Asian Journal of Chemistry Vol. 15, No. 1 (2003), 466–470

Spectrophotometric Characterisation of Doped Pr(III) Ion in Saturated Alcoholic Solution of Some Thiosemicarbazone Derived from Carbonyl Compounds

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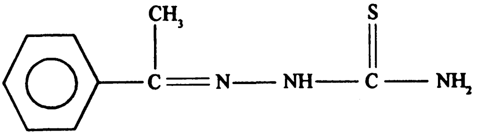
The stereo-environment of doped Pr(III) ion in saturated solution of some thiosemicarbazones of carbonyl compounds in alcoholic media has been discussed on the basis of various electronic spectral parameters. The various electronic parameters, *viz.*, Judd-Ofelt intensity parameter (T_λ), Slater-Condon (F_k), Landés (ζ_{4f}), intensity of hypersensitive band ($^3P_2$) for Racah's (E_k) as well as bonding parameters $b^{1/2}$ for Pr(III) ion doped in alcoholic saturated solution of thiosemicarbazones derived from thiosemicarbazide and acetophenone, *o*-hydroxy acetophenone, *m*-hydroxy acetophenone, *o*-amino acetophenone, *m*-amino acetophenone and benzaldehyde.

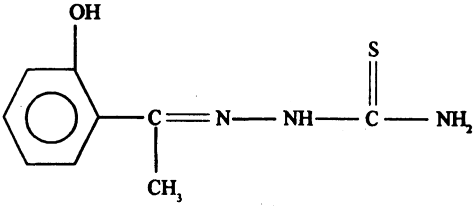
Key Words: Spectrophotometric, Doped Pr(III) ion, Thiosemicarbazone.

INTRODUCTION

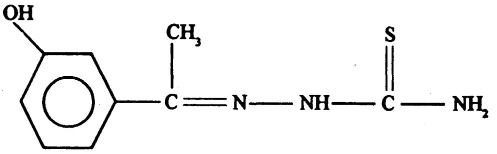
In the present discussion the study has been made on the basis of utility of some lanthanide substituted thiosemicarbazones of carbonyl compounds, owing to their immense medicinal application[1–3], on the basis of Judd-Ofelt and Slater-Condon theory. Since in the field of science and technology the doped study of certain systems finds immense application[4–9], therefore, on the basis of Judd-Ofelt[10–12] intensity as well as other electronic spectral parameters a correlation of $f \leftrightarrow f$ transition for Pr(II) ion doped in saturated solution of some thiosemicarbazones of carbonyl compounds and the stereo-environment around Pr(III) ion has been attempted. A saturated solution in alcoholic media has been made by dissolving some thiosemicarbazones derived from carbonyl compounds at room temperature (30 ± 2°C) and a constant amount of Pr(III) chloride has been added to each of the solutions. Characterisation of some of the electronic parameters for Pr(III) ion doped in saturated alcoholic solution of these compounds was made spectrophotometrically. On the basis that Pr(III) ion yields four bands in visible region, viz., $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$, 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 $f \leftrightarrow f$ transition in lanthanides.



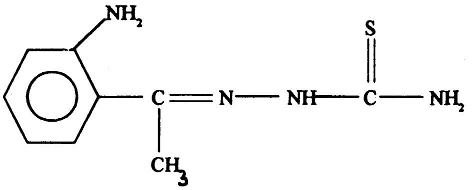
(1) Acetophenone thiosemicarbazone.



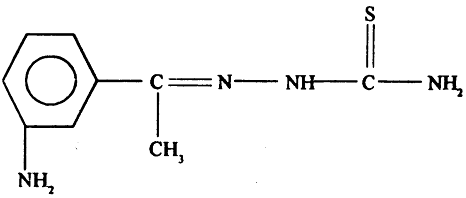
(2) *o*-Hydroxy acetophenone thiosemicarbazone.



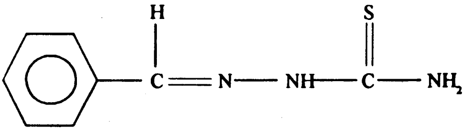
(3) *m*-Hydroxy acetophenone thiosemicarbazone.



(4) *o*-Amino acetophenone thiosemicarbazone.



(5) *m*-Amino acetophenone thiosemicarbazone.



(6) Benzeldehyde thiosemicarbazone.

EXPERIMENTAL

Equal molar concentration of thiosemicarbazide and acetophenone, *o*-hydroxy acetophenone, *m*-hydroxy acetophenone, *o*-amino acetophenone, *m*-amino acetophenone and benzaldehyde etc. were refluxed for 5 to 6 h at temperature 70–80°C; thiosemicarbazones derived as such were crystallized and various saturated solutions[18–21] of above compounds and 0.014 M of $PrCl_3 \cdot 6H_2O$ (99.9% purity, supplied by Indian Rare Earths, Udyogmandalam, Kerala) were added to each of the solutions. The solution spectra of these systems were recorded by using standard spectrophotometer[17–19] (Spectronics-20) in the visible region. The calculation for various electronic parameters was made by computerized statistical method reported earlier[18, 19].

