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Synthetic and spectral studies of some 4*f*-metal complexes

GENDA SINGH and T. R. RAO*
Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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Abstract—Salicylaldehyde(N-benzoyl)glycyl hydrazone (SalBzGH) has been synthesized and characterized. Metal complexes of the empirical formula [Ln(SalBzGH-2H)OH$(H_2O)_2$] where Ln = Y, Pr, Nd, Sm, Eu, Gd and Dy, have been synthesized and their structures studied by infrared, far-infrared, absorption, emission and NMR spectra. ^{1}H and ^{13}C NMR spectra indicate the presence of dynamic equilibrium between two isomers of SalBzGH over the 298–368 K temperature range and stabilization of a single isomer upon complexation with Ln(III). The hypersensitive band profile of the Nd(III) complex indicates a change in metal coordination number due to solvation, while an increase of temperature results in a decrease of ε_{max} of the hypersensitive band. The emission spectrum of [Eu(SalBzGH-2H)OH$(H_2O)_2$] at 77 K indicates a low site symmetry. SalBzGH coordinates through imidolic oxygen, azomethine nitrogen and phenolate oxygen.

INTRODUCTION

THE rare earth complexes in which strong fluorescence has been observed have almost exclusively Sm^{3+}, Eu^{3+}, Tb^{3+} or Dy^{3+} as the central metal ion whereas hypersensitive absorptions are observed exclusively in Nd^{3+}, Eu^{3+}, Er^{3+} and Ho^{3+}. The ability of certain trivalent lanthanide ions, Ln(III), to luminesce in solid or solution at room temperature renders them attractive as substitutional probe ions for the study of Ca(II)- and Mg(II)-binding species of biological interest [1, 2]. The Eu(III) ion is particularly useful in this regard in that it possesses nondegenerate ground ($^7F_0$) and emitting ($^5D_0$) states and its size and coordination number are equivalent to those of the Ca(II) ion. Previous work reported from our laboratory pertains to the absorption, IR, ^{1}H NMR and ^{13}C NMR spectral studies on the Nd(III), Sm(III) and Pr(III) adducts as well as neutral complexes of lanthanide chlorides and isothiocyanates with hydrazide [3] and hydrazones [4–8]. In this paper we report the preparation and spectral studies of neutral complexes of lanthanide(III) with salicylaldehyde(*N*-benzoyl)glycyl hydrazone (Fig. 1). The compounds of the composition [Ln(SalBzGH-2H)OH$(H_2O)_2$] where Ln = Y(III), Pr(III), Nd(III), Sm(III)–Dy(III) were studied by various spectral techniques.

EXPERIMENTAL

Ligand synthesis

All the chemicals used were of B.D.H. or S. Merck grade. Hydrated lanthanide chlorides (99.9% purity) obtained from M/s Indian Rare Earths Ltd, Kerala (India) were used as such. Salicylaldehyde(*N*-benzoyl)glycyl hydrazone was prepared by refluxing *N*-benzoylglycine hydrazide (25 mmol in 50 ml of methanol) and salicylaldehyde (50 mmol in 50 ml of methanol) for *ca* 6 h. The light yellow crystals, obtained on slow cooling of the reaction mixture to room temperature were separated by filtration, washed repeatedly with cold methanol and recrystallized from hot methanol, m.p. 249°C.

Analysis

Found: C, 64.40; H, 5.10; N, 14.21; N_2H_4, 10.68%. $C_{16}H_{15}N_3O_3$ requires: C, 64.65; H, 5.05; N, 14.14; N_2H_4, 10.77%.

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* Author to whom correspondence should be addressed.

