

Printed in India.

Analytical Chemistry

## SPECTRAL, MAGNETIC AND ANTIFUNGAL ACTIVITIES OF SOME NOVEL LANTHANON CHELATES OF SCHIFF BASES CONTAINING OXYGEN AND NITROGEN DONOR ATOMS

C. P. GUPTA, VIBHA SURI, R. P. MATHUR and R. K. MEHTA

Department of Chemistry, University of Jodhpur, Jodhpur, India

(Received 3 September 1981)

Lanthanon chelates of the type  $[LnL_3]$  and  $[LnL_3']$  where  $Ln = La(III)$ ,  $Pr(III)$ ,  $Nd(III)$ ,  $Sm(III)$ ,  $Ho(III)$  and  $Er(III)$  and  $L =$  acetylacetonethiosemicarbazide (AAS) and  $L' =$  Benzoylacetonethiosemicarbazide (BAS) have been isolated in solid state and are characterized by their spectral, magnetic and antifungal activities. The electronic spectra of these chelates have been analysed in the light of LSJ terms and involving characteristic  $f-f$  transitions. The ligands and their resulting chelates have been shown to be toxic against the two pathogenic fungi, viz., *Aspergillus niger* and *Draschelera australiensis* and the results revealed that the toxicity decreases on chelation or metallation. Overall, the benzoylacetonesemicarbazide lanthanon chelates are more toxic to fungi than the corresponding lanthanon derivatives of Acetylacetonesemicarbazide.

**Keywords:** Lanthanon Chelates; Schiff Base; Donor Atom; Pathogenic Fungi

### INTRODUCTION

AMONGST the ligands containing nitrogen and sulphur donor atoms, the Schiff bases and thioureas respectively are more important in respect of their remarkable pharmacological activity (Dey, 1974). The group N-C-S is chiefly responsible for the pharmacological activity (Horsfall, 1945) of such materials. The microbio-activity of such materials lies in their tendency for chelation with traces of metal ions (Erlenmeyer, *et al.*, 1953).

In the present communication, we submit the results of spectral, magnetic and antifungal activities of the lanthanon chelates of the newly synthesised ligands namely Acetylacetonethiosemicarbazide (AAS) and Benzoylacetonethiosemicarbazide (BAS). The antifungal activities of AAS and BAS and their lanthanon chelates have been investigated against the pathogenic fungi *Aspergillus niger* and *Draschelera australiensis*.

### EXPERIMENTAL

The ligands AAS and BAS were synthesised from Acetylacetone, Benzoylacetone and thiosemicarbazide by the method already reported (Gupta *et al.*, 1979a, b). The materials, apparatus and methods used in elemental analysis, spectral and magnetic studies were the same as described previously (Gupta *et al.*—*In Press*).

The ligands (AAS & BAS) and their lanthanon chelates were dissolved in acetone to prepare the solutions of different concentrations (e.g., 100 & 200 ppm w/v) and these were introduced in potato-dextrose-sugar medium. The petriplates were inoculated with a block of 5mm diameter of *Aspergillus niger* and *Draschelera australiensis* and each treatment was replicated thrice. For four days at 28 °C, the plates were incubated and from the average diameter of fungal colony (Vincent, 1959) the growth inhibition percentage was evaluated.

## RESULTS AND DISCUSSION

The 1:2 (metal-ligand) stoichiometry is established on the basis of analytical results (Table I). Thus, they may be represented as  $[LnL_2]$  or  $[LnL'_2]$  where Ln = La(III), Pr(III), Nd(III), Sm(III), Ho(III) and Er(III) L =  $(C_8H_{11}N_3OS)$  or L' =  $(C_{11}H_{13}N_3OS)$ , which is also supported by elemental analyses, molecular wt. and thermogravimetric data. The non-electrolytic character (Geary, 1971) of the lanthanon chelates is evident from the low molar conductance (2.5–7.3 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) in dioxane.

TABLE I

Colour, molecular wt. and magnetic moments of AAS and BAS—lanthanon chelates

Chelate	Colour	Mole. wt.		$\mu_{eff}$ B. M. 308°K
		Found	Calcd.	
[LaL <sub>2</sub> ]	Dirty white	463	483	Diamagnetic
[PrL <sub>2</sub> ]	Creamish	470	485	3.31
[NdL <sub>2</sub> ]	Orange	469	489	3.60
[SmL <sub>2</sub> ]	Offwhite	475	494	1.42
[HoL <sub>2</sub> ]	Pale orange	488	509	10.29
[ErL <sub>2</sub> ]	Pink	492	511	9.38
[LaL' <sub>2</sub> ]	Gray	590	607	Diamagnetic
[PrL' <sub>2</sub> ]	Yellow	592	609	3.37
[NdL' <sub>2</sub> ]	Pale yellow	597	612	3.65
[SmL' <sub>2</sub> ]	White	601	618	1.48
[HoL' <sub>2</sub> ]	Orange	617	633	10.35
[ErL' <sub>2</sub> ]	Pinkish white	619	635	9.43

All gave satisfactory elemental analyses.

