

Synthetic and structural studies of some trivalent lanthanide metal complexes of *o*-hydroxyacetophenone (N-benzoyl)glycyl hydrazone

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Abstract. *o*-Hydroxyacetophenone (N-benzoyl)glycyl hydrazone (*o*-HABzGH) forms complexes of the types $[M(o\text{-HABzGH})Cl_2(H_2O)_2]Cl$ and $[M(o\text{-HABzGH-}2H)OH(H_2O)_2]$, where $M = Y(III), Gd(III), Tb(III)$ and $Dy(III)$. The complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility, infrared, electronic, 1H NMR and ^{13}C NMR spectral techniques. The nephelauxetic ratio (β), covalency (δ), bonding parameter ($b^{1/2}$) and angular overlap parameter (η) have been calculated from $Dy(III)$ complexes. Infrared and NMR spectral studies show that *o*-HABzGH acts as a neutral bidentate ligand in the adduct complexes and as a dinegative tridentate one in the neutral complexes. A coordination number of six has been proposed for the metal ion in all the complexes.

Keywords. Lanthanide metal complexes; *o*-hydroxyacetophenone (N-benzoyl)glycyl hydrazone complexes; hexa-coordinated Ln complexes.

1. Introduction

Metal complexes of amino acids containing catecholic or phenolic side chains have recently attracted much attention mainly due to their potentially multidentate ligational behaviour (Birch and Manahan 1967; Gergely *et al* 1971; McAuliffe and Murray 1973). In continuation of our previous work (Rao *et al* 1985, 1986, 1988) we have extended our studies to the lanthanide metal complexes of a potential multidentate ligand, viz., *o*-hydroxyacetophenone (N-benzoyl)glycyl hydrazone (abbreviated as *o*-HABzGH) and the present paper deals with the synthesis and structural studies of complexes of *o*-HABzGH with $Y(III)$, $Gd(III)$, $Tb(III)$ and $Dy(III)$.

2. Experimental

2.1 Materials

Metal chlorides (99.90% pure) were obtained from the Indian Rare Earths Ltd., Kerala. All other chemicals used were from BDH or S Merck.

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o-Hydroxyacetophenone (N-benzoyl)glycyl hydrazone was prepared as reported earlier (Rao *et al* 1985) (m.p. 180°; lit. 180°C). Analysis – found: C, 65.62; H, 5.47; N, 13.48; N₂H₄, 10.29%. Calculated for C₁₇H₁₇N₃O₃: C, 65.88; H, 5.49; N, 13.41; N₂H₄, 10.33%.

2.2 Synthetic outlines

All the adduct complexes of the empirical formula M(*o*-HABzGH)Cl₃·2H₂O were prepared by mixing together hot ethanolic solutions of the hydrated metal chloride and *o*-HABzGH in ≈ 1:1 molar ratio and heating the reaction mixture under reflux for 2 h. Addition of about 10 ml of acetonitrile to the reaction mixture in each case resulted in the formation of a gummy solid which, after decanting the supernatant solution, was redissolved in ethanol and macerated with acetonitrile; successive repetitions of this process yielded crystalline complexes which were filtered, washed with an acetonitrile–ethanol mixture and dried in *vacuo*.

All the neutral complexes of the empirical formula M(*o*-HABzGH-2H)(OH)·2H₂O were prepared by mixing together aqueous ethanolic solutions of the appropriate metal chloride and *o*-HABzGH (≈ 1:1 molar ratio) and raising the pH of the solution to ~ 7.5 by adding LiOH solution. The resulting products were digested on a water bath for about 1 h, filtered, washed successively with aqueous ethanol, ethanol and diethyl ether and dried at room temperature.

2.3 Analyses of the complexes

C, H and N were determined by microanalysis. The metal ions, after destroying the organic matter with aquaregia followed by treatment with sulphuric acid, were estimated volumetrically by EDTA titration (Lyle and Rahaman 1963) using Eriochrome Black-T as indicator. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. H₂O content was determined by the weight loss suffered on heating the complexes in the temperature range 80–160°C.

2.4 Physical measurements

Microanalysis was carried out using a Perkin–Elmer 240C microanalyser. The molar conductance was measured at room temperature on a WTW conductivity meter. Magnetic susceptibility measurements were carried out on a Cahn–Faraday electrobalance using Hg[Co(NCS)₄] as the calibrant. Electronic spectra were recorded on a Cary-23 spectrophotometer while IR spectra were obtained using a Perkin–Elmer 783 spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded on a Jeol FX-90Q multinuclear NMR spectrometer.