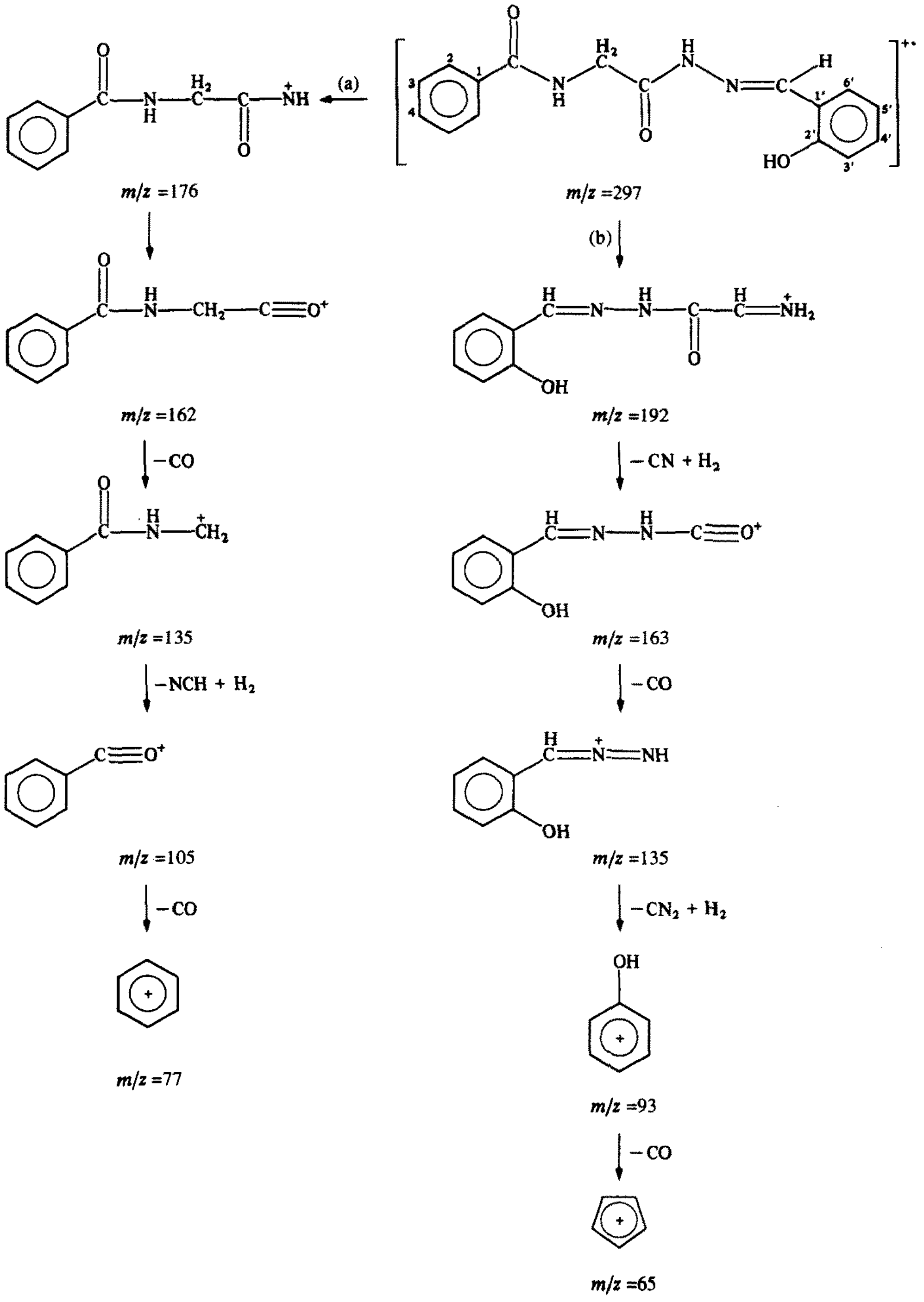

Fig. 1. Fragmentation pattern of SalBzGH.

Synthesis and analysis of the complexes

*Hydroxomono(salicylaldehyde(*N*-benzoyl)glycyl hydrazonato) diaqua lanthanide(III)* [Ln(SalBzGH-2H)OH(H_2O)$_2$] (Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb and Dy). These complexes were prepared by mixing together aqueous ethanolic solutions of the appropriate metal chloride (2.0 mmol in *ca* 20 ml), SalBzGH (2.0 mmol) and KOH (4.0 mmol in *ca* 20 ml) and adjusting the pH of the solution to ~7.5. The precipitated complexes were digested in a water bath for *ca* 1 h, filtered, washed successively with aqueous ethanol, ethanol and diethyl ether and dried at room temperature.

All the complexes were analysed for metal, N_2H_4 and nitrogen according to the procedures reported earlier [8]. The details of the equipment used for the physical measurements are also the same as reported earlier [6]. The emission spectrum of the Eu(III) complex was recorded using an Amnico–Bowman spectrofluorometer (SPF) using 360 nm excitation energy.

Results and Discussion

Characterization of the ligand

SalBzGH shows two strong bands at 1700 and 1640 cm^{-1} in the Nujol mull spectrum due to $\nu(\mathrm{C{=}O})$ of the carbonyl groups of the hydrazone and benzamide moieties, respectively. Of the four medium intensity bands appearing in the spectrum at 1565, 1325, 1540 and 1305 cm^{-1} the former two may be assigned to amide II and amide III frequencies of the hydrazone carbonyl group of SalBGH while the latter two to those of the benzamide carbonyl group [9]. The band at 3420 cm^{-1} is due to $\nu(\mathrm{NH})$ whereas a broad band at 3210 cm^{-1} indicates a hydrogen-bonded phenolic group.