Decomposition temperature was 290–370 °C.

The magnetic moment values observed for AAS and BAS chelates are respectively 3.34 and 3.38 (Pr(III)); 3.66 and 3.68 B.M. (Nd(III)); 1.45 and 1.43 B.M. (Sm(III)); 10.32 and 10.34 B. M. (Ho(III)) and 9.40 and 9.45 B.M. (Er(III)) at 303 °K which are in good agreement with those reported for lanthanide sulphates (Figgis, 1967). The effect of temperature on the magnetic moment of lanthanon chelates was found negligible.

## Visible Spectra

The visible spectra of these materials were analysed to obtain the nephelauxetic ratio ( $\beta$ ), bonding parameter ( $b^{1/2}$ ) and  $\delta$  ( $4f$ -ligand mixing). The nephelauxetic ratio ( $\beta$ ) as determined by the method of Jorgensen *et al.* (1964) was used for the corresponding transitions. *The effect of the chelation on the free ion is the red shift of electronic transitions. It may, therefore, be concluded that involvement of  $4f$ -orbitals in bonding is negligible due to perturbing effect of ligand.* The bands observed in visible spectra of Pr(III), Nd(III), Sm(III), Ho(III) and Er(III) chelates may be due to transition from ground level  $^3H_4$ ,  $^4I_{9/2}$ ,  $^6H_{5/2}$ ,  $^5I_8$  and  $^4I_{15/2}$  to the excited  $J$  levels of  $4f^n$  configuration, respectively. The relevant spectral parameters viz.,  $(1 - \beta)$ ,  $\delta$  and  $b^{1/2}$  at corresponding transitions are summarized in Table II.

TABLE II

Electronic spectral data and relevant bonding parameters of AAS & BAS chelates

Ion	AAS Chela- tes Cm <sup>-1</sup>	BAS Chela- tes Cm <sup>-1</sup>	J level	(1- $\beta$ ) $\times 10^2$		$\delta$ (%)		$b^{1/2}\times 10^{-1}$	
				AAS Chela- tes	BAS Chela- tes	AAS Chelates	BAS Chelates	AAS Chelates	BAS Chelates
Pr(III)	22170	22280	$^3H_4 \rightarrow ^3P_2$	0.69	0.24	0.6915	0.2460	0.074	0.060
	21130	21210	$\rightarrow ^3P_1$	1.04	0.85	1.0507	0.8619	0.081	0.057
	20530	20640	$\rightarrow ^3P_0$	0.69	0.57	0.6998	0.5710	0.084	0.053
	16910	17080	$\rightarrow ^1D_2$	1.35	0.62	1.3506	0.6340	0.092	0.089
Nd(III)	19560	19680	$^4I_{9/2} \rightarrow ^4G_{5/2}, ^4H_{9/2}$	0.47	0.36	0.4750	0.3691	0.042	0.048
	18720	18900	$\rightarrow ^4F_{7/2}, ^4S_{3/2}$	1.21	0.62	1.2201	0.6276	0.085	0.072
	17150	17330	$\rightarrow ^4F_{9/2}$	0.59	0.49	0.5980	0.4900	0.096	0.046
	14470	14470	$\rightarrow ^4G_{5/2}, ^2G_{7/2}$ *	0.73	0.73	0.7311	0.7311	0.066	0.066
	13390	13440	$\rightarrow ^4G_{7/2}$	1.16	0.81	1.1630	0.8319	0.058	0.067
	12390	12480	$\rightarrow ^4G_{9/2}$	0.86	0.50	0.8810	0.5169	0.060	0.066
Sm(III)	24680	24820	$^6H_{5/2} \rightarrow ^4F_{9/2}$	0.89	0.33	0.8920	0.3346	0.043	0.043
	23790	23880	$\rightarrow ^6P_{5/2}$	0.34	1.01	0.3555	1.0107	0.067	0.056
	21430	21550	$\rightarrow ^4I_{13/2}$	1.02	0.41	1.0280	0.4202	0.060	0.051
Ho(III)	22270	22390	$^5I_8 \rightarrow ^5G_6, ^5F_1$ *	1.02	1.00	1.0200	1.0069	0.061	0.072
	19000	19165	$\rightarrow ^5F_4$ *	0.79	1.00	0.7990	1.0056	0.065	0.062
	15610	15730	$\rightarrow ^5F_5, ^5S_2$	0.13	1.06	0.1398	1.0667	0.084	0.079
	13380	13470	$\rightarrow ^5I_4$	0.89	0.16	0.8911	0.1805	0.030	0.091
Er(III)	22180	22270	$^4I_{15/2} \rightarrow ^4F_{5/2}$	0.54	0.14	0.5507	0.1502	0.065	0.061
	20620	20780	$\rightarrow ^4F_{7/2}$	1.34	0.58	1.3462	0.5878	0.071	0.067
	19210	19360	$\rightarrow ^2H_{11/2}$	0.85	1.32	0.8511	1.3200	0.069	0.089
	15290	15360	$\rightarrow ^4F_{9/2}$	1.23	1.01	1.2376	1.0123	0.084	0.074

