

NOTE

Electronic Spectral Studies on Nd³⁺ Doped Sulphonanilide System Part II

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Six 3-carboxy/carboalkoxy-4-hydroxy-5-nitro-N-alkyl benzene-sulphonanilide (alkoxy = methoxy and ethoxy, alkyl = methyl and ethyl) have been synthesised. Their interaction with Nd³⁺ ion in the form of doped model has been discussed in terms of Slater-Condon, Landé and Judd-Ofelt parameters. The involvement of 4f-orbitals in the Nd³⁺ doped systems including deviation in symmetry has been discussed.

It has been well established that sulphur-containing ligands have versatile pharmacological activity, which increases on complexation with metal ions¹. Most important of them are sulphonanilide derivatives which have immense anti-bacterial activity. The complexing behaviour of lanthanide ions has not been studied extensively as compared to the transition metal ions. In continuation with our studies, we have undertaken the synthesis of sulphonanilides and an attempt has been made to characterize Nd³⁺ doped sulphonanilides on the basis of Judd-Ofelt, Slater-Condon and other theories. The complexing ability with respect to thermodynamic stability is poor in case of lanthanide complexes; so doped lanthanide ion in saturated solution of ligand has been undertaken as a system for electronic spectral study. The present work infers covalency in metal-ligand bonding in the systems undertaken. The study also provides some useful information regarding metal-ligand interaction and change in symmetry around lanthanide ion.

Sulphonanilides (Fig. 1) have been synthesised by the method reported in the literature^{2,3}.

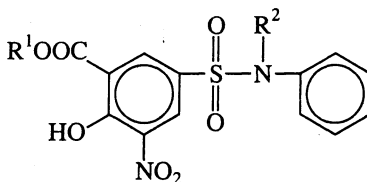


Fig. 1

where

L	L ₁	L ₂	L ₃	L ₄	L ₅	L ₆
R ¹	H	CH ₃	C ₂ H ₅	H	CH ₃	C ₂ H ₅
R ²	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅

The IUPAC names of ligands are as follows:

- L₁ 3-Carboxy-4-hydroxy-5 nitro-N-methyl benzenesulphonanilide
- L₂ 3-Carbomethoxy-4-hydroxy-5 nitro-N-methyl benzenesulphonanilide
- L₃ 3-Carboethoxy-4-hydroxy-5 nitro-N-methyl benzenesulphonanilide
- L₄ 3-Carboxy-4-hydroxy-5 nitro-N-ethyl benzenesulphonanilide
- L₅ 3-Carbomethoxy-4-hydroxy-5 nitro-N-ethyl benzenesulphonanilide
- L₆ 3-Carboethoxy-4-hydroxy-5 nitro-N-ethyl benzenesulphonanilide

Preparation of Doped Systems: In the present work six systems of lanthanide ion doped in saturated solutions of these ligand have been prepared by adding 0.1 g NdCl₃·6H₂O salt (supplied by Indian Rare Earth Ltd.) per 10 mL of ligand solution. The solution spectrum of each system has been recorded in the range 350–950 nm by using standard spectrophotometer.

The values of various spectral parameters including oscillator strength, energy, Slater-Condon nephelauxetic ratio, Landé and bonding parameters, etc. have been reported in Table-1. The observed change in the various energy and intensity parameters shows that the $f \leftrightarrow f$ transition resulting from spin-orbit interaction in Nd³⁺ ion is due to the interaction of f-orbital with the ligand present in the saturated solution. The calculation of various parameters involves Slater-Condon-Landé and Judd-Ofelt theories as reported by earlier workers⁴⁻⁶. Red-shift has been observed in all energy bands as compared to the free ion thereby establishing the validity of Slater-Condon-Landé theory. The r.m.s. deviation in energy varies from ± 64.14 to ± 91.95 in all the systems. The intensities of observed bands have been given in terms of oscillator strength (P). The r.m.s. deviation is very small varying from ± 1.83 to 2.45 suggesting the validity of Judd-Ofelt theory for $f \leftrightarrow f$ transition. T_4/T_6 value varies from 1.33 to 1.60. It indicates variation in symmetry around doped Pr³⁺ ion in saturated ligand solution. The % rF_2 varies from 1.39 to 2.03 indicating decrease in inter-electronic repulsion between metal and ligand. The values of nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) with little variation in it suggests that the 4f-orbitals are very slightly involved in the bonding in saturated solutions doped with Pr³⁺ ion. The % $r\zeta_{4f}$ varies from 3.31 to 6.38 indicating decrease in spin-orbit interaction in metal-ligand bonding.

Other parameters have also been computed so as to indicate variation in electronic-spectral characterization.

TABLE-1
VALUES OF VARIOUS PARAMETERS FOR Nd³⁺ DOPED SULPHONANILIDES

Ligand	T ₄ /T ₆	F ₂	F ₄	F ₆	ζ _{4f}	% r(C) _{4f}	% rF ₂	β	b ^{1/2}	E _{exp} *	P _{exp} × 10 ⁶ *
L ₁	1.60	325.78	54.10	5.26	827.62	6.38	1.63	0.9825	0.093	17241	24.80
L ₂	1.44	326.23	53.11	5.23	843.71	4.56	1.49	0.9839	0.089	17241	23.30
L ₃	1.51	324.44	53.82	5.19	854.78	3.31	2.03	0.9785	0.103	17241	25.00
L ₄	1.40	325.43	53.71	5.24	836.27	5.39	1.73	0.9814	0.096	17182	31.30
L ₅	1.33	326.56	53.27	5.29	836.98	5.32	1.39	0.9849	0.086	17182	30.00
L ₆	1.47	326.49	53.08	5.27	846.15	4.28	1.41	0.9847	0.087	17241	20.02

*values of hypersensitive peak ⁴G_{5/2}

ACKNOWLEDGEMENTS

Authors are thankful to Dr. G.K. Joshi and Dr. H.K. Pandey of Department of Chemistry, Dungar College, Bikaner for their valuable suggestions and help.

REFERENCES

1. L. Bhal, J.P. Tandon and S.K. Sinha, *Curr. Sci. (India)*, **55**, 566 (1984).
2. Vertkes Migradichian, *Organic Synthesis*, Vol. 2, Reinhold Publishing Corporation, New York, p. 1961 (1957).
3. S.S. Shrimali, N.D. Sharma, S. Kumar and B.C. Joshi, *Rev Roum. Chim.*, **23**, 613 (1978).
4. B.K. Gupta, G.K. Joshi and P.R. Bhati, *Indian J. Pure and Appl. Phys.*, **28**, 525 (1990).
5. Neelam Naulakha, K.P. Soni and P.R. Bhati, *Asian J. Chem.*, **12**, 151 (2000).
6. M.P. Goutam, Ashok Yadav and S.M. Limaye, *Asian J. Chem.*, **10**, 415 (1998).

(Received: 2 January 2001; Accepted: 4 May 2001)

AJC-2345