The ^{1}H NMR spectrum of SalBzGH shows doubling of the signals due to different conformers. Of the several spectra recorded as a function of temperature, the one at 368 K corresponds to a single conformer of SalBzGH. Reproduction of the spectra in ascending and descending orders of temperatures over the range 298–368 K supports the presence of dynamic equilibrium of SalBzGH between the two conformers.

The ^{13}C NMR spectrum in DMSO-d_6 shows as many as 20 resonance signals corresponding to the 16 carbon atoms present in the molecule indicating the presence of conformers. The signals observed at 169.89(s), 166.54 and 165.5(d), and 147.25(s) ppm correspond to C_α, $C_{\alpha'}$ and NCH, respectively. All the other signals observed are given in Table 4.

Mass spectrum

In the mass spectrum (Fig. 2) of SalBzGH, the base peak obtained at $m/z = 297$ corresponds to the molecular ion. All the major peaks of the spectrum can be explained following the fragmentation path (Fig. 1).

Characterization of the complexes

A summary of the analytical results and physical data is given in Table 1. It can be observed that the ligand SalBzGH reacts with Ln(III) chlorides independently of mole ratio, at *ca* 80°C in aqueous ethanol at pH ~7.5 to give $[\mathrm{Ln(SalBzGH\text{-}2H)OH(H_2O)_2}]$ where Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb and Dy. The formation of these deprotonated

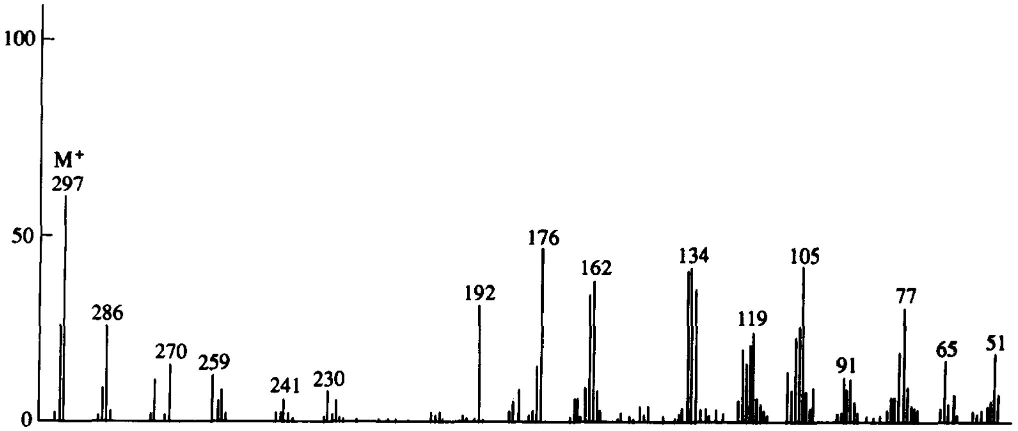

Fig. 2. Mass spectrum of SalBzGH.

Table 1. Analytical data, general behaviour and magnetic moments of SalBzGH complexes

Complex and colour (m.p. °C)	UV spectra (mμ)		Found (calc.) %					μ_{eff} (B.M.)
	λ_{max}	ε_{max}	C	H	N	M	N_2H_4	
[Y(SalBzGH-2H)OH(H_2O)$_2$]	281	22 290	44.01	4.14	9.60	20.50	7.41	Diamagnetic
Yellow (>300)	292	22 910	(44.05)	(4.13)	(9.61)	(20.41)	(7.32)	
	316	16 890						
	367	11 770						
[Pr(SalBzGH-2H)OH(H_2O)$_2$]	281	17 110	39.23	3.50	8.60	28.50	6.39	3.67
Yellow (>300)	291	15 840	(39.27)	(3.48)	(8.59)	(28.57)	(6.53)	
	322	10 750						
	362	5860						
[Nd(SalBzGH-2H)OH(H_2O)$_2$]	280	20 880	39.04	3.48	8.53	29.51	6.45	4.31
Yellowish green (284 d)	290	18 720	(39.01)	(3.45)	(8.53)	(29.30)	(6.50)	
	323	13 940						
	368	3710						
[Sm(SalBzGH-2H)OH(H_2O)$_2$]	281	18 970	38.60	3.40	8.45	30.78	6.35	2.20
Yellow (279 d)	290	17 530	(38.53)	(3.41)	(8.43)	(30.43)	(6.42)	
	323	12 380						
	364	5900						
[Eu(SalBzGH-2H)OH(H_2O)$_2$]	281	15 810	38.38	3.41	8.42	30.59	6.48	3.16
Yellow (>300)	292	14 270	(38.40)	(3.40)	(8.40)	(30.49)	(6.40)	
	322	9800						
	365	4290						
[Gd(SalBzGH-2H)OH(H_2O)$_2$]	281	19 170	38.01	3.38	8.30	31.09	6.25	7.82
Yellow (>300)	291	18 190	(37.99)	(3.36)	(8.31)	(31.18)	(6.33)	
	321	12 760						
	363	17 030						
[Tb(SalBzGH-2H)OH(H_2O)$_2$]	280	16 150	37.94	3.36	8.31	31.17	6.28	8.80
Yellow (272 d)	290	15 960	(37.88)	(3.35)	(8.29)	(31.39)	(6.31)	
	322	10 500						
	371	3900						
[Dy(SalBzGH-2H)OH(H_2O)$_2$]	281	13 800	37.56	3.33	8.25	32.06	6.32	9.22
Yellow (>300)	292	13 320	(37.61)	(3.33)	(8.23)	(31.94)	(6.27)	
	321	8570						
	360	6240						