\*Hypersensitive transition (Red shift).

Nd(III) chelates in DMSO exhibited hypersensitivity. Excepting the hypersensitive transition  $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$  small differences in band position were

observed, Red shift with smaller values for  $\delta$ -parameter are also observed for  ${}^6I_8 \rightarrow {}^6G_8$ ,  ${}^5F_1$  and  ${}^6F_4$  transition of Ho(III) chelates. In the case of Er(III) chelates, no red shift was observed but the  ${}^4I_{15/2} \rightarrow {}^4F_{7/2}$   ${}^4F_{9/2}$  transitions appear unaffected by chelate formation or showed a very slight red shift.

### Antifungal Activity

Amongst the two ligands tested, Benzoylacetone thiosemicarbazide (BAS) has been found to be more toxic than acetylacetone thiosemicarbazide (AAS) (per cent growth inhibited at 100 and 200 ppm, for *Aspergillus niger* fungi AAS/BAS = 52 and 68/66 and 82 and for *Draschelera australiensis* fungi AAS/BAS = 48 and 112/74 and 114). It may be due to one benzene ring in the BAS alongwith a enolic oxygen at  $\beta$ -position. The hydroxy group increases the toxicity of the ligands and according to Horsfall (1945) the hydrogen of enolic group is highly reactive so as to enable the toxicant to combine with the constituents of the fungus resulting in the inhibition of its function.

The lanthanon chelates displayed lower fungitoxicity as compared to the ligands (AAS & BAS) [percentage growth inhibited at 100 and 200 ppm, for *Aspergillus niger* fungi Ln(AAS/BAS)<sub>2</sub> = 28-39, 42-59 and 61-72/45-53, 64-73 and 75-83, and for *Draschelera australiensis* fungi Ln (AAS/BAS)<sub>2</sub> = 32-49, 52-63 and 68-81/46-59, 67-80 and 75-91]. It seems that the sulphur and nitrogen of thioketo ( $>C=S$ ) and azomethine ( $>C=N$ ) groups in the ligands are freely available for combination with the fungi cells and thus their growth is checked. But on chelation with the lanthanons these coordination sites get occupied and naturally their toxicity diminishes. Besides the solubility of the fungicides, the fineness of the particles are equally important with the toxicity determination. Perhaps this might be the additional parameter for the lower activity of lanthanon thiosemicarbazones derivatives. Both AAS & BAS, are more soluble in organic solvents than their lanthanon chelates and therefore, these are absorbed easily by the fungal hyphae.

### ACKNOWLEDGEMENT

The authors express their gratitude to the CSIR (New Delhi) for the award of Post-Doctoral Fellowship to one of them (CPG).

### REFERENCES

- Dey, K. (1974) *J. scient. ind. Res.*, **33**, 76.  
 Erlenmeyer, H., Baumler, J., and Routh, W. (1953) *Helv. Chim. Acta*, **36**, 974.  
 Figgis, B. N. (1967) *Introduction of Ligand Fields*. John Wiley & Sons, New York, 326.  
 Geary, W. L. (1971) *Coord. Chem. Rev.*, **7**, 81.  
 Gupta, C. P., Sankhla, N. K., and Mehta, R. K. (1979 a) *J. inorg. nucl. Chem.*, **41**, 1392.  
 ——— (1979b) *J. prakt. Chem.*, **321**, 691.  
 Gupta, C. P., Sharma, K. G., and Mehta, R. K. (*In press*), *Acta. Chim. Aca. Hung. Sci.* (Budapest).  
 Horsfall, J. (1945) *Bot. Rev.*, **5**, 557.  
 Jorgensen, C. K., Pappalardo, R., and Rittershaus, E. (1964) *Z. Naturf.*, **19a**, 424.  
 Vincent, J. M. (1959) *Farmer's Bull. U.S.D.A. Inhibitors' Nature*, P. 850.