viz.*

$^2P_{1/2} \leftarrow {}^4I_{9/2}$, $^4G_{11/2} \leftarrow {}^4I_{9/2}$, $^4G_{9/2} \leftarrow {}^4I_{9/2}$, $^2G_{9/2} \leftarrow {}^4I_{9/2}$, $^4G_{7/2} \leftarrow {}^4I_{9/2}$,
($\sim$23148 cm^{-1}) ($\sim$21598 cm^{-1}) ($\sim$21229 cm^{-1}) ($\sim$19531 cm^{-1}) ($\sim$19157 cm^{-1})

$^4G_{5/2} \leftarrow {}^4I_{9/2}$, $^4F_{9/2} \leftarrow {}^4I_{9/2}$, $^4F_{7/2} \leftarrow {}^4I_{9/2}$, $^4F_{5/2} \leftarrow {}^4I_{9/2}$, $^4F_{3/2} \leftarrow {}^4I_{9/2}$
($\sim$17240 cm^{-1}) ($\sim$14663 cm^{-1}) ($\sim$13260 cm^{-1}) ($\sim$12315 cm^{-1}) ($\sim$11428 cm^{-1})

The energies of the bands observed have been reacalculated by applying the Slater-Condon Lande's equation. The comparison of the observed and the recalculated values of the various energy levels (Tables 5–7) shows the average r.m.s. deviation of the order ± 43 cm^{-1} to ± 91 cm^{-1} which indicates good results even though the radial eigen function has been assumed to be hydrogenic and also best fit for the partial regression method. The red shifts in all the energy bands from that of free ion support the complexation.

The various energy parameters $F_k(K = 2,4,6)$ i.e Slater Condon parameter, β Nephelauxetic ratio, ζ_{4f} Lande's parameter and $b^{1/2}$ bonding parameter (extent of covalency in the complexes) and $\%^rF_2$ have been reported in the Table 8. In the complexes of Nd (III) the decrease in parametric value of F_k, E^k and ζ_{4f} indicates the decrease in inter-electronic repulsion and spin-orbit interactions which suggest expansion of the central metal ion orbital on complexation and is in accordance with the theory of f ↔ f transition reported earlier.[2–7]

The average value of F_4/F_2 for Nd(III) complexes (0.15859) is larger than those calculated by using Hartee and Fock[12] method (= 0.13), but they are nearer to the value for free ion (= 0.1531). The same trend has been observed for the ratio F_6 / F_2(= 0.016).

The values of nephelauxetic ratio $\beta < 1$ and bonding parameter $b^{1/2}$ indicate covalent bonding in Nd (III) complexes. The small value of $b^{1/2}$ and little variation in it suggest that the 4f orbitals are very slightly involved in the bonding of lanthanide complexes. Since lanthanide ion complexes are kinetically less stable and complexation reaction is just similar to solvation reaction ($MgCl_2 \cdot 6NH_3$) of alkaline earth metal ion so the present study finds a very little covalency in the metal-ligand bonding of the complexes. Thus the present spectral characterizations of the complexes are found to be much more important as these complexes involve a very little crystal field.

Spectral Intensities

The intensities of the observed bands have been given in terms of oscillator strength (P). The observed values of oscillator strength have been compared with those of the calculated ones (using Judd-Ofelt equation). The r.m.s. deviation varies within the range of 1.04×10^{-6} to 3.39×10^{-6} has been reported in the

Tables (2–4). The small deviation for the calculated and observed (P) values suggests the validity of Judd-Ofelt equation for f <–> f transitions for the complexes under study.

The ratio T_4 / T_6 is fairly constant and has been reported along with T_2 in the Table 11. In the present study, T_4 / T_6 ratio suggests qualitatively to have a common symmetry is slightly varied and hence the various complexes can be grouped according to the ratio value.

The hypersensitive transition (which is sensitive to environmental change) ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ exhibits (Table 11) the increase in intensity with increase in covalency of the complexes. The hypersensitivity has been found to be proportional to nephelauxetic ratio β. It also decreases with decreasing frequency of the transition. This is in confirmation of the earlier observation reported by Peacock[11].

In the present series of Nd (III) complexes the following inferences have been derived with respect to their spectral characterizations described in terms of various spectral parameters.

(a) Order in terms of ζ_{4f}

The trend in the decrease of ζ_{4f} values or increase in % $^r\zeta_{4f}$ value for the Nd^{3+} complexes in comparison to free ion value (= 884.00 cm^{-1}) varies between 3.96 to 5.91 and has been given as follows.

(i) β keto imine complexes derived from methyl acetoacetate and ethyl acetoacetate with various phenylenediamine.

