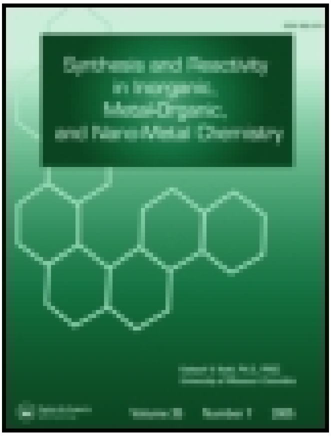

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Lanthanide Complexes of 2-Aminobenzophenone-2-thenoylhydrazone: Synthesis and Structural Characterization

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LANTHANIDE COMPLEXES OF 2-AMINOBENZOPHENONE-2-THENOYLHYDRAZONE: SYNTHESIS AND STRUCTURAL CHARACTERIZATION

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ABSTRACT

Trivalent lanthanide complexes of the general formula $[Ln(Habth)_2Cl_2]Cl$ [Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III); Habth = 2-aminobenzophenone-2-thenoylhydrazone] were prepared and characterized using magnetic moments, molar conductance and UV-VIS, IR and emission spectroscopy.

INTRODUCTION

Reaction[1] of 3d-metal chlorides with Habth (Fig. 1) yielded the complexes $VO(Habth)_2SO_4$, $M(Habth)_2Cl_2$ [M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)], $VO(abth)_2$ and $M(abth)_2$ [M = Co(II), Ni(II), Cu(II) and Zn(II)]. The Schiff base is bonded as neutral, monodentate ligand through the carbonyl oxygen in $VO(Habth)_2SO_4$, as neutral, bidentate ligand through the carbonyl oxygen and azomethine nitrogen in $M(Habth)_2Cl_2$, as uninegative, bidentate ligand through the imidol oxygen and azomethine nitrogen in $VO(abth)_2$ and as uninegative, tridentate ligand through the imidol oxygen, azomethine and amine nitrogens in $M(abth)_2$ complexes. The

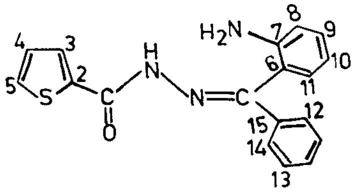

Fig.1. Structure of Habth

complexes were proposed to have octahedral geometry, except the vanadyl complexes, which have square pyramidal stereochemistry. This work is now extended to study the bonding properties of the Schiff base towards 4f-metal ions and investigate the structure of the resulting complexes. The results are reported in this paper.

EXPERIMENTAL

2-Aminobenzophenone and 2-thenoylhydrazine (Aldrich Chemie, Germany) and hydrated metal chlorides (Indian Rare Earths Ltd. Kerala, India) were used as obtained. The other chemicals used were of British Drug House or of equivalent grade.

Preparation of the Schiff Base

Habth was prepared by reacting EtOH solutions of 2-aminobenzophenone (10 mmol, 1.97 g, 10 mL) and 2-thenoylhydrazine (10 mmol, 1.42 g, 10 mL) containing a catalytic amount of CH_3COOH (0.1 mL) under reflux for ∽4 h. A yellow crystalline compound separated after keeping the reaction solution at room temperature for∽3 h. It was recrystallized from hot EtOH solution. Yield 2.4 g, 75%, m p 209-12°C [Found: C, 66.8; H, 4.6; N, 12.9; N_2H_4, 9.9; Calcd. for $C_{18}H_{15}N_3OS$: C, 67.3; H, 4.6; N, 13.0; N_2H_4, 10.0]. The Schiff base was also characterized by IR, ^1H and ^{13}C NMR spectra. The IR spectrum shows bands at 1660, 1535, 1630, 1600 and 970 cm^{-1} which were assigned to amide I, amide II,

ν(C=N), ρ(NH_2) and ν(N-N) modes, respectively. The PMR spectrum of Habth in DMSO-d_6 exhibits signals at δ 11.09 (1H, s), 5.09 (2H, s) and 8.71 - 7.33 (12H, m) which are assigned to NH, NH_2 and aromatic protons, respectively. The ^{13}C NMR spectrum of the Schiff base shows signals at 195.67 and 148.49 ppm which are assigned to carbonyl and azomethine carbons. The signals for the aromatic carbons are assigned as C_2 = 137.64, C_3 = 132.37, C_4 = 132.07, C_5 = 128.89, C_6 = 127.93, C_7 = 127.03, C_8 = 125.87, C_9 = 116.19, C_{10} = 115.19, C_{11} = 113.46, C_{12} = 129.39, C_{13} = 128.12, C_{14} = 126.12, C_{15} = 120.56 ppm, respectively.

