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Electronic Spectral Study and Thermodynamic Characterization of Doped Nd(III) Ions in various Semicarbazones

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The saturated organic ligand environment produced by various semicarbazones, around Nd(III) ion, has been studied with respect to hypersensitive transition involved in doped system. The various energy parameters such as Racah (E^k), Slater-Condon (F_k), Lande parameter (ζ_{4f}) and the intensity parameters such as oscillator strength (P), Judd-Ofelt parameter (T_λ) have been computed using partial and regression method. The bonding parameter ($b^{1/2}$) and nephelauxetic ratio (β) have also been evaluated.

Key Words: Semicarbazones, Doped Nd(III), Electronic.

INTRODUCTION

The coordination chemistry of semicarbazones has been of vital importance due to their biological and analytical applicability[1, 2]. The energy and intensity parameters of lanthanon chelates with variety of ligands have widely been studied for the interpretation of sharp line like bands arising from the transition among different levels of $4f^n$ configuration[3, 4]. Doped study of certain systems finds immense application[5–7], therefore, this paper deals with the study of various energy and electronic parameters, *viz.*, Judd-Ofelt intensity (T_λ), Slater-Condon (F_λ), Lande's (ζ_{4f}) intensity of hypersensitive band ($^3P_2$) and Racah's (E_k) as well as bonding parameters $b^{1/2}$ for Nd(III) ion doped in alcoholic saturated solution of semicarbazones derived from carbonyl compounds. In these studies, a saturated solution in alcoholic media has been made by dissolving some semicarbazones derived from carbonyl compounds at room temperature and a constant amount of Nd(III) chloride has been added to each of the solutions. Spectrophotometry has been used for the characterization and determination of electronic parameters for Nd(III) ion doped in saturated alcoholic solution. Several bands including $^4G_{5/2}$ are characterized for Nd(III) ion in the visible region and the change in the intensity of these bands is indicated by red shift caused by the change in coordination environment around the ion resulting from $f \longleftrightarrow f$ transition in lanthanides.

EXPERIMENTAL

Synthesis of ligands: Seven semicarbazones were synthesized by refluxing semicarbazide in equimolar ratio with 3,4-dimethoxybenzaldehyde, 2,5-dimethoxybenzaldehyde, benzilidine acetophenone, benzophenone, *m*-nitro benzophenone, acetophenone and benzaldehyde respectively for 5 to 6 h at temperature 70–80°C. Each compound was purified and crystallized in ethanol.

Preparation of saturated ligands solution contain doped Nd(III) ion: The saturated solutions of 3,4-dimethoxybenzaldehyde semicarbazone (3,4-DMB-SC), 2,5-dimethoxybenzaldehyde semicarbazone (2,5-DMB-SC), benzildine-acetophenone semicarbazone (BAP-SC), benzophenone semicarbazone (BP-SC), *m*-nitrobenzophenone semicarbazone (m-NB-SC), acetophenone semicarbazone (AP-SC) and benzaldehyde semicarbazone (B-SC) were prepared by dissolving in ethanol separately and 0.014 M of $NdCl_3 \cdot 6H_2O$ were added to each of the solutions.

The solution spectra of these systems were recorded by using standard spectrophotometer (Spectronic-20) in the visible region. The calculation for various electronic parameters was made by computerized statistical method reported earlier[8]. All chemicals used were of AR grade, $PrCl_3 \cdot 6H_2O$ (99.9% purity) supplied by Indian Rare Earths (India).

RESULTS AND DISCUSSION

The value of energies (E) for peaks of various transitions and the parameters of all the compounds summarized in Tables 1 and 2. The decrease in values of the Slater-Condon, Lande and the Racah parameters of the doped system as compared to those of the free metal ion may be attributed to chelation of Nd(III) ion with the ligand present in the surrounding environment and this in turn indicates the expansion of metal orbital, which is in accordance with $f \longleftrightarrow f$ transitions. The decrease in the value of the Lande parameter (ζ_{4f}) is more than the Slater-Condon (F_k) parameter indicating that the ligand affects the spin orbit coupling more than electrostatic repulsion. The order of Slater-Condon parameter is found to be $F_2 > F_4 > F_6$. The observed values of F_6/F_2 are less than F_4/F_2. The solution spectra are analyzed by resolving each band into Gaussian curve shape to enable evaluation of oscillator strength. The observed oscillator strength has maximum contribution from the induced electric dipole mode in comparison to magnetic dipole and electric quadripole modes. Comparing the values of energies with corresponding energy level in free metal ion has identified the bands for the different transitions.

Nephelauxetic ratio has been found less than one for all the complexes; this reflects the mixing of metal-ligand orbitals and the covalent nature of metal-ligand bond may be concluded. To establish the validity of the theory given by Judd-Ofelt[7] with reference to the result obtained for the systems. T_2, T_4 and T_6 are Judd-Ofelt parameters (T) that have been further used to classify the symmetry environment around Nd(III) ion. The values of oscillatory strength were calculated. The r.m.s. deviations with respect to oscillator strength were in the acceptable range.