d Decomposition temperature.
SalBzGH shows λ_{max} at 281 (18 800), 291 (17 600) and 323 (14 960) mμ.

complexes may be represented by the following equation:

$$LnCl_3 \cdot nH_2O + SalBzGH + 3KOH \xrightarrow{\text{aq. ethanol}} [Ln(SalBzGH\text{-}2H)OH(H_2O)_2]nH_2O + 3\,KCl$$

In all the complexes the ligand is present in its semi-enolized di-deprotonated form due to amide $\rightleftharpoons$ imidol tautomers as a function of pH. All the complexes are stable at room temperature and are soluble only in coordinating solvents like pyridine, dimethylformamide and dimethylsulphoxide. The electrical conductance data in DMF (Ω_M values of 9–25 ohm^{-1} cm^2 mol^{-1}) indicate that all the complexes are non-electrolytes [10]. The weight loss suffered by the complexes on heating them in the 100–180°C temperature range corresponds to two water molecules. All the complexes are light yellow in colour.

Magnetic moments

The room temperature magnetic moments of the complexes corrected for diamagnetism show very little deviation from van Vleck values [11] indicating minor participation of 4*f*-electrons in bond formation. However, the enhanced magnetic moment of the Nd(III) complex may be due to an increase in covalency. The Sm(III) complex shows a marginally higher moment which may presumably include temperature-dependent magnetism on account of low *J*-separation [12].

Infrared spectra

The IR spectra of all the complexes have shown some band shifts which indicate the coordination mode of the ligand. In particular, there are some characteristic vibrations of the coordinated ligand in the enol form that are much more diagnostic of the formation of neutral complexes.

The positions of amide I (1640), II (1540) and III (1305) cm^{-1} bands arising from the >C=O group of the benzamide moiety remained almost unaltered in the spectra of all the complexes compared to those of SalBzGH suggesting non-involvement of the above group in coordination [13]. However, such amide bands (1700, 1565 and 1325 cm^{-1}, respectively) of the hydrazone >C=O group totally disappeared from the spectra of the complexes and a sharp band diagnostic of >C=N—N=C< group appeared at 1610 cm^{-1} [14] which indicates destruction of the hydrazone carbonyl group through amide$\rightleftharpoons$imidol tautomerism and subsequent coordination of the imidol oxygen. Coordination of the imidol group in the complexes is further supported by the appearance of new peaks characteristic of $\nu(NCO^-)$ in the 1530–1510 and 1370–1365 cm^{-1} regions of these spectra [15]. The ν(N—N) band occurring at 965 cm^{-1} in SalBzGH undergoes a hypsochromic shift (~35 cm^{-1}) in the spectra of all the complexes supporting coordination through azomethine nitrogen. Coordination of the phenolate oxygen may be indicated on the basis of the observed hypsochromic shift (1275–1300 cm^{-1}) of the $\nu(C—O)_{phenolic}$ mode and the disappearance of the in-plane and out-of-plane deformation modes of the phenolic —OH group [16]. The band at 1200 cm^{-1} is assigned to M—OH bending [17].

The FT-far-IR spectrum (50–640 cm^{-1} region) of $[Nd(SalBzGH\text{-}2H)OH(H_2O)_2]$ shows a strong band at 435 cm^{-1} which may be assigned to the wagging mode of vibration (e_w) of the coordinated water molecules [17]. Further, the fine spectrum consisting of a doublet (430 and 433 cm^{-1}) suggests that both the water molecules are in *cis*-configuration to each other. The broad and strong band observed at 254–266 cm^{-1} which was absent in the spectrum of SalBzGH is indicative of ν(Nd—O) vibration [18, 19], while the medium intensity band at 170 cm^{-1} is assignable to the ν(Nd—N) mode [20].

Absorption spectra

Intra-ligand and charge-transfer transitions. The UV absorption spectral bands of SalBzGH and its complexes along with the assignments are included in Table 1. SalBzGH shows bands at 244, 297, 301 and 361 nm in Nujol and at 281, 292 and 323 nm in DMSO solution due to the presence of >C=N, >C=O and phenolic chromophores in the molecule. Complexation with Ln(III) has been found to shift the band positions and to increase the ε_{max} values. At pH ~13 the phenolic group of SalBzGH is shifted to 385 nm ($\varepsilon = 19\,680\ mol^{-1}\,cm^{-1}$) presumably due to the formation of the $SalBzGH^{2-}$ ion and the availability of one extra pair of electrons resulting in the bathochromic and hypochromic shifts of the signal [21]. The observed shifts in the ligand bands and the appearance of a new broad band at 350–500 nm in the Nujol mull spectra of the complexes may be taken as evidence of coordination of SalBzGH (in anionic form) to the metal ion.

In order to get charge-transfer bands, the experimental data were taken on chelate samples vs ligand reference in a double beam mode and the base line for the ligand reference vs ligand sample was found to be very nearly flat in the region of interest. The absorption bands of rare-earth ions in this region are relatively much weaker in intensity and so, it is concluded that the observed spectra are of charge-transfer origin. This charge-transfer may occur due to the transition from the filled π-level of the ligand to the vacant outer orbitals of the lanthanide ions. This is based on the fact that electronic transitions from the π-levels can occur at lower energy than similar transitions from lanthanide ions [22]. In the latter case, these transitions would have to arise from the 4*f*-orbitals, which have considerably higher ionization energies than the ligands.

f-f Transitions. The electronic spectral data of some of the selected complexes are reported in Table 2. The nephelauxetic effect has been correlated with the covalency of the metal–ligand bonding [23, 24], and Sinha's parameter (δ) [25] is usually supposed to be a measure of the covalency. The absorption spectrum of the neodymium(III) complex shows the expected red shift in comparison to the aqua metal ion. Adsorption intensities have been determined by the area under the absorption curve and oscillator strengths calculated from the reduced expression [26, 27]:

$$P=(4.31\times10^{-9})\frac{9\eta^2}{(\eta^2+2)^2}\int\varepsilon(\bar{\nu})\mathrm{d}\nu,$$

where η is the refractive index of the solution and $\varepsilon(\bar{\nu})$ is the molar extinction coefficient at wavenumber $\bar{\nu}$ in cm^{-1}. While the oscillator strengths (Table 2) corresponding to all the observed bands of [Nd(SalBzGH-2H)OH(H_2O)$_2$] are larger than those reported for the aquo-ion [28], the P value of the band due to the transition ${}^4I_{9/2}\rightarrow{}^4G_{5/2}$, ${}^2G_{7/2}$ requires a special mention since there is an eight fold increase. Thus, it indicates a greater sensitivity of the hypersensitive band to the changes in the electronic environment. Obviously, the larger value is due to the interaction of the Nd^{3+} ion with the enolic form of SalBzGH leading to a greater covalency of the metal–ligand bonding and a higher oscillator strength [28]. Higher oscillator strength is sometimes a manifestation of lower symmetry of complexes [9, 26]. The hypersensitive band of Nd(III) complexes has been used for probing the coordination environment about the metal ion [26]. The Nujol mull spectral features of [Nd(SalBzGH-2H)OH(H_2O)$_2$] resemble those of six-coordinated Nd(DPPD)$_3$ [27] while the spectral profile of the DMF/DMSO solution spectrum (Fig. 3) indicates a seven coordination due to its close similarity to that of Nd(tfaa)$_3\cdot H_2O$ reported by KARRAKER [27]. The effect of environment on the hypersensitive transitions was examined by measuring the spectra at different temperatures. In the case of the Nd(III) complex, there has been a significant reduction in the absorption coefficient ($\varepsilon_{\max}$) as a function of temperature in the range 25–75°C, with no considerable change in the band position. Such a behaviour was reported in the case of neodymium complexes of hydroxy acids [30] where the oscillator strengths are found to be influenced by temperature effects supporting the presence of dynamic coupling due to structures with inversion symmetry [31]. Various spectral parameters calculated from the hypersensitive transition energy are included in Table 2. In the absence of a ν_{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 per cent) is expressed as $\delta=(1-\beta)100/\beta$ where β is the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The positive value of δ indicate covalent bonding in the Nd(III) complex.