Preparation of Complexes

The complexes were prepared by refluxing an EtOH solution (30 mL) of 2-aminobenzophenone-2-thenoylhydrazone (2 mmol, 0.65 g) with the hydrated metal chloride (1 mmol) for ~ 4 h. All the complexes were isolated as gummy solids by adding acetonitrile to the reaction solution. The gummy solid was redissolved in the minimum amount of ethanol and reprecipitated with acetonitrile. Then it was rubbed several times with acetonitrile to obtain a crystalline compound.

Analyses and Physical Measurements

The metal contents in the complexes were determined volumetrically by EDTA titrations[2] using Eriochrome Black - T as indicator after destroying the organic matter with aqua regia. Hydrazine was determined volumetrically[3] by the potassium iodate method after hydrolysing the complex with 6 - 8 N HCl for ~ 4 h. Chloride was determined gravimetrically[3] as AgCl.

The molar conductance of the complexes was determined on a WTW conductivity meter using a commercial conductivity 'dip cell'. Room temperature magnetic susceptibility measurements were made on a Cahn-Faraday electrobalance using $Hg[Co(NCS)_4]$ as calibrant. The experimental magnetic susceptibility was corrected for diamagnetism using Pascal's constants[4]. IR spectra of the Schiff base and the complexes were recorded on a JASCO FT/IR- 5300 spectrophotometer. UV-VIS spectra were recorded on a Shimadzu-160A spectrophotometer while the emission spectra of the complexes were recorded in the solid state on a Perkin-Elmer MPF-44B fluorescence spectrophotometer, after exciting with 335 nm radiation.

RESULTS AND DISCUSSION

The reaction between the hydrated lanthanide chloride and the Schiff base may be shown as:

$$LnCl_3 \cdot nH_2O \quad + \quad 2\,Habth \quad = \quad [Ln(Habth)_2Cl_2]Cl \quad + \quad n\,H_2O$$

The resulting complexes are soluble in ethanol, methanol, DMF and DMSO. They melt within the temperature range 128-240°C. The complexes are found to be 1:1 electrolytes in 10^{-3} M ethanol solutions implying that one of the chloride ions is out of the coordination sphere.

IR Spectra

Habth exhibits bands at 1660, 1630, 1600 and 970 cm^{-1} in the infrared spectrum which are assigned to $\nu(C=O)$, $\nu(C=N)$, $\beta(NH_2)$ and $\nu(N-N)$ modes, respectively. A bathochromic shift of $\nu(C=O)$, $\nu(C=N)$ and $\beta(NH_2)$ modes[6] and a hypsochromic shift of $\nu(N-N)$[7] suggest coordination through the carbonyl oxygen, azomethine nitrogen and amine nitrogen. The observed lowering in absorption due to $\nu(NH)$ at 3559 - 3414 cm^{-1} to 3318 - 3433 cm^{-1} may be due to hydrogen bonding between -NH and Cl. Thus it may be concluded that Habth bonds to the metal ion in a tridentate fashion through the carbonyl oxygen, azomethine nitrogen and amine nitrogen.