3. Results and discussion

A summary of the analytical results and the melting/decomposing temperatures is presented in table 1. It can be observed from the data that the ligand *o*-HABzGH reacts with metal chlorides as a neutral ligand in ethanol and as a dinegative anion in aqueous solutions in the presence of LiOH. Thus, increase of pH by the requisite

Table 1. Analytical data, general behaviour and magnetic moments of *o*-HABzGH complexes.

Complex	Colour	M.P. (°C)	Found (Calcd) (%)						μ_{eff} (B.M.)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
			N	M	Cl	N ₃ H ₄				
[Y(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	White	246 ^d	7.76 (7.74)	16.35 (16.39)	19.20 (19.63)	5.75 (5.90)	—	diamagnetic	1050	
[Gd(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	Cream	> 300	6.90 (6.88)	25.70 (25.75)	17.30 (17.44)	5.17 (5.24)	—	7.55	114.4	
[Tb(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	Cream	286 ^d	6.87 (6.86)	25.98 (25.96)	17.14 (17.39)	5.19 (5.23)	—	9.67	99.0	
[Dy(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	Cream	> 300	6.81 (6.81)	26.45 (26.39)	17.39 (17.28)	5.15 (5.19)	—	9.46	108.0	
[Y(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	Yellow	> 300	9.30 (9.31)	19.81 (19.72)	—	7.17 (7.10)	—	diamagnetic	8.2	
[Gd(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	Yellow	> 300	8.10 (8.09)	30.04 (30.28)	—	6.23 (6.16)	—	8.27	7.8	
[Tb(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	Yellow	> 300	8.08 (8.06)	30.49 (30.51)	—	6.04 (6.14)	—	9.25	7.4	
[Dy(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	Yellow	> 300	8.00 (8.01)	31.00 (30.98)	—	6.04 (6.10)	—	8.02	7.6	

^d Decomposes

quantity of LiOH solution may facilitate the deprotonation of the ligand possibly through amide \rightleftharpoons imidol tautomerism, thereby, enabling the ligand to behave as a dinegative species.

All the adduct complexes are moderately hygroscopic and are soluble in water, methanol, ethanol, DMF and DMSO while the neutral complexes are stable at room temperature and are soluble only in coordinating solvents like pyridine, DMF and DMSO. The electrical conductance data in 0.001 M DMF solutions (table 1) indicate that all the adduct complexes show 1:1 electrolytic behaviour while the neutral complexes are all non-electrolytes (Geary 1971). The weight loss suffered by the complexes on heating then in the 80–160°C temperature range corresponds to two water molecules in each case. Thus, based on the analytical data, electrical conductance and thermal studies, the empirical formulae $[M(o\text{-HABzGH})Cl_2(H_2O)_2]Cl$ and $[M(o\text{-HABzGH-2H})OH(H_2O)_2]$, may tentatively be assigned to the adducts and neutral complexes of the metals respectively.

3.1 Magnetic moments

The room temperature magnetic moments of the complexes (table 1) show a small deviation from Van Vleck values (Van Vleck and Frank 1929) indicating a little participation of $4f$ -electrons in the metal–ligand bond formation.

3.2 Electronic spectra

The absorption spectra of Dy(III) complexes were recorded as nujol mulls and the spectral data along with various calculated parameters are given in table 2. The spectra of the complexes show a shift of the spectral bands toward lower frequency compared to those of the aqua ion (Carnall *et al* 1968) suggesting a decrease in the inter-electronic repulsion parameter (β) due to the crystal-field effect upon complexation. The various parameters were calculated using the literature procedure (Rayar and Jorgensen 1966; Tandon and Mehta 1970). The value of β (less than unity) and the positive values of the bonding parameter ($b^{1/2}$), covalency (δ) and covalency angular overlap parameter (η) suggest a weak covalent bond between the metal ion and *o*-HABzGH.

Table 2. Electronic spectral data of Dy(III) complexes of *o*-HABzGH.