TABLE-1

COMPUTED VALUES OF ENERGY (cm^{-1}) OF OSCILLATOR STRENGTH FOR Nd(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS SEMICARBAZONES OF CARBONYL COMPOUNDS

Compound	$^2P_{1/2}$		$^4G_{11/2}$		$^4G_{9/2}$		$^2G_{9/2}$		$^4G_{7/2}$	
	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
Nd-3,4-DMB-SC	0.600	0.590	0.950	0.180	2.690	1.420	0.530	0.360	4.210	3.120
Nd-2,5-DMB-SC	1.230	1.460	0.620	0.230	4.380	2.450	1,380	0.550	7.590	6.120
Nd-BAP-SC	1.120	1.150	0.510	0.180	3.430	1.920	1.110	0.430	5.710	4.930
Nd-BP-SC	0.960	0.910	0.430	0.220	3.160	1.960	0.770	0.460	5.910	4.590
Nd-MNB-SC	0.930	0.940	0.470	0.210	3.010	1.900	0.830	0.450	4.800	4.430
Nd-AP-SC	0.950	1.200	0.470	0.290	4.480	2.500	0.870	0.600	6.760	5.570
Nd-B-SC	1.120	1.370	1.720	0.380	5.150	3.100	0.780	0.770	7.720	6.720

Compound	$^4G_{5/2}$		$^4F_{9/2}$		$^4F_{7/2}$		$^4F_{5/2}$		$^4F_{3/2}$		σ_{rms}
	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	
Nd-3,4-DMB-SC	11.000	12.200	0.790	0.440	4.210	3.760	2.520	4.950	1.700	2.130	1.050
Nd-2,5-DMB-SC	23.470	25.100	1.770	0.390	2.570	2.400	2.820	6.170	3.740	4.520	1.530
Nd-BAP-SC	19.900	21.300	1.180	0.300	1.730	1.790	2.100	4.780	2.810	3.540	1.180
Nd-BP-SC	18.600	20.300	1.100	0.500	3.940	3.980	3.020	6.010	2.000	3.080	1.300
Nd-MNB-SC	16.600	18.100	1.190	0.460	3.840	3.610	2.800	5.780	2.650	3.130	1.170
Nd-AP-SC	17.900	19.600	2.910	0.640	5.070	5.220	5.070	7.950	2.970	4.070	1.510
Nd-B-SC	21.400	24.200	1.170	0.900	7.620	7.540	5.750	10.400	3.440	4.820	1.960

TABLE-2

COMPUTED VALUES OF ENERGY (F_k, ζ_{4f}, E_k, %r ζ_{4f}, β and $b^{1/2}$) Nd(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS SEMICARBAZONES OF CARBONYL COMPOUNDS

Compound	F_2 (in cm^{-1})	F_4 (in cm^{-1})	F_6 (in cm^{-1})	% rF_2	ζ_{4f} (in cm^{-1})	% r ζ_{4f}	E^1 (in cm^{-1})	E^2 (in cm^{-1})	E^3 (in cm^{-1})	β	$b^{1/2}$
Nd-3,4-DMB-SC	330.770	50.36	5.30	0.1170	874.42	1.0830	5049.61	24.20	490.54	0.9986	0.0263
Nd-2,5-DMB-SC	330.900	49.95	5.33	0.0774	873.17	1.2247	5047.54	24.03	490.82	0.9969	0.0388
Nd-BAP-SC	331.000	50.20	5.33	0.0156	873.69	1.1660	5045.01	24.09	491.13	0.9976	0.0346
Nd-BP-SC	330.560	50.46	5.30	0.1784	880.21	0.4278	5043.22	24.26	489.50	0.9979	0.0316
Nd-MNB-SC	331.140	49.77	5.33	0.0054	882.14	0.2102	5040.64	24.35	489.53	0.9987	0.0253
Nd-AP-SC	330.770	50.36	5.30	0.1170	873.69	1.1660	5045.01	24.09	491.13	0.9976	0.0346
Nd-B-SC	331.140	49.77	5.33	0.0054	882.14	0.2102	5040.64	24.35	489.53	0.9967	0.0253

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RESEARCH

In search of the truth and in order to provide and arouse,
May you possess an untamed desire to discover and invent!
In the quest for knowledge and the love for perfection,
May you continue to observe, analyze, deduce and conclude!
In the depth of the heart and for the pleasure of the mind,
May you preserve and exercise the zeal and the willingness,
To plan, observe and record, and to devise and modify,
To question and contemplate, to propose and accept or reject!
May you remain unperturbed when the challenges abound!
May you not submit or give in when the endeavours fail!

May you soon reclaim and start afresh to try again!
And may you as always be ready for the serendipity!

May you not distort or lie, suppress or exaggerate!
May you not rush or delay to present and disseminate!
May you not be driven by ego and the glory of the self!
And may you excite and delight as the horizon extends!

Behold! The children of Adam created in the best of the mould,
Achieving the heights, opening the mind and nourishing the soul!
As they engage in discovering the signs in nature and within!
And sinking to the lowest of the low as they reject and deny!

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