Table 1. Analytical Data, Magnetic Moments and Molar Conductance of Habth Complexes

Complex (Empirical formula)	Colour	M.p./°C	Found (Calcd.) %			μ_{eff} (B.M.)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	Yield (%)
			M	Cl	N_2H_4			
$[La(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2LaCl_3)$	Pale yellow	204–06	13.3 (13.7)	10.1 (10.5)	6.9 (6.3)	-	41.8	50
$[Pr(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2PrCl_3)$	Dirty yellow	238–40	13.6 (14.1)	10.3 (10.7)	6.9 (6.4)	3.9	52.1	70
$[Nd(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2NdCl_3)$	Dirty yellow	195–200	14.1 (14.4)	10.1 (10.6)	6.8 (6.4)	3.4	39.5	75
$[Sm(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2SmCl_3)$	Yellow	128–31	14.6 (14.9)	10.1 (10.6)	6.7 (6.4)	2.0	32.8	65
$[Eu(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2EuCl_3)$	Bright yellow	135–40	15.1 (15.1)	10.3 (10.6)	6.5 (6.3)	3.6	37.3	70
$[Gd(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2GdCl_3)$	Pale yellow	158–60	15.3 (15.5)	10.0 (10.5)	6.4 (6.3)	7.1	44.1	73
$[Tb(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2TbCl_3)$	Yellow	138–42	15.1 (15.6)	10.2 (10.5)	6.5 (6.3)	9.4	38.4	60
$[Dy(Habth)_2Cl_2]Cl$ $(C_{36}H_{30}N_6O_2S_2DyCl_3)$	Pale yellow	150–54	15.5 (15.9)	10.1 (10.4)	6.6 (6.3)	10.1	49.7	70

Table 2. Infrared Spectral Bands/ cm^{-1} and their Assignments

Complex	ν(C=O)	ν(C=N)	ν(N-N)	$\beta(NH_2)$
Habth	1660m	1630sh	970w	1600w
$[La(Habth)_2Cl_2]Cl$	1640s	1620w	1020m	1585w
$[Pr(Habth)_2Cl_2]Cl$	1655w	1626s	1024m	1586w
$[Nd(Habth)_2Cl_2]Cl$	1655w	1626s	1057m	1588m
$[Sm(Habth)_2Cl_2]Cl$	1657w	1620s	1026m	1586w
$[Eu(Habth)_2Cl_2]Cl$	1657w	1626w	1026m	1585w
$[Gd(Habth)_2Cl_2]Cl$	1655w	1628m	1026m	1591m
$[Tb(Habth)_2Cl_2]Cl$	1650w	1624m	1026m	1591w
$[Dy(Habth)_2Cl_2]Cl$	1650w	1628m	1026m	1591m

Magnetic Susceptibilities

The magnetic susceptibilities of the complexes, except those of samarium(III) and europium(III), show little deviation from the Van Vleck values[8], indicating slight participation of 4f-electrons in bond formation. The slightly higher μ_{eff}[9] values observed in case of samarium(III) and europium(III) complexes may include temperature dependent magnetism on account of low J-J separation.

Electronic Spectral Studies

Habth exhibits bands at 27025, 30770, 37735 and 42555 cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ and/ or $n \rightarrow \pi^*$ transitions. The lanthanide complexes show absorption bands at 28325- 27395 and 42550- 39215 cm^{-1} due to the above absorptions. The La(III) complex does not show f-f transitions as it has a $4f^0$ configuration. The complexes of Eu(III), Gd(III), Tb(III) and Dy(III) also do not give f-f transitions. However, the electronic spectra of Pr(III), Nd(III) and Sm(III) complexes have been analysed (Table 4).

The f-f transitions[10] are weakly allowed due to some mixing of excited states of opposite parity into the ground state that is configuration interaction. This small mixing is increased on complexation if the energy of the excited state is lowered. This also increases due to the increase in the covalent nature of the metal-ligand bond. This absorption intensity presented as oscillator strength (P) was calculated from the expression:

$$P = 4.31 \times 10^{-9} \left[9\eta / (\eta^2 + 2)^2\right] \int \epsilon \nu \, d\nu$$