Complex	Band max (cm^{-1})	Assignments	Calculated parameters
$[Dy(o\text{-HABzGH})Cl_2(H_2O)_2]Cl$	13700	${}^6H_{15/2} \rightarrow {}^6F_{1/2}$	$\beta = 0.9872$
	14925	$\rightarrow {}^6H_{3/2}$	$b^{1/2} = 0.08$
	16950	$\rightarrow {}^6H_{1/2}$	$\eta = 0.006$
	22830	$\rightarrow {}^4G_{11/2}$	$\delta\% = 1.29$
$[Dy(o\text{-HABzGH-2H})OH(H_2O)_2]$	13736	${}^6H_{15/2} \rightarrow {}^6F_{1/2}$	$\beta = 0.9982$
	14950	$\rightarrow {}^6H_{3/2}$	$b^{1/2} = 0.03$
	16950	$\rightarrow {}^6H_{1/2}$	$\eta = 0.001$
			$\delta\% = 0.18$

3.3 Infrared spectra

Infrared frequencies of selected groups in the spectra of *o*-HABzGH and its complexes are given in table 3. *o*-HABzGH in its nujol mull spectrum exhibits two strong bands at 1695 and 1640 cm^{-1} due to $\nu(\text{C}=\text{O})$ of the carbonyl groups of the hydrazone and benzamide moieties respectively. Of the four medium intensity bands appearing in the spectrum of the ligand at 1550, 1305, 1540 and 1300 cm^{-1} , the former two may be assigned to amide II and amide III frequencies of the hydrazone carbonyl group, while the latter two to those of the benzamide carbonyl group (Marcotrigiano and Pellacani 1975).

The positions of the amide I, II and III bands arising from the $>\text{C}=\text{O}$ group of the benzamide moiety remain almost unaltered in the spectra of all the complexes as compared to those of the uncoordinated *o*-HABzGH suggesting the non-involvement of the above group in coordination with the metal ions (Nagano *et al* 1964). However, such amide bands of the hydrazide $>\text{C}=\text{O}$ group appear at 1660–1650, 1530 and 1320 cm^{-1} in the spectra of $[\text{M}(\textit{o}\text{-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$, while all of them disappear from the spectra of $[\text{M}(\textit{o}\text{-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$ indicating carbonyl group coordination in the former case (Nagano *et al* 1964) and its destruction through amide \rightleftharpoons imidol tautomerism and subsequent coordination of the imidol oxygen in the latter. The coordination of the imidol group in $[\text{M}(\textit{o}\text{-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$ is further supported by the appearance of new peaks in the 1520–1515 and 1370–1365 cm^{-1} regions diagnostic of $\nu(\text{NCO}^-)$ (Rao 1963). Coordination of the azomethine nitrogen is suggested on the basis of the observed hypsochromic shift of $\sim 25 \text{ cm}^{-1}$ in the $\nu(\text{N}-\text{N})$ band in the spectra of all the complexes as compared to that at 940 cm^{-1} in *o*-HABzGH (Braibanti *et al* 1968).

Phenolic oxygen coordination may be inferred on the basis of the disappearance of the in-plane and out-of-plane deformation modes of the phenolic $-\text{OH}$ group in the spectra of all the neutral complexes (Inomata *et al* 1974). The appearance of a new band at 1150 cm^{-1} in the neutral complexes is suggestive of an MOH bending mode (Nakamoto 1978). The non-ligand bands appearing in the regions 415–400 and 305–290 cm^{-1} in the spectra of all the complexes are tentatively assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes respectively (Nakamoto and Martel 1960).

3.4 ^1H and ^{13}C NMR spectra

The ^1H NMR spectra of *o*-HABzGH and its Y(III) complexes were recorded in DMSO- d_6 . In the spectrum of *o*-HABzGH the signals obtained at δ 13.09, 11.09, 8.90, 3.71 and 2.38 are respectively assignable to phenolic $-\text{OH}$, imine protons of hydrazone and benzamide moieties, methylene and methyl protons. The aromatic protons are observed at δ 7.85–6.90. In the spectrum of $[\text{Y}(\textit{o}\text{-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ the signal due to the imide (NH) proton of the hydrazide moiety undergoes a downfield shift (δ 11.16) with slight broadening, suggesting the involvement of the carbonyl oxygen and the azomethine nitrogen of the hydrazide moiety in the coordination with the metal ion. However, in the spectrum of $[\text{Y}(\textit{o}\text{-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$, the signals due to the phenolic and imine (hydrazide moiety) protons disappear totally, while those of the aromatic protons appear with broadening at almost the same positions as in the ligand suggesting the loss of the amide proton of the hydrazide moiety through enolization, deprotonation of the phenolic $-\text{OH}$ and subsequent coordination of the ligand as a dinegative tridentate species, bonding through the enolic oxygen,

Table 3. Infrared spectral data (cm^{-1}) of *o*-HABzGH complexes.