RESULTS AND DISCUSSION

The analytical data of thiosemicarbzones are given in Table-1. The absorption at 1600 cm^{-1} in the thiosemicarbazones can be attributed to ν(C=N) of imine nitrogen which is in agreement with early reports[13, 14]. The bands observed in 1630–1130 cm^{-1} region are assigned to ν(C=S)[15, 16]. The computed values of various parameters have been given in Tables 2 and 3. The present study shows that the $f \leftrightarrow f$ transition resulting from spin orbit interaction in Pr(III) is due to interaction with the ligand present in the saturated solution which is remarkably manifested in terms of change in the energy of various electronic parameters. The decrease in computed values of spin orbit interaction parameter (ζ_{4f}), oscillator strength of $^3P_2$ band, Judd-Ofelt parameter (T_λ) and Slater-Condon parameter (F_k) in comparison to free ion values clearly reflects symmetry change around the metal ion in the solution. The T_4/T_6 ratio reflects the change in stereo-environment around the metal ion present in the solution and thereby change in coordination number. Therefore, the change in the surrounding environment around the metal ion involving the suitable interaction between the metal ion and ligand has been well characterized by decrease in the various interelectronic replusions and spin-orbit interactions.

TABLE-1
ANALYTICAL DATA (%) OF THIOSEMICARBAZONES

Compounds	C	H	N	S
1.	55.95	5.69	21.76	16.58
2.	51.67	5.26	20.09	15.31
3.	51.67	5.26	20.09	15.31
4.	51.92	5.76	26.92	15.38
5.	51.92	5.76	26.92	15.38
6.	53.63	5.02	23.46	17.87

The parametric values provide useful information regarding the coordination behaviour of Pr(III) ion. The coordination behaviour varies as the change in ratio of T_4/T_6 takes place. Similar values indicate the similar stereo-environment around Pr(III) due to solute-interaction present in the solution.

TABLE-2

COMPUTED VALUES OF ENERGY (cm^{-1}) OF OSCILLATOR STRENGTH T_λ AND T_4/T_6 FOR Pr(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS THIOSEMICARBAZONES OF CARBONYL COMPOUNDS

Compounds	$^3P_2 \times 10^{-6}$		$^3P_1 \times 10^{-6}$		$^3P_0 \times 10^{-6}$		$^1D_2 \times 10^{-6}$		$T \times 10^{-10}$			T_4/T_6
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	T_2	T_4	T_6	
1.	24.40	24.44	10.50	10.50	6.32	6.29	6.21	6.21	–223	23.2	73.9	0.31
2.	29.50	29.50	10.90	10.90	5.94	5.92	7.23	7.23	–319	23.2	90.7	0.26
3.	31.90	31.90	10.60	10.60	5.60	5.57	7.49	7.49	–422	22.5	98.6	0.23
4.	26.60	26.60	9.36	9.36	4.52	4.50	5.87	5.87	–430	19.1	82.0	0.23
5.	29.00	29.00	9.48	9.48	4.73	4.71	5.93	5.93	–579	19.7	89.6	0.22
6.	30.00	30.00	9.76	9.76	5.26	5.23	6.09	6.09	–622	20.7	93.6	0.22

TABLE-3

COMPUTED VALUES OF F_k, ζ_{4f}, E_k, % γF_2, β AND $b^{1/2}$ Pr(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS THIOSEMICARBAZONES OF CARBONYL COMPOUNDS

Compounds	F_2	F_4	F_6	% rF_2	ζ_{4f}	% $r\zeta_{4f}$	E^1	E^2	E^3	β	$b^{1/2}$
Pr^{3+} Free Ion	322.09	44.46	4.87	—	738.00	—	4729.00	24.78	478.13	—	—
1.	309.39	42.71	4.67	3.94	719.11	2.95	4542.42	23.76	459.26	0.9605	0.1404
2.	311.81	43.04	4.71	3.19	662.39	3.19	4577.95	23.94	462.85	0.9680	0.1263
3.	312.16	43.09	4.71	3.08	660.11	10.91	4583.19	23.97	463.38	0.9691	0.1241
4.	312.70	43.16	4.72	2.91	654.88	11.62	4591.04	23.01	464.17	0.9708	0.1207
5.	311.70	43.03	4.70	3.22	671.70	9.35	4576.41	23.93	462.69	0.9677	0.1269
6.	313.16	43.23	4.73	2.77	629.27	15.07	4597.80	24.05	464.86	0.9722	0.1177

The values of Slater-Condon parameter (F_k) in the present system decrease from free ion value and show close similarity whereas Lande's parameter (ζ_{4f}) which shows spin-orbit interaction has been found to show much variation. This shows that spin-orbit interactions in $f \leftrightarrow f$ transition are much more affected in comparison to inter-electronic interaction. The intensity of hypersensitivity band also shows similar trend.

The study provides useful information regarding stereo-environment around Pr(III) ion as significantly exhibited by T_4/T_6 ratio. The nephelauxetic ratio as indicated by the values of $b^{1/2}$ also reflects some bonding character in the form of change in stereo-environment around the central metal ion.

The various other electronic parameters reported in Tables 2 and 3 have their usual significance as reported earlier by Soni *et al.*[20, 21].

ACKNOWLEDGEMENTS

Authors are thankful to Prof. R.P. Mathur, H.K. Pandey and Anil Gupta, Department of Chemistry, Dungar College, Bikaner for their valuable suggestions and help. One of the authors K.P. Soni is also thankful to University Grants Commission for financial assistance.

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(*Received*: 21 August 2002; *Accepted:* 28 September 2002) AJC-2863