where η is the refractive index of the solvent and ϵ is the molar extinction coefficient of the wave length ν.[11,12] The oscillator strengths [Table 3] corresponding to all the observed bands of $[Nd(Habth)_2Cl_2]Cl$ are larger than those reported for the aquo ions[13]. However, the three to nine- fold increase in the oscillator strength values may be attributed to the interaction of Nd^{3+} ion with Habth leading to a greater covalency of the metal ligand bonding[13]. In the absence of the $\nu_{\text{free ion}}$ value, the ionic or covalent character may be expressed relative to the aquo complex in a δ - scale where the parameter δ (in percent) is expressed as $\delta = (1 - \beta)\,100/\beta$ and β is the $\nu_{\text{complex}}/\nu_{\text{aquo}}$ ratio. The positive value of δ indicates covalent bonding in the Nd(III) complex. The Nujol mull and ethanol solution spectra of the neodymium(III) complex show almost similar profiles with sharper features in the latter. It may, therefore, be inferred that there is no change in coordination due to solvation effects[11]. The profile of the bands in the Nd(III) complex closely resembles that of the eight-coordinated Nd(III) complex reported by Karraker[12] and as is also proposed by IR studies in conjunction with the molar conductance.

Emission Spectra

The spectra of all the complexes except that of lanthanum were recorded. The complexes do not fluoresce or fluoresce only

Table 3. Oscillator Strength Values for the Neodymium(III) Complex

Complex	Spectral range	Assignments	Oscillator strengths for complex ($\mathcal{P}$x 10^6)	Oscillator strengths for Nd^{3+} aquo ion ($\mathcal{P}$ x 10^6)
$[Nd(Habth)_2Cl_2]Cl$	11415-11670	$^4I_{9/2} \longrightarrow {}^4F_{3/2}$	21.16	3.02
	12280-12805	$\longrightarrow {}^4F_{5/2}$	83.13	9.22
	13045-13725	$\longrightarrow {}^4F_{7/2}, {}^4S_{3/2}$	77.80	8.88
	14685-15330	$\longrightarrow {}^4F_{9/2}$	13.60	0.83
	15790-16405	$\longrightarrow {}^2H_{11/2}$	13.60	0.39
	15935-17645	$\longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$	54.40	10.50

Table 4. Electronic Spectral Data of Habth Complexes

Complexes	Bands/cm^{-1}	Assignments	Calculated parameters
$[Pr(Habth)_2Cl_2]Cl$	16778	$^3H_4 \longrightarrow {}^1D_2$	$\bar{\beta}$ = 0.9676
	20703	$\longrightarrow {}^3P_o$	$b^{1/2}$ = 0.1271
	21276	$\longrightarrow {}^3P_1$	δ % = 3.3412
	22421	$\longrightarrow {}^3P_2$	η = 0.0165
$[Nd(Habth)_2Cl_2]Cl$	11560	$^4I_{9/2} \longrightarrow {}^4F_{3/2}$	
	12578	$\longrightarrow {}^2H_{9/2}$	$\bar{\beta}$ = 0.9915
	13513	$\longrightarrow {}^4F_{7/2}, {}^4S_{3/2}$	$b^{1/2}$ = 0.0652
	14706	$\longrightarrow {}^4F_{9/2}$	δ % = 0.8573
	15625	$\longrightarrow {}^2H_{11/2}$	η = 0.0043
	17391	$\longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$	
	19231	$\longrightarrow {}^4G_{9/2}$	
$[Sm(Habth)_2Cl_2]Cl$	20964	$^6H_{5/2} \longrightarrow {}^4I_{11/2}$	$\bar{\beta}$ = 0.9907
	24875	$\longrightarrow {}^4K_{11/2}$	$b^{1/2}$ = 0.0881
			δ % = 0.9387
			η = 0.0047

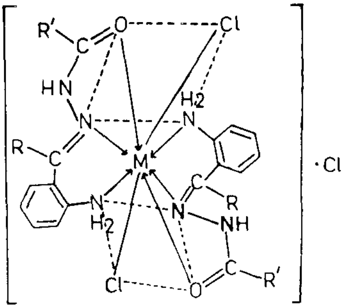

Fig. 2. Structure of $[Ln(Habth)_2Cl_2]Cl$.

very weakly at liquid nitrogen temperature due to internal quenching through strong coupling of the ions with the crystal forces[14,15]. This may also be due to the bulky nature of the ligand which acts as effective "sink" for tunnelling away of the energy and thus reducing the fluorescence yield drastically.

Based on these studies an eight-coordinate structure (Fig. 2) for these complexes may be proposed.

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