

## Synthetic and Structural Studies of 4f-Metal Complexes of Oxalic Bis(Cyclohexylidenehydrazide)

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Oxalic bis(cyclohexylidenehydrazide) (ObCH) gave, by reaction with 4f-metal chlorides, complexes of the type  $[Ln(ObCH)Cl_2]Cl \cdot H_2O$ , where  $Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III),$  and  $Y(III)$ . The complexes have been studied by conductance, magnetic, electronic, i.r. and  $^1H$  n.m.r. spectral techniques. I.r. and n.m.r. spectra indicate tetradentate coordination of ObCH through carbonyl oxygens and azomethine nitrogens with a polymeric linkage. Six coordination is proposed in the complexes.

### INTRODUCTION

The chemical properties of hydrazones have been intensively investigated in recent years, owing to their coordinative capability<sup>1</sup>, their pharmacological activity<sup>2</sup> and their use in analytical chemistry as metal extracting agents<sup>3</sup>. Oxalic bis(cyclohexylidenehydrazide) (ObCH) has received special interest mainly due to the potentially multidentate ligational behaviour and its use in the analysis of 3d-metals<sup>4,5</sup>. The spectrophotometric properties of its complexes<sup>6,7</sup> are also of vivid interest. Although a few papers<sup>8-10</sup> have appeared on transition metal complexes of acylhydrazones derived from oxalyhydrazide apart from one on Cu(II) complexes of oxalic bis(cyclohexylidenehydrazide)<sup>11</sup>. The present paper describes the ligational behaviour of oxalic bis(cyclohexylidenehydrazide) with 4f-metal ions.

### EXPERIMENTAL

All the chemicals used were of BDH or S. Merck. Hydrated lanthanide chlorides (99.99%) obtained from Indian Rare Earths Ltd., Kerala (India) were used without further purification. Oxalic bis(cyclohexylidenehydrazide) was purchased from Sigma Chemical Company, U.S.A. Purified solvents were made anhydrous, where necessary, applying standard literature method<sup>12</sup>.

*Dichloromonakis[oxalic bis(cyclohexylidenehydrazide)] lanthanide(III) chloride hydrate*,  $[Ln(ObCH)Cl_2]Cl \cdot H_2O$  [ $Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy$  and  $Y$ ] were prepared by mixing MeOH solutions of ObCH (2.0 mmol in ca. 20 cm<sup>3</sup>) and the appropriate lanthanide chloride (2.0 mmol in ca. 20 cm<sup>3</sup>) and digesting the reaction mixture for ca. 1 hr. The complexes formed

were filtered, washed repeatedly with MeOH and ether and dried in *vacuo*.

The procedures for analysing the metal, chloride, hydrazine and H<sub>2</sub>O contents were essentially the same as described in our previous paper<sup>13</sup>. Details of the equipment used for various physico-chemical studies were the same as reported earlier<sup>13</sup>.

## RESULTS AND DISCUSSION

The summary of the analytical results is presented in Table 1. All the complexes are insoluble in water and common organic solvents but are largely soluble in coordinating solvents such as DMF and DMSO. However, a few complexes are sparingly soluble even in DMF and DMSO. The electrical conductance data in 10<sup>-3</sup>M DMF solutions or saturated solutions in DMF indicate that all the complexes are 1 : 1 electrolytes<sup>14</sup>. The complexes are non-melting below 300°C. The weight loss on heating the complexes to 80–160°C corresponds to one water molecule. The presence of lattice water is suggested in the following discussion on i.r. spectra. Thus, the empirical formula [Ln(ObCH)Cl<sub>2</sub>]Cl.H<sub>2</sub>O may tentatively be assigned to the complexes. The non-melting and sparingly soluble behaviour of the complexes is suggestive of their polymeric nature.

The room temperature magnetic moments of all the complexes corrected for diamagnetism<sup>15</sup> show very little deviation from Van Vleck values<sup>16</sup> indicating a little participation of the 4f-electrons in bond formation. The slightly higher values observed in the Sm(III) and Eu(III) complexes may presumably include temperature dependent magnetism on account of low J-separation<sup>17,18</sup>.

