



RESEARCH ARTICLE

LANTHANIDE COMPLEXES OF SCHIFF BASES DERIVED FROM FERROCENE KETO ACID AND 2-QUINOLINOYL AND 8-QUINOLINOYL HYDRAZINES

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ABSTRACT

Lanthanide(III), Cerium(III), Praseodymium(III), neodymium(III), Samarium(III), gadolinium(III), terbium(III), dysprosium(III) and yttrium(III) complexes of Schiff bases derived from ferrocenyl keto acid and 2-quinolinoyl hydrazine (H₂L) and Ferrocenyl keto acid and 8-quinolinoyl hydrazine (H₂L¹) have been prepared. The complexes are of the type [Ln(HL)L](H₂O)_n, [Ln(HL¹)L¹](H₂O)_n (n=1-2) and [Ln(HL¹)L¹] and these have been characterized on the basis of elemental analysis, conductance measurements. Magnetic moments thermal analysis, infrared and electronic absorption spectra. Nephelauxetic ratio (β) and covalency factor (b1/2) have been determined for neodymium(III) complexes, which indicate some covalent character in these complexes.

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INTRODUCTION

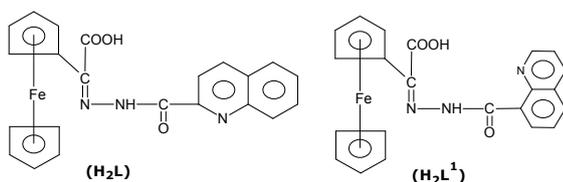
In the past decade, the lanthanide coordination chemistry was one of the most focused areas of research (Procházková, et al., (2016), Chen and Ma, (2015), Yang, et al., (2014). The intriguing structures (Han, et al., (2014), Wen, et al., (2015), Tian, et al., (2014) and the potential uses in a wide variety of areas as diagnostic tools in biology (Caki, et al., 2015) catalysis (Zhou et al., 2014), luminescence (Lahoud et al., 2016) and magnetism (Cristóvão and Hnatejko, 2015) reinforce the interest of chemists in these areas of research. A few years ago our research group initiated a project concerning rare earth metal chemistry ((a) Tamboura, et al, 2004, (b) Haba, et al., 2006) in a search for unusual molecular materials (Tamboura, et al., 2012) By use of an acyclic Schiff's base in presence of acetate groups, it is possible to introduce two identical or different lanthanide ions and to study their physicochemical properties (Sun et al., (2016) Costes et al., (2004) The flexibility and the multiple coordination site of the acyclic ligand provides several possible structure with lanthanide ions (Vigato and Tamburini, (2004), Casellato et al., (2004). The carboxylate groups can adopt various coordination modes, which may cause the generation of novel structures (de Oliveira et al., (2013), Wang et al., (2008).

Hydrazones are Schiff base precursors with a triatomic moiety connection of -C=N-NH. The chemistry of hydrazine derivatives has been intensively investigated in recent years. Complexes of Lanthanons with the Schiff base derived from 2-Acetyl pyridine and N-benzoyl glycine hydrazide have been prepared and characterized on the basis of elemental analysis, molar conductance, magnetic, electronic, infrared, 1H and 13C-NMR spectral techniques. The nephelauxetic ratio (β), the bonding parameter (b1/2), Sinhas parameter (δ%) and angular overlap parameter (η) have been calculated from the electronic spectra of Pr(III), Nd(III) and Sm(III) complexes infrared and NMR-spectra indicate coordination through the azomethine nitrogen; pyridine ring nitrogen and carbonyl oxygen of the hydrazone moiety. An eight coordinated structure has been proposed for the complexes (Rao & Genda, 1990). Interaction of some bivalent (Cu, Ni, Zn, Co) and trivalent (La, Pr, Nd, Gd, Dy and Y) metal ions with cytidine and uridine in the presence of amino carboxylic acids (imino diacetic acid nitrilo triacetic acid and ethylene diamine tetra acetic acid/has been investigated by pH-measurements at 35°C and 0.10M (KNO₃) ionic strength. Influence of charge on the structure and stability of metal nucleoside complexes has been described. The differences in the stabilities of the binary and ternary systems have been measured in terms of Δlog K. Based on the Δlog K values, the mode of bonding in various complexes has been discussed. The factors responsible for

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differences in the stabilities of cytidine and uridine ternary systems have been identified (Ravindra Reddy & K.Sudhakar, 1990). Several complexes of lanthanons chlorosulphates with triphenyl phosphine (TPP) triphenyl phosphine oxide (TPPO), triphenyl Arsilene (TPA) and triphenyl Arsilene oxide (TPAO) have been isolated and characterized by magnetic moment, infrared and reflectance spectral studies (S.Aftab, *et al.*, 1990). A modified method for the evaluation of spectral parameters of 4f–4f transitions in Pr(III) and Nd(III) complexes have been discussed. A new hypersensitive band ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ is observed apart from the usual hypersensitive ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ band in the case of Nd(III)–nucleoside/nucleotide system and this has also been taken into considerations in the evaluation of parameters. A new correction parameters Tc is used in explaining the spectral data of Nd(III); it makes the interpretation of spectral data in solution more meaningful. This method has been tested for the spectra of ~200 complexes of Pr^{3+} and an equal number of Nd^{3+} complexes (Mishra, *et al.*, 1990). 2–quinolinoyl hydrazine (H_2L) and 8–quinolinoyl hydrazine (H_2L^1) schiff bases have attracted attention (Dutta & Sarkar, J.(1981), Dutta & Md. Hossain, (1982) because of their flexidentate and ambiprotic behaviour we here report study of complexes of some lanthanides with the following two ligands.



Experimental

The ligands were prepared, first 1–acetyl ferrocene alcoholic solution was oxidized by selenium dioxide to get the keto aldehyde which on further oxidation yield keto acid, this on condensation with 2–quinolinyl hydrazine and 8–quinolinoyl hydrazine in equimolar ratio gave the desired products (Dutta & Md. Hossain, (1982), Dutta & Das, (1983) .

General method of synthesis of the complexes

Hydrated lanthanon nitrate (0.001 mol) was dissolved in warