

Studies on some rare earth metal complexes: Ten- and six-coordinated complexes of an unsymmetrical aminoacid derivative

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Abstract. 2,4-Dihydroxybenzaldehyde(N-benzoyl)glycyl hydrazone, H₃dhhbgh, has been synthesized and characterized. Rare earth metal complexes of the empirical formulae, [Ln(H₃dhhbgh)₂Cl₂]Cl·nH₂O and [Ln(dhhbgh)(H₂O)₂], where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Y(III) have been synthesized and characterized by elemental analyses, molar conductances, magnetic susceptibilities, electronic, infrared and NMR spectral studies. Various bonding parameters (β , $b^{1/2}$, % δ and η) calculated from the electronic spectra of Pr(III), Nd(III), Sm(III) and Dy(III) complexes suggest a weak covalent bond between the metal and ligand. The theoretical oscillator strengths (P_{calcd}) and a set of three intensity parameters ($T_{\lambda=2,4,6}$) computed from the Judd–Ofelt equation are found to be in good agreement with experimental values. On the basis of the spectral profiles of the hypersensitive transitions (${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$) in the Nd(III) complexes, coordination numbers ten and six have been proposed for the Ln(III) ions in the adduct and deprotonated complexes respectively.

Keywords. Lanthanide metal complexes; 2,4-dihydroxybenzaldehyde(N-benzoyl)glycyl hydrazone; hypersensitive transitions.

1. Introduction

The chemistry of lanthanides has assumed considerable importance owing to their increasing use in the construction of superconductors (Gopalakrishnan *et al* 1987) and as ideal probes in studies on biological systems (Richardson 1982). Rare earth metal ions with their characteristic magnetic and spectral properties are suitable for studying various natural systems as potential probes. This is particularly true in the investigation of metal-containing macromolecules in which the metal ion is spectroscopically silent. Considerable interest has recently been evinced in the study of metal complexes of aminoacids containing catecholic or phenolic side chains mainly due to the potentially multidentate ligational behaviour of aminoacids (Birch and Manhan 1967; Weber and Simon 1971; Gergely *et al* 1971; Van der Helm and Tatsch 1972; McAuliffe and Murray 1973). This interest has led us to the synthesis and spectral studies on Ln(III) complexes and in continuation of our earlier work on rare earth metal complexes of various N, O-donor ligands, derived from tyrosine and glycine (Rao *et al* 1986, 1989; Rao and Khan

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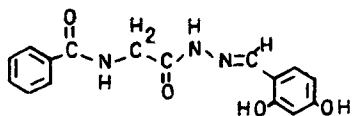


Figure 1. Structure of $H_3dhbbgh$.

1987; Rao and Singh 1989; Rao and Kumar 1994). We report here the results of our structural investigations on the Ln(III) complexes of 2,4-dihydroxybenzaldehyde(N-benzoyl)glycyl hydrazone, $H_3dhbbgh$ (figure 1).

2. Experimental

2.1 Materials and methods

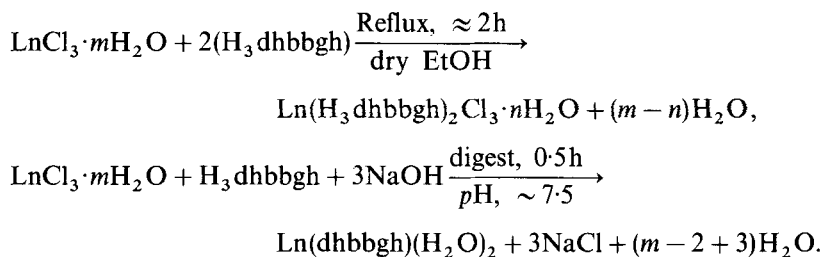
Chemicals of standard purity were used. Hydrated lanthanide trichlorides of 99.9% purity, supplied by the Indian Rare Earth Ltd., India were used as such. (N-benzoyl)glycyl hydrazide (BzGH) was prepared as reported earlier (Rao *et al* 1989). The ligand, $H_3dhbbgh$, was prepared by refluxing BzGH (4.95 g/25.0 mmol in 50 cm³ dry ethanol) and 2,4-dihydroxybenzaldehyde (3.45 g/25.0 mmol in 25 cm³ dry ethanol) for \approx 6 h. The white crude product, obtained on slow cooling of the reaction mixture to room temperature, was filtered off, washed repeatedly with cold ethanol and recrystallised from hot ethanol to get an yield of 5.75 g (73%) with a melting point of 236°C. Analysis: Found—C, 61.72; H, 4.21; N, 13.47; N₂H₄, 10.25%. Calcd. for C₁₆H₁₃N₃O₄—C, 61.73; H, 4.20; N, 13.49; N₂H₄, 10.27%; Mass spectrum, M⁺ ion peak at $m/z = 314$ (6.1% intensity); base peak at $m/z = 209$ (1.2% intensity).

2.2 Preparation and analyses of the complexes

2.2a Addition complexes: Dichlorobis(2,4-dihydroxybenzaldehyde(N-benzoyl)glycyl hydrazone) lanthanide(III) chloride hydrates, [Ln($H_3dhbbgh$)₂Cl₂]Cl.nH₂O, were obtained by mixing together absolute ethanolic solutions of the appropriate metal chloride (0.74 g/2.0 mmol in 20 cm³) and ligand (1.24 g/4.0 mmol in 20 cm³) and refluxing the reaction mixture for \approx 2 h. Addition of 10 cm³ of acetonitrile to the resulting solution yielded a gummy solid which was macerated in acetonitrile, dissolved in dry ethanol and reprecipitated by adding acetonitrile. Multiple repetitions of the process finally yielded crystalline complexes, which were filtered off and washed several times with a mixture of acetonitrile and ethanol (50:50 v/v), and dried in a desiccator at room temperature.

2.2b Neutral/deprotonated complexes: Monokis(2,4-dihydroxybenzaldehyde(N-benzoyl)glycyl hydrazone) diaqua lanthanides(III), [Ln(dhbbgh)(H₂O)₂], were prepared by mixing together aqueous solutions of the metal chlorides (0.74 g/2.0 mmol in 30 cm³ of water) and $H_3dhbbgh$ (1.24 g/4.0 mmol in 20 cm³ of water) and adjusting the pH of the resultant solution to 7.0–7.5 by adding NaOH solution (0.32 g/8.0 mmol in 30 cm³ of water). The precipitated complexes were digested on a water bath for \approx 1/2 h, suction-filtered, washed successively with water, aqueous methanol and diethyl ether, and dried at room temperature. The reaction conditions may be represented by the

following equations:



2.3 Physical measurements

C, H and N microanalyses were done on a Perkin–Elmer 240 C analyzer. Molar conductances were measured at room temperature on a WTW conductivity meter. Room temperature magnetic susceptibility measurements were carried out on a Cahn–Faraday electrobalance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Electronic spectra were recorded on UV-Vis-NIR (Cary-2390 and Shimadzu-160A) spectrophotometers. Infrared spectra were run on a FT-IR (JASCO-5300) spectrophotometer and NMR spectra on a Jeol. FX-90Q (90 MHz) and Bruker VM-40C (400 MHz) multinuclear spectrometers. Mass spectra of the ligands were recorded on a Shimadzu GC MS-QP 1000A mass spectrometer.

The theoretical oscillator strengths (P_{calcd}) were successfully computed by using the well-known Judd–Ofelt equation,

$$P_{\text{calcd}} = \Sigma T_{\lambda} v (f^N \Psi_j U^{(\lambda)} f^N \Psi'_j)^2 / (2J + 1),$$

where v is the energy of transition expressed in wave numbers (cm^{-1}), T_{λ} ($\lambda = 2, 4, 6$) are the adjustable phenomenological Judd–Ofelt parameters, which may be calculated by least square analysis using the matrix elements given in the literature, and the unit tensor operator, $U^{(\lambda)}$, connects the initial and final states, Ψ_j and Ψ'_j .

3. Results and discussion

3.1 Characterization of complexes

As borne out by the elemental analyses and various physical data (*vide* table 1), the ligand reacts with metal chlorides as a neutral ligand in ethanol and as a trinegative anion in aqueous solutions in the presence of NaOH in 1:2 and 1:1 metal to ligand stoichiometries. Thus, increase of pH by adding the requisite quantity of NaOH may facilitate the deprotonation of the ligand possibly through amide-imidol tautomerism, thereby enabling the ligand to behave as a trinegative species.

All the addition 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 in coordinating solvents like pyridine, DMF and DMSO. The electrical conductance data (*vide* table 1) indicate 1:1 ratio and non-electrolytic behaviour for adduct and neutral complexes respectively (Geary 1971). The weight loss suffered by the representative adduct (at 80–120°C) and neutral (at 80–160°C) complexes corresponds to one/two (presumably lattice-held) and two water molecules, respectively.

Table 1. Analytical data and general behaviour of Ln(III) complexes of H₃dhhbgh.

Complex*	Colour (% Yield)	m.pt. (°C)	Elemental analyses Found (Calcd.) (%)				μ_{eff} (BM)
			N	M	Cl	N ₂ H ₄	
I	Yellow (74)	242	9.42 (9.44)	15.26 (15.60)	11.85 (11.95)	7.17 (7.19)	Dia.
II	Orange (87)	236–238	9.47 (9.42)	15.68 (15.79)	11.89 (11.92)	7.14 (7.17)	3.46
III	Yellow (62)	198	9.35 (9.38)	15.89 (16.11)	11.80 (11.88)	7.13 (7.14)	4.05
IV	Pale yellow (69)	221	9.33 (9.32)	16.47 (16.68)	11.91 (11.79)	7.08 (7.10)	2.25
V	Yellow (73)	213	9.26 (9.30)	16.56 (16.82)	11.73 (11.77)	7.03 (7.08)	3.19
VI	Yellow (56)	195–197	9.03 (9.01)	16.61 (16.97)	11.57 (11.48)	6.87 (6.90)	7.83
VII	Yellow (61)	238	9.04 (9.05)	17.40 (17.12)	11.30 (11.45)	6.86 (6.89)	9.68
VIII	Cream (75)	247	9.01 (9.02)	17.23 (17.44)	11.37 (11.41)	6.58 (6.87)	10.67
IX	Yellow (59)	207	10.02 (10.00)	10.21 (10.58)	12.60 (12.66)	7.55 (7.62)	Dia.
X	Yellow (64)	> 300	8.64 (8.66)	28.38 (28.62)		6.57 (6.59)	Dia.
XI	Yellow (61)	> 300	8.62 (8.62)	29.17 (28.91)		6.52 (6.56)	3.31
XII	Yellow (78)	289 ^d	8.55 (8.56)	28.72 (29.40)		6.47 (6.52)	4.02
XIII	Cream (73)	267 ^d	8.43 (8.46)	29.45 (30.27)		6.42 (6.44)	2.53
XIV	Yellow (68)	> 300	8.40 (8.43)	29.82 (30.49)		6.38 (6.42)	3.71
XV	Pale yellow (55)	> 300	8.31 (8.34)	31.15 (31.32)		6.33 (6.35)	7.82
XVI	Yellow (61)	277 ^d	8.30 (8.31)	31.12 (31.45)		6.09 (6.33)	9.66
XVII	Yellow (77)	281 ^d	8.23 (8.25)	31.42 (31.93)		6.07 (6.28)	10.48
XVIII	Yellow (58)	> 300	9.64 (9.65)	20.04 (20.42)		7.33 (7.35)	Dia.

*I–IX represent adduct complexes with empirical formula, [Ln(H₃dhhbgh)₂Cl₂]Cl·3H₂O and X–XVIII represent deprotonated complexes with empirical formula, [Ln(dhhbgh)(H₂O)₂];

^d Dia.—diamagnetic.

3.2 Magnetic moments

The room temperature magnetic moments (*vide* table 1) of all the complexes, except that of Sm(III), show a little deviation from Van Vleck values (Van Vleck and Frank 1929), indicating some participation of 4*f*-electrons in bond formation. The Sm(III) complexes, however, show much deviation in their μ_{eff} values from Van Vleck values. Complex behaviour which includes the temperature-dependent magnetic moment is

expected in the case of Sm(III), since the energy difference between the ground state (${}^6H_{5/2}$) and the next higher J level leads to the thermal population of the higher energy levels and susceptibilities due to first-order Zeeman effect (Sinha 1966; Mark 1978).

3.3 Infrared spectra

The IR spectrum (recorded as KBr pellet) of H_3 dhhbgh shows two sets of bands at 1670, 1579, 1325 cm^{-1} and 1630, 1545, 1305 cm^{-1} due to $\nu(C=O)$, amide-II and amide-III modes of hydrazone and benzamide $>C=O$ groups respectively. The bathochromic shifts in the $\nu(C=O)$ and amide-II bands and the hypsochromic shifts in the amide-III band in the spectra of the adduct complexes suggest coordination of the hydrazone $>C=O$ group (Nagano *et al* 1964). However, the absence of such amide bands in the spectra of the neutral complexes and the appearance of a new band diagnostic of a $>C=N-N=C<$ group at 1610 cm^{-1} (Sayed and Iskander 1971) indicates the destruction of the hydrazone carbonyl group through amide \rightleftharpoons imidol tautomerism and subsequent bonding through imidolic oxygen after deprotonation. Coordination of the imidol group in the present deprotonated complexes was further inferred by the appearance of new peaks characteristic of $\nu(NCO^-)$ in the 1543–1540 and 1385 cm^{-1} regions (Rao 1963). The $\nu(N-N)$ band observed at ≈ 970 cm^{-1} in the spectrum of H_3 dhhbgh suffered a hypsochromic shift (≈ 20 cm^{-1}) in all the present complexes and suggests coordination through azomethine nitrogen (Braibanti *et al* 1968). The interaction of phenolic/phenolate oxygens in the adduct and neutral complexes may be invoked on the basis of the hypsochromic shifts of $\nu(C-O)_{phenolic}$ mode (ligand 1163, 1130 cm^{-1} ; adducts, 1174–1185, 1130 cm^{-1} ; deprotonated, 1220–1226, 1162–1176 cm^{-1}) Inomata *et al* 1974). Further, a broad intensity band in 3300–3150 cm^{-1} region in the adduct complexes indicate the presence of water molecules, preferably lattice-held. However, in addition to the above band, a medium intensity band observed at 800 cm^{-1} in all the neutral complexes supports the evidence of coordinated water molecules (Nakamoto 1978). In all the present complexes, the medium intensity band observed at 420 cm^{-1} may be assigned to the $\nu(M-N)$ mode (Nakamoto 1978).