The absorption spectra of Pr(III), Nd(III) and Sm(III) complexes were recorded on nujol mulls as well as in DMF solution. The spectral data along with various calculated parameters are given in Table 2. Among the trivalent lanthanide ions, neodymium(III) has been used most frequently as an absorption probe of lanthanide-ligand interactions. The absorption bands associated with the nearly degenerate <sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>G<sub>5/2</sub> and <sup>2</sup>G<sub>7/2</sub> transitions of Nd(III) exhibit strong hypersensitive behaviour<sup>19–21</sup> making it especially suitable for probing the coordination environment around the neodymium(III) ion. The total intensity, intensity distribution and energy barycentre of this band are strongly modulated by ligand coordination properties. The data given in Table 2 clearly demonstrate the hypersensitive behaviour of the <sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>G<sub>5/2</sub>, <sup>2</sup>G<sub>7/2</sub> transition and its features in solid state differ markedly from those of the solution state spectrum. A six coordination may be assigned for [Nd(ObCH)Cl<sub>2</sub>]Cl.H<sub>2</sub>O in its solid state based on the striking resemblance of the hypersensitive band with that of six coordinate [Nd(thd)<sub>3</sub>] [thd = (CH<sub>3</sub>)<sub>3</sub>CCOCHCOC(CH<sub>3</sub>)<sub>3</sub>] in benzene reported by Karraker<sup>22</sup>. A spectral change presumably due to increase in coordination number has been observed in the spectrum

TABLE I  
ANALYTICAL DATA, COLOUR AND MAGNETIC  
MOMENTS OF ObCH COMPLEXES

Complex	Colour	M.pt. (°C)	Found (Calcd.) %			$\mu_{\text{eff}}$ (B.M.)	Molar conductance (ohm <sup>-1</sup> cm <sup>-2</sup> mol <sup>-1</sup> )
			N	M	Cl		
[La(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Colourless	> 300	10.40 (10.34)	26.05 (25.65)	19.80 (19.65)	11.90 (11.81)	77.0
[Pr(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Green	> 300	10.41 (10.30)	25.90 (25.93)	19.70 (19.58)	11.75 (11.76)	80.2
[Nd(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Blue	> 300	10.33 (10.24)	26.60 (26.36)	19.51 (19.46)	11.80 (11.69)	79.8
[Sm(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Light yellow	> 300	110.11 (10.12)	27.01 (27.15)	19.17 (19.25)	11.42 (11.56)	79.8
[Eu(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Cream	> 300	10.10 (10.09)	27.40 (27.41)	19.10 (19.19)	11.47 (11.53)	72.0
[Gd(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Colourless	> 300	10.01 (10.00)	28.23 (28.10)	19.23 (19.01)	11.10 (11.42)	83.1
[Tb(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Cream	> 300	10.01 (9.97)	28.35 (28.29)	19.03 (18.95)	11.50 (11.39)	83.1
[Dy(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Cream	> 300	9.93 (9.91)	28.90 (28.80)	19.04 (18.82)	11.50 (11.32)	83.5
[Y(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Colourless	> 300	11.34 (11.39)	18.04 (18.10)	21.71 (21.65)	13.16 (13.01)	81.0

of the above complex recorded in DMF solution and the resulting features in the hypersensitive band region and the band corresponding to the transition  ${}^4I_{5/2} \rightarrow {}^4G_{7/2}$  are similar to those of a seven coordinate  $[Nd(thd)_3HFAA]$  [ $HFAA = CF_3COCHCOCF_3$ ] in  $C_2H_5OH$  reported by Karraker<sup>22</sup>.

TABLE 2  
ELECTRONIC SPECTRAL DATA OF ObCH COMPLEXES

Complex	Band max. (cm <sup>-1</sup> )		Assignments	Calculated parameters	
	Solid	Solution		Solid	Solution
[Pr(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	16810	16695	${}^3H_4 \rightarrow {}^1D_2$	$\beta = 0.9895$	$\beta = 0.9860$
	20490	20530	$\rightarrow {}^2P_0$	$b^{1/2} = 0.0725$	$b^{1/2} = 0.0837$
	21100	20095	$\rightarrow {}^3P_1$	$\eta = 0.00053$	$\eta = 0.0071$
	22270	22220	$\rightarrow {}^3P_2$	$\delta\% = 1.06114$	$\delta\% = 1.4209$
[Nd(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	11520	11470	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	$\beta = 0.9942$	$\beta = 0.9849$
	12550	12410	$\rightarrow {}^4F_{5/2}$	$b^{1/2} = 0.0538$	$b^{1/2} = 0.0869$
	13550	13330	$\rightarrow {}^4F_{7/2}$	$\eta = 0.0029$	$\eta = 0.0076$
	14705	14555	$\rightarrow {}^4F_{9/2}$	$\delta\% = 0.5834$	$\delta\% = 1.5331$
	17180	17020	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$		
	19085	19010	$\rightarrow {}^4G_{7/2}$		
	19500	19455	$\rightarrow {}^4G_{9/2}$		
	21010	20830	$\rightarrow {}^4G_{11/2}$		
	23365	23200	$\rightarrow {}^2P_{1/2}$		
[Sm(ObCH)Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	20835	—	${}^6H_{5/2} \rightarrow {}^4I_{11/2}$	$\beta = 0.9897$	$\beta = 0.9905$
	21370	21360	$\rightarrow {}^4I_{13/2}$	$b^{1/2} = 0.0717$	$b^{1/2} = 0.0696$
	23810	23805	$\rightarrow {}^4P_{9/2}$	$\eta = 0.0052$	$\eta = 0.0049$
	24510	24570	$\rightarrow {}^4F_{9/2}$	$\delta\% = 1.0410$	$\delta\% = 0.9795$

\*For Nd(III) the spectral parameters were calculated from the hypersensitive bands.

The slight bathochromic shift in the hypersensitive band has been attributed by Jørgensen<sup>23</sup> to the effect of crystal field upon interelectronic repulsion among the 4f-electrons, *i.e.*, lowering of the interelectronic repulsion parameters ( $\beta$ ) on complexation.

A noteworthy feature of the solution state spectra of Pr(III) and Nd(III) complexes is that the magnitude of the bathochromic shifts of the absorption bands based on those of the aqueous solutions are slightly larger compared to similar shifts obtained in the solid state spectra. Various spectral parameters, *viz.*, nephelauxetic effect ( $\beta$ ), bonding para-

meter ( $b^{1/2}$ ), angular overlap parameter ( $\eta$ ) and covalency ( $\delta\%$ ) have been calculated<sup>24-26</sup> from the solid as well as solution state spectra. The values of  $\beta$  (less than unity) and positive values of  $b^{1/2}$ ,  $\eta$  and  $\delta\%$  suggest weak covalent bond between metal and ObCH.

The I.R. assignments of the ligand and the complexes have been based on those proposed for various oxalyldihydrazones by Wiles and Suprunchuk<sup>28</sup>. The acetonitrile solution spectrum of ObCH shows strong peaks at 1680, 1540 and 1280  $\text{cm}^{-1}$  which may be assigned to the amide I, II and III frequencies respectively. These amide bands occur in the complexes in the 1665-1660, 1515-1510 and 1315-1300  $\text{cm}^{-1}$  regions respectively. Thus, the observed bathochromic shifts in the amide I and II bands coupled with a hypsochromic shift in the amide III band suggest the coordination of  $>\text{C}=\text{O}$  groups with the metal ion. Further, the medium intensity band at 1630  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  in ObCH suffers a bathochromic shift of 10-20  $\text{cm}^{-1}$  in all the complexes. A weak to medium intensity band appearing at 930  $\text{cm}^{-1}$  in the spectrum of ObCH may be assigned to  $\nu(\text{N}-\text{N})$  which appears in the spectra of the complexes in 965-960  $\text{cm}^{-1}$  region suggesting a monodentate coordination of the N-N moiety<sup>29</sup>. The new bands arising in the spectra of the complexes at 1620-1600 (apart from that of  $\nu_{\text{C}=\text{N}}$ ) and 890  $\text{cm}^{-1}$  may respectively be assigned to HOH bending and  $\nu(\text{H}_2\text{O})$  of lattice water<sup>30</sup>. The medium intensity bands appearing in 445-415 and 350-330  $\text{cm}^{-1}$  regions may tentatively be assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  modes<sup>31</sup>.

The  $^1\text{H}$  n.m.r. spectra of ObCH and its lanthanum(III) complex were recorded in  $\text{DMSO}-d_6$  solutions. The signal appearing in the spectrum of ObCH at  $\delta$  10.9 is assigned to the imino proton while those at  $\delta$  2.33 and 1.67 are due to the ring protons. The signal due to the imino proton shifts downfield to  $\delta$  11.0 with concomitant broadening in the spectrum of La(III) complex suggesting the coordination of both the carbonyl oxygens and azomethine nitrogens.

Based on the analytical, conductance, magnetic and spectroscopic data, polymeric structure as shown in Fig. 1 may tentatively be proposed for the present complexes.

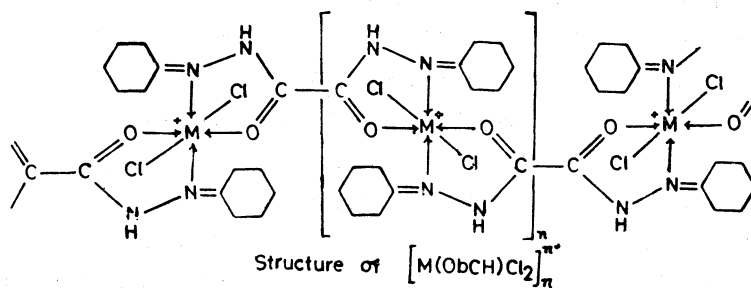


Fig. 1.

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