Table 2. Electronic spectral data of Nd(III) complex of SalBzGH

Band max (cm^{-1})			Oscillator strength	
Nujol	DMF solution	Assignments	$P\times10^6$	Calculated parameters*
10 930–11 695	11 300–11 630	${}^4I_{9/2}\rightarrow{}^4F_{3/2}$	10.94	
11 975–12 785	12 150–12 660	$\rightarrow{}^4F_{5/2}$	13.85	
12 990–13 795	12 990–13 700	$\rightarrow{}^4F_{7/2}$, ${}^3S_{3/2}$	18.61	$\beta=0.986$
14 285–14 925	14 685–14 925	$\rightarrow{}^4F_{9/2}$	5.07	$b^{1/2}=0.084$
16 315–17 700	16 395–17 545	$\rightarrow{}^4G_{5/2}$, ${}^2G_{7/2}$	64.62	$\delta\%=1.44$
18 350–19 160	18 520–19 050	$\rightarrow{}^4G_{7/2}$	13.86	
19 160–19 685	19 050–19 510	$\rightarrow{}^4G_{9/2}$	11.73	
19 685–21 645	—	$\rightarrow{}^4G_{11/2}$	—	

* Parameters calculated from Nujol mull spectra.

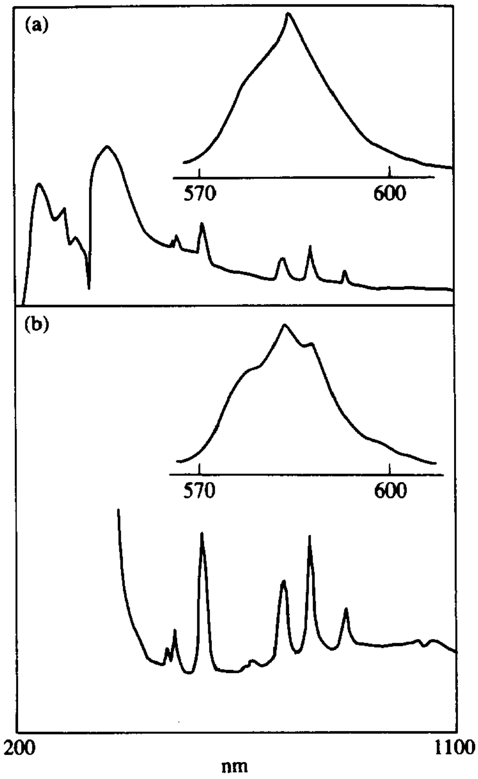

Fig. 3. Absorption spectra of [Nd(SalBzGH-2H)OH(H_2O)$_2$]: (a) in Nujol; (b) in DMF solution, and their expanded hypersensitive bands.

Fluorescence/emission spectra provide valuable information relating to coordination numbers, nature of bonding and symmetry in lanthanide complexes. The small splittings that characterize certain lanthanide emission lines are useful for establishing, by a group theoretical method, the local site symmetry of the metal ion in the complex [32]. Eu(III) complexes are often studied in preference to other lanthanides, since the low J values of the strongest emission lines ($^5D_J \to {}^7F_{J'}$, $J = 0, 1$; $J = 0, 1, 2$) give rise to a smaller number of closely spaced energy levels than is observed with most other lanthanide ions. The emission spectrum of [Eu(SalBzGH-2H)OH(H_2O)$_2$] at 77 K shows that emission arises mainly from transitions originating at the $^5D_0$ level. The spectrum shows a very weak line at 17 256 cm^{-1} associated with the $^5D_0 \to {}^7F_0$ transition which was assumed to be forbidden. The $^5D_0 \to {}^7F_1$ transition (16 783 cm^{-1}) consists of three components, two of which are attributable to an E species. The region of $^5D_0 \to {}^7F_2$ (16 180 cm^{-1}) also contains an equal number of peaks, two of which are attributable to an E species (both electric and magnetic dipole components) and one to A_1 species (electric dipole component). Based on the above observations, a low site symmetry may be proposed for the complex [33].

The total charge on the ligand attached to the central metal ion was calculated using the equation [34]

$$\nu = 0.76P^2 + 2.29P + 17\,273$$

where P is total charge on ligand and ν is the shifting of the band corresponding to the transition $^5D_0 \to {}^7F_0$ in cm^{-1} from 17 273 cm^{-1} and was found to be -3.01. The intensity ratio, $\eta_{\mathrm{Eu}^+} = {}^5D_0 \to {}^7F_2 / {}^5D_0 \to {}^7F_1$ was found to be 2.08 which corresponds to a role of covalency in the metal–ligand bond [35].

Table 3. ^{1}H NMR spectral data (δ) of SalBzGH and the Y(III) complex

Protons	SalBzGH (298 K)	SalBzGH (368 K)	$[Y(SalBzGH\text{-}2H)OH(H_2O)_2]$ (298 K)
—CH_2—	4.05^{d}, 4.43^{d}	4.19^{d}	3.85^{s}
C_6H_5CONH—	8.66^{t}, 8.88^{t}	8.48	9.10^{t}
RN*H*CO—	10.05^{s}, 11.12^{s}	10.71	—
—C_6H_4OH	11.45^{s}, 11.71^{s}	11.3^{s}	—
—NC*H*—	8.28^{s}, 8.42^{s}	8.43^{s}	8.52^{s}
Ring	7.90^{m}	7.90^{m}	7.61^{s}
	7.52	7.52	7.23^{s}
	7.19	7.24	7.00^{d}
	6.95	6.95	6.62^{m}
	6.86	6.86	6.67^{d}

s Singlet; d doublet; t triplet; m multiplet.

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

The ^{1}H NMR spectra (in $^{2}H_6$-DMSO) of SalBzGH and $[Y(SalBzGH\text{-}2H)OH(H_2O)_2]$ were recorded at room temperature. The resonances observed (Table 3) in the spectrum of SalBzGH at δ 11.7(s) and 11.45(s) due to —C_6H_4OH, and δ 11.12(s) and 10.05(s) due to —CON*H* N=C< were found to completely disappear from the spectrum of the Y(III) complex. The above observations are in strong support of deprotonation of the —C_6H_5OH and the hydrazidic —N*H*— groups presumably through amide$\rightleftharpoons$imidol tautomerism. Thus, the spectrum of Y(III) complex involving coordination of dinegative species of SalBzGH through imidolic oxygen, phenolate oxygen and azomethine nitrogen is expected to be devoid of signals of the two protons in question. The downfield shift of the —N=C*H*— resonance also supports the interaction of azomethine nitrogen in the complex. However, the two triplets of $C_6H_5CONHCH_2$— appearing at δ 8.88 and 8.66 and characterizing the two conformers of SalBzGH coalesce into a single broad peak centred at δ 8.91 in the complex. The non-retention of the doubling feature indicates the absence of two different conformers in the Y(III) complex and the negligible shift is consistent with non-coordination of the above group. Further, there was a high-field shift of the resonance signals due to the salicyloyl ring protons in the Y(III) complex, such a shift may be due to an increase in electron density through electron delocalization in the di-deprotonated form of the ligand. This indirectly supports coordination in the deprotonated form of SalBzGH.

The assignments of the proton-noise-decoupled ^{13}C NMR spectra have been made applying the principle of substituent additivity [21] and the numbering scheme of the carbon atoms is as shown in Fig. 1. The ^{13}C NMR spectrum recorded at RT (Table 4) is compatible with two different conformers of SalBzGH while that at 368 K corresponds to a single isomer and hence the latter has been used for comparison. The spectrum of $[Y(SalBzGH\text{-}2H)OH(H_2O)_2]$ characterizing downfield shifts of —*C*(O)NHN=C< and —C(O)NHN=*C*< atoms support coordination through carbonyl oxygen and azomethine nitrogen [36]. The upfield shifts of the salicyloyl ring carbon atoms indirectly support coordination through dinegative species of SalBzGH involving electron delocalization [37]. However, the resonance signals due to the C_6H_5CONH— and the phenyl ring carbon atoms suffer no shift in the complex which indicates non-interaction of the benzamide carbonyl group with the metal ion.

CONCLUSION

The bonding sites of SalBzGH in its Ln(III) complexes were discussed applying various physico-chemical techniques. SalBzGH, involving a dynamic equilibrium between two different conformers over the temperature range 298–368 K, has been found to become stabilized in a single conformer upon complexation with metal ion. The

Table 4. ^{13}C NMR spectral data* of SalBzGH and the Y(III) complexes

Carbon atoms	SalBzGH (298 K)	SalBzGH (368 K)	[Y(SalBzGH-2H)OH(H_2O)$_2$] (298 K)
C_α	169.89	—	171.04
$C_{\alpha'}$	166.54, 165.51	166.59	165.61
—H_2C—	42.26, 41.34	41.23	42.26
—NCH—	147.25	—	153.62
C_1	131.27	130.68	131.92
C_2	128.29	127.75	128.45
C_3	127.31	126.78	127.31
C_4	133.84, 133.61	133.95	133.38
$C_{1'}$	126.45	—	—
$C_{2'}$	157.28, 156.35	156.72	158.69
$C_{3'}$	118.59, 116.32	115.34	113.45
$C_{4'}$	141.19	—	141.57
$C_{5'}$	120.06, 119.30	118.87	119.79
$C_{6'}$	129.38	128.56	131.48

* Measured in ppm w.r.t. DMSO-d_6 (39.50 ppm).

empirical formula [Ln(SalBzGH-2H)OH(H_2O)$_2$] has been proposed for the present complexes with a dinegative tridentate functional ligand and a six-coordinated metal ion with low site symmetry.

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REFERENCES

[1] F. S. Richardson, *Chem. Rev.* **82**, 541 (1982).
[2] J. C. G. Bunzli, *Inorg. Chim. Acta* **139**, 219 (1987).
[3] T. R. Rao, I. A. Khan and R. C. Aggarwal, *Proc. Indian Acad. Sci. (Chem. Sci.)* **97**, 13 (1986).
[4] T. R. Rao, G. Singh and I. A. Khan, *Trans. Met. Chem.* **14**, 15 (1989).
[5] T. R. Rao and G. Singh, *Synth. React. Inorg. Met.-Org. Chem.* **20**, 263 (1989).
[6] T. R. Rao and G. Singh, *Trans. Met. Chem.* **14**, 471 (1989).
[7] T. R. Rao and G. Singh, *Proc. Indian Acad. Sci. (Chem. Sci)* **101**, 219 (1989).
[8] T. R. Rao and G. Singh, *Indian J. Chem.* **29A**, 154 (1990).
[9] G. Marcotrigiano and G. C. Pellacani, *Inorg. Nucl. Chem. Lett.* **11**, 643 (1975).
[10] W. J. Geary, *Coord. Chem. Rev.* **7**, 81 (1971).
[11] J. H. van Vleck and A. Frank, *Phys. Rev.* **34**, 1494 (1929).
[12] B. N. Figgis and J. Lewis, *Techniques of Inorganic Chemistry*, Vol. 4, p. 137. Interscience, New York (1965).
[13] K. Nagano, H. Kinoshita and A. Hirakawa, *Chem. Pharm. Bull.* **12**, 1198 (1964).
[14] E. El-Gayel and M. F. Iskander, *J. Inorg. Nucl. Chem.* **33**, 107 (1971).
[15] C. N. R. Rao, *Chemical Application of Infrared Spectroscopy*, p. 265. Academic Press, New York (1963).
[16] Y. Inomata, T. Inomata and T. Moriwaki, *Bull. Chem. Soc. Jap.* **47**, 818 (1974).
[17] K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 4th edn, p. 230. Interscience, New York (1978).
[18] J. R. Ferraro, *Low Frequency Vibration of Inorganic and Coordination Compounds*. Plenum Press, New York (1971).
[19] J.-C. G. Bunzli, E. Moret and J.-R. Yersin, *Helv. Chim. Acta* **61**, 762 (1978).
[20] J.-P. Roche and P. V. Huong, *Bull. Soc. Chim. Fr.* 4521 (1972).
[21] A. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th edn, pp. 264, 308. Wiley, New York (1981).
[22] E. A. Boudreax and W.-G. Chen, *J. Inorg. Nucl. Chem.* **39**, 595 (1977).
[23] C. K. Jørgensen, *Prog. Inorg. Chem.* **4**, 73 (1962).
[24] J. L. Ravan and C. K. Jørgensen, *J. Phys. Chem.* **70**, 2845 (1966).
[25] S. P. Sinha, *Spectrochim. Acta* **22**, 57 (1966).
[26] D. G. Karraker, *Inorg. Chim.* **6**, 1863 (1967).
[27] D. G. Karraker, *Inorg. Chem.* **7**, 473 (1968).
[28] K. Iftikhar, *Inorg. Chim. Acta* **129**, 261 (1987).

[29] D. G. Karraker, *J. Inorg. Nucl. Chem.* **33**, 3713 (1971).

[30] P. Krumholtz, *Spectrochim. Acta* **10**, 274 (1958).

[31] D. E. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev.* **18**, 199 (1976); and Refs therein.

[32] R. E. Whan and G. A. Grosby, *J. Molec. Spectrosc.* **8**, 315 (1962).

[33] J. H. Forsberg, *Coord. Chem. Rev.* **10**, 195 (1973); and Refs therein.

[34] M. Albin and W. Dew Horroks Jr, *Inorg. Chem.* **24**, 895 (1985).

[35] A. Seminara and A. Musumeci, *Inorg. Chim. Acta* **95**, 291 (1984).

[36] G. Paolucci, G. Marangoni, G. Bandoli and D. A. Clemente, *J. Chem. Soc., Dalton Trans.* 1304 (1980).

[37] P. Domiano, C. Pelizzi, G. Predieri, C. Viglani and G. Palla, *Polyhedron* **3**, 281 (1984).