3.4 NMR spectra

The 1H and ${}^{13}C$ NMR spectra of ligand and its diamagnetic complexes were recorded in DMSO- d_6 solutions at room temperature. The 1H NMR spectrum of H_3 dhhbgh exhibits resonance signals at δ 10.26 (broad singlet) and δ 8.73 (triplet) corresponding to the $-NH$ protons of hydrazone and benzamide moieties respectively. This assignment was further confirmed by the disappearance of the above signals after deuterium exchange. The two phenolic protons were observed at δ 11.46 and all the ring protons appeared as a broad multiplet at δ 6.66–8.20. A noteworthy feature of the spectrum is the presence of isomeric signals due to benzamide $-NH$ (δ , 8.73t, 8.83t), $-NH-CH_2-$ (δ , 4.23d, 4.56d), $-NCH-$ (δ , 8.40s, 8.53s) and $C_6H_3(OH)_2$ (δ , 11.46s, 11.72s). The presence of two sets of signals for each of the above protons suggests two possible isomers of H_3 dhhbgh caused by rotation about the C–N bonds at both the benzoyl and aldehyde ends. It is well-known that restricted rotation about the carbon-to-nitrogen bond in a number of amides leads to the existence of geometrical isomers (Lewin *et al* 1975). The present case is similar those of salicylaldehyde (N-benzoyl) glycylic hydrazone (Rao and Singh 1991) and furfural (N-benzoyl) glycylic hydrazone (Lonibala 1992) where two isomers were shown in each case. These isomers are usually non-separable due to the relatively low barrier to rotation (Stewart and Sidall 1970).

The ^1H NMR spectral features of the La(III) complexes suggest coordination through hydrazone $\text{C}=\text{O}/\text{C}-\text{O}^-$ oxygen and/or azomethine nitrogen and phenolic/phenolate oxygen(s) on the basis of considerable shifts in hydrazidic $-\text{NH}-$ ($\approx 0.6, \delta$) (adduct complex) and ring protons. Further, the spectra of both adducts and neutral complexes reveal the existence of single isomer upon complexation.

The signals in the proton-noise decoupled ^{13}C NMR spectrum of the ligand were assigned by adopting the principle of substituent additivity (Silverstein *et al* 1981) and the spectrum shows the resonance signals due to $> \text{C}=\text{O}$ (benzamide), $> \text{C}=\text{O}$ (hydrazide), $> \text{C}=\text{N}$ and $-\text{CH}_2-$ groups at 169.61, 165.28, 148.37 and 40.78 ppm, respectively. However, the signals observed at 127.45–133.89 ppm and 102.74–160.51 ppm may be assigned to benzamide and aldehyde ring carbons. These features also confirm the presence of two different isomers of the parent ligand while one isomer was stabilized upon complex formation. The ^{13}C NMR spectra of La(III) complexes show considerable shifts when compared to the spectrum of the free ligand suggesting coordination of ligand through hydrazone/imidol carbonyl oxygen, azomethine nitrogen and two phenolic/phenolate oxygens.

3.5 Electronic spectra

The absorption spectra of the Pr(III), Nd(III), Sm(III) and Dy(III) complexes were recorded as nujol mulls as well as ethanolic (2×10^{-3} M) solutions. The spectral data along with the various bonding parameters are given in table 2. All the absorption bands of the present complexes show weak perturbations due to complex formation and increase in intensity compared to the aquo metal ions, presumably due to the nephelauxetic effect (Carnall *et al* 1968). The absorption band associated with the nearly degenerate $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transitions of Nd(III) is known to exhibit strong hypersensitive behaviour (Choppin *et al* 1966; Peacock 1975), making it especially suitable for probing the coordination number around the Nd(III) ion. The spectral profiles of the above transition (solid as well as solution states) in the present Nd(III) complexes resemble that of ten (in case of adduct complex) and six (in case of deprotonated complex) coordinated complexes, as reported by Karraker (1967). Temperature variation (28–75°C) studies in methanol solution proved to have no effect on the hypersensitive band profiles and oscillator strengths of the present Nd(III) complexes. A similar environment around the Nd(III) ion in the solid and solution states (at room temperature) of the present Nd(III) complexes may be inferred from the identical spectral profiles of the hypersensitive band in both the states.

The absorption intensities were determined experimentally by the area method and the experimental oscillator strengths ($P \times 10^6$) were calculated for all the solution state spectral bands of the complexes being studied, using the reduced expression (Karraker 1967, 1968). These values show an increase in comparison to the aquo metal ions, which is most probably due to the lowering of molecular symmetry (Jorgensen and Judd 1964; Judd 1966). Further, the oscillator strengths calculated theoretically from the Judd–Ofelt equation ($P_{\text{calcd}} \times 10^6$) were found to be in reasonable agreement with the experimental values (*vide* table 2). A set of three intensity parameters (T_2, T_4 and T_6) were calculated in each case by substituting the values of P_{exptl} and matrix elements in the Judd–Ofelt equation, as reported earlier (Singh *et al* 1994). The trend in the T_λ parameters, $T_2 > T_4 > T_6$, shows that the T_2 has the maximum value for most of the complexes under discussion. These maxima may be explained in terms of the higher sensitivity of the T_2 parameter to the ligand environment (Carnall *et al* 1968), than that of the other two parameters.

Table 2. Electronic spectral data (cm^{-1}) of Pr(III), Nd(III), Sm(III) and Dy(III) complexes.

Complex	Nujol	MeOH	$S'L'J'$	$P \times 10^6$ Exptl. (Calcd.)	T_λ	Bonding parameters
II	6351		3F_3		$T_2 = 6.646$	$\beta = 0.996$
	6942		3F_4		$T_4 = 0.485$	$b^{1/2} = 0.046$
	9807	9762	1G_4	0.26(0.85)	$T_6 = 2.587$	$\% \delta = 0.432$
	16836	16871	$^1D_2^*$	3.64(3.02)		$\eta = 0.002$
	20484	20586	3P_0	2.11(1.95)		
	21331	21285	$^3P_1, ^1I_6$	5.37(5.49)		
	22527	22544	$^3P_2^*$	9.11(9.20)		
III	11481	11485	$^4F_{3/2}$	5.83(4.77)	$T_2 = 11.279$	$\beta = 0.996$
	12428	12452	$^4F_{5/2}, ^2H_{9/2}$	19.36(20.46)	$T_4 = 2.565$	$b^{1/2} = 0.042$
	13476	13513	$^4F_{7/2}, ^4S_{3/2}$	24.79(24.05)	$T_6 = 1.984$	$\% \delta = 0.345$
		14480	$^4F_{9/2}$	1.30(1.76)		$\eta = 0.004$
	17096	17152	$^4G_{5/2}, ^2G_{7/2}^*$	33.97(33.96)		
	19175	19083	$^2K_{13/2}$	12.85(12.81)		
		21516	$^4G_{7/2}^*$ $^4G_{9/2}$ $^4G_{11/2}$			
IV	6309		$^6F_{1/2}^*$		$T_2 = 5.549$	$\beta = 0.995$
	6563		$^6H_{15/2}, ^6F_{3/2}$		$T_4 = 0.545$	$b^{1/2} = 0.050$
	6997		$^6F_{5/2}$		$T_6 = 0.360$	$\% \delta = 0.513$
		9225	$^6F_{9/2}$	1.98(1.83)		$\eta = 0.002$
	10440	10579	$^6F_{11/2}$	0.34(0.33)		
	24826	$^6P_{3/2}$	4.12(4.35)			
VIII	7751		$^6H_{9/2}, ^6F_{11/2}$		$T_2 = 34.552$	$\beta = 0.989$
	9049	9091	$^6F_{9/2}, ^6H_{11/2}$	3.16(3.12)	$T_4 = 0.664$	$b^{1/2} = 0.071$
	10989	10989	$^6F_{7/2}$	2.63(2.71)	$T_6 = 0.485$	$\% \delta = 0.231$
	12500	12366	$^6F_{5/2}$	1.87(1.71)		$\eta = 0.003$
	13157		$^6F_{3/2}$			
	22102		$^4I_{15/2}$			
23306	23281	$^4G_{11/2}$	0.245(0.106)			
XI	6435		3F_3		$T_2 = 15.259$	$\beta = 0.998$
	6928		3F_4		$T_4 = 2.819$	$b^{1/2} = 0.033$
	9896	9791	1G_4	0.35(0.86)	$T_6 = 0.665$	$\% \delta = 0.220$
	16821	16888	$^1D_2^*$	2.96(2.87)		$\eta = 0.001$
	21266	21165	$^3P_1, ^1I_6$	4.73(4.86)		
		22312	$^3P_2^*$			

(Continued)

Table 2. (Continued)

XII	11494	11490	${}^4F_{3/2}$	4.32(9.90)	$T_2 = 2.060$	$\beta = 0.989$
	12500		${}^4F_{5/2}, {}^2H_{9/2}$		$T_4 = 0.562$	$b^{1/2} = 0.076$
	13505	13513	${}^4F_{7/2}, {}^4S_{3/2}$	24.06(23.59)	$T_6 = 1.333$	$\% \delta = 0.551$
	17241	17246	${}^4G_{5/2}, {}^2G_{7/2}^*$	35.17(34.96)		$\eta = 0.004$
	19112	19074	${}^2K_{13/2}, {}^4G_{7/2}^*$			
XIII	6357		${}^6F_{1/2}^*$		$T_2 = 27.762$	$\beta = 0.994$
	6578		${}^6H_{15/2}, {}^6F_{3/2}$		$T_4 = 1.225$	$b^{1/2} = 0.046$
	6993		${}^6F_{5/2}$		$T_6 = 0.479$	$\% \delta = 0.431$
	8024		${}^6F_{7/2}$			$\eta = 0.002$
		9267	${}^6F_{9/2}$	2.32(2.38)		
	10431	10582	${}^6F_{11/2}$	1.13(2.01)		
	24875	${}^6P_{3/2}$	4.01(4.11)			
XVII	7782		${}^6H_{9/2}, {}^6F_{11/2}$		$T_2 = 72.210$	$\beta = 0.997$
	9076	9101	${}^6F_{9/2}, {}^6H_{7/2}$	2.20(2.54)	$T_4 = 16.595$	$b^{1/2} = 0.027$
	10979	10863	${}^6F_{7/2}$	2.58(3.04)	$T_6 = 3.688$	$\% \delta = 0.253$
	12352		${}^6F_{5/2}$			$\eta = 0.003$
	13150	13157	${}^6F_{3/2}$	1.85(1.54)		
	22079		${}^4I_{15/2}$			

*Hypersensitive transitions

The various bonding parameters were calculated using the literature procedure (Rayan and Jorgensen 1966; Tandon and Mehta 1970). The value of nephelauxetic ratio (β) (less than unity) and the positive values of the bonding parameter ($b^{1/2}$), covalency ($\% \delta$) and covalency angular overlap parameter (η) suggest a weak covalent bond between the metal ion and ligand.

4. Conclusions

The ligand, H_3 dhbbgh, was found to react with Ln(III) ions forming both adduct and deprotonated complexes at different pH values. Elemental analyses and molar conductance data suggest the empirical formulae, $[Ln(H_3 dhbbgh)_2 Cl_2] \cdot n H_2 O$ and $[Ln(dhbbgh)(H_2 O)_2]$ for the adduct and deprotonated complexes respectively. Various bonding parameters calculated from the electronic spectra suggest the predominantly ionic nature of the complexes, which in turn is consistent with the magnetic moments, where some participation of f -electrons was inferred. The IR and NMR data strongly suggest the varying denticity of the ligand with variation of pH, as mono- and bidentate towards Ln(III) ions, by offering hydrazone carbonyl oxygen and azomethine nitrogen as common bonding sites with one and two phenolate oxygen(s) in deprotonated and adduct complexes respectively. The electronic spectral profiles in the hypersensitive band region (≈ 585 nm) of the Nd(III) complexes suggest ten- and six-coordination number for the adduct and deprotonated complexes. 1H and ${}^{13}C$ NMR spectral data, besides confirming the bonding sites inferred from the IR spectral studies, provided valuable information regarding the existence of two geometrical isomers in the ligand.

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