(b) MeAA > EtAA

$$\begin{array}{ll} \text{for (c) Nd–MeAA} & \multirow{2}{*}{\Bigg]\ \text{trend is}} \quad \text{MPD > OPD > PPD} \\ \text{(d) Nd–EtAA} & \quad\quad\quad\quad\quad \text{MPD > PPD > OPD} \end{array}$$

(ii) Schiff base complexes derived from ethyl vanilline, veratraldehyde and 2,5-dimethoxy benzaldehyde with various phenylenediamine has found in the following order.

(f) In terms of amine is

OPD > MPD > PPD

this may be probably due to steric hindrance.

(b) The order in terms of $b^{1/2}$

β-keto imine metal complexes derived from methyl and ethyl β keto esters (CO) and o^-, m^- and p^- phenylenediamine shows following trends

CO–PPD > CO–OPD > CO–MPD
CO–OPD > CO–PPD > CO–MPD

When the carbonyl compounds used are veratraldehyde, ethyl vanilline and 2,5-dimethoxy benzaldehyde.

(c) Order in terms of T_4 / T_6 ratio with respect to various phenylenediamine

(i) PPD > OPD > MPD

When the carbonyl compound used for the formation of ligands are methyl and ethyl β keto-ester

(ii) OPD > PPD > MPD

When the carbonyl compounds used for the formation of ligands are veratraldehyde, ethyl vanilline and 2,5-dimethoxy benzaldehyde.

IR Studies

The IR spectra of these complexes show broad and medium intensity band in the region 3400–3300 cm^{-1} which is due to lattice water. Bending and rocking modes of vibration of water about 1020 cm^{-1} and 835 to 820 cm^{-1} respectively are further activated by coordination with metal ion examined by earlier worker[13]. Medium to sharp and very sharp band appearing in the region 1245 cm^{-1} in the complexes are due to O–H deformation.

A weak to strong and very sharp band in the region 1615 cm^{-1} to 1660 cm^{-1} is due to C=N stretching vibration in the Nd (III) complexes have also been reported[14]. The shift of C–O stretching vibration of the phenolic part of ethyl vanilline schiff-bases have been observed at 1435 to 1460 cm^{-1} supports the coordination of oxygen with metal. A vibration mode appearing in the 820 to 770 cm^{-1} and absent in the respective ligands is assigned to metal nitrogen bond[15,16].

Thus the nitrogen of imine group and oxygen of phenolic group are coordinated and the analytical data of the complexes suggest that the complexes may be assigned the formula

(i) $[M(L_1)(H_2O)_4(Cl)]$ and (ii) $[M(L_2)(H_2O)_4Cl_3]$

ACKNOWLEDGEMENTS

The authors are highly thankful to U.G.C. New Delhi for financial support in carrying out the research project. They extended their thanks to Sh. B.K. Gupta and other learned colleagues of the Department of Chemistry, Dungar College, Bikaner who have imparted their full co-operation and interest in the work.

REFERENCES

1. W.T. Carnall, P.R. Fields and B.G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
2. B.R. Judd, *Phys. Rev.*, **127**, 750 (1962).
3. G.S. Ofelt, *J.Chem. Phys.*, **37**, 511 (1962).
4. S.P. Tandon and P.C. Mehta, *J. Chem. Phys.*, **52**, 4313 (1970).
5. S.N. Misra and G.K. Joshi, *Indian J. Pure and Applied Phys.*, **19**, 279 (1981).
6. S.S.L. Surana, Megh Singh and S.N. Misra , *J. Inorg. Nucl. Chem.*, **42**, 61 (1980).

7. R.D. Peacock, *J. Chem. Soc. A*, 2028 (1971); molec. Phys., **25**, 817 (1973); *Chem Phys. Lett.*, **16**, 590 (1973).
8. Cyril H. Gaulden, Method of Statistical Analysis, Asia Publishing House, Bombay, Ch.8, p. 134 (1964).
9. M. Shameen Ansari and N.A. Ahmed, *J. Inorg. Nucl. Chem.*, **38**, 1232 (1976).
10. Vogel, A Text Book of Pract. Org. Chem. (Ed. B.S. Furnished et al., edition, IV, ELBS, 661.
11. R.D. Peacock, Structure and Bonding, Vol. 22, Springer-Verlag, Berlin, p. 88 (1975).
12. A.G. Freeman and R.E. Watson, *Phys. Rev.*, **127**, 2053 (1962).
13. J. Fujita, K.Nakamoto and Kobayashi, *J. Am. Chem. Soc.*, **78**, 3963 (1956).
14. R.A. Henry and W.M. Dehn, *J. Am. Chem. Soc.*, **71**, 2297 (1949).
15. C.L. Garg, K.C. Narasimahan and B.N. Tripathi, *J. Inorg. Chem.*, **33**, 3847 (1971).
16. S.L. Gupta, R.C. Saxena, Om Prakash and A.N. Pandey, *Indian J. Pure Appl. Phys.*, **17**, 407 (1979).

(*Received*: 1 March 1992; *Accepted*: 5 February 1993) AJC–543