Complex	Benzamide moiety			Hydrazide moiety			$\nu(\text{N}-\text{N})$
	Amide I	Amide II	Amide III	Amide I	Amide II	Amide III	
<i>o</i> -HABzGH	1640	1540	1300	1695	1550	1305	940
[Y(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	1640	1540	1300	1660	1530	1320	965
[Gd(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	1640	1540	1300	1655	1530	1320	965
[Tb(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	1635	1540	1300	1660	1530	1320	970
[Dy(<i>o</i> -HABzGH)Cl ₂ (H ₂ O) ₂]Cl	1640	1545	1300	1660	1530	1320	960
[Y(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	1640	1540	1300	—	—	—	960
[Gd(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	1640	1540	1300	—	—	—	960
[Tb(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	1640	1540	1300	—	—	—	965
[Dy(<i>o</i> -HABzGH-2H)OH(H ₂ O) ₂]	1640	1540	1300	—	—	—	960

azomethine nitrogen and phenolic oxygen. However, the signal due to the imine proton of the benzamide moiety (δ 8.90) shifts slightly to the upfield region in the complexes suggesting the non-involvement of the benzamide carbonyl group in coordination.

The 22.49 MHz proton-noise-decoupled ^{13}C NMR spectra of *o*-HABzGH and its Y(III) complexes were recorded in $\text{DMSO-}d_6$ and the chemical shifts are given in table 4. In $[\text{Y}(\textit{o}\text{-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ the signals due to the carbonyl carbon and the azomethine carbon of the hydrazide moiety undergo a downfield shift suggesting the involvement of the above groups in coordination (Domiano *et al* 1984). In the $[\text{Y}(\textit{o}\text{-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$ the signal corresponding to the carbonyl carbon of the hydrazide moiety (C_α) is not discernible. Nevertheless, the signal due to the azomethine carbon undergoes a downfield shift suggesting coordination of the group with the metal ion. Further, the signal due to the carbonyl carbon of the benzamide moiety remains almost at the same position suggesting the non-involvement of the group in coordination with the metal ion.

Thus, ^1H and ^{13}C NMR spectral data suggest coordination of the carbonyl oxygen

Table 4. 22.49 MHz proton noise-decoupled ^{13}C NMR spectral data^{a,b} of *o*-HABzGH and its Y(III) complexes.

Carbon atom	<i>o</i> -HABzGH	$[\text{Y}(\textit{o}\text{-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$	$[\text{Y}(\textit{o}\text{-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$
C_α	166.76	170.01	—
C_β	166.32	165.67	165.93
$-\text{CH}_2-$	41.39	41.34	41.34
$-\text{CH}_3$	13.55	12.60	13.19
NC	155.21	156.32	156.16
C_1	131.43	132.06	131.32
C_2	128.35	128.29	128.29
C_3	127.32	127.20	127.28
C_4	133.87	133.97	133.97
$\text{C}_{1'}$	119.30	118.75	119.70
$\text{C}_{2'}$	158.52	158.69	158.80
$\text{C}_{3'}$	117.19	116.84	116.48
$\text{C}_{5'}$	118.49	118.17	119.07
$\text{C}_{6'}$	131.00	131.42	130.94

^a Measured in ppm w.r.t. $\text{DMSO-}d_6$ (39.50 ppm); ^b numbering scheme of the carbon atoms in the ligand is shown in figure 1.

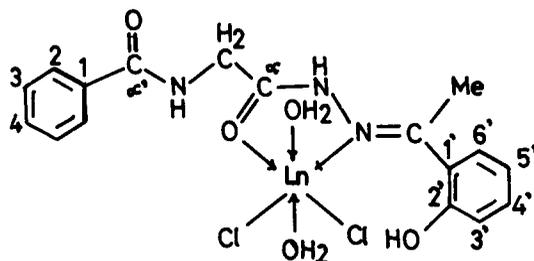


Figure 1. Structure of $[\text{Ln}(\textit{o}\text{-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]^+$.

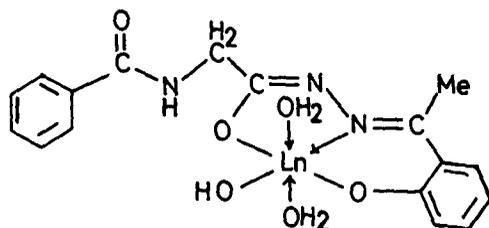


Figure 2. Structure of $[\text{Ln}(\text{o-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_3]$.

and azomethine nitrogen, and the non-coordination of the benzamide carbonyl group. This inference is consistent with that drawn from IR spectra.

Based on elemental analysis and various physico-chemical studies, the empirical formulae $[\text{M}(\text{o-HABzGH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ and $[\text{M}(\text{o-HABzGH-2H})\text{OH}(\text{H}_2\text{O})_2]$ have been tentatively proposed for the adducts and neutral complexes respectively with six-coordination around the metal ion (figures 1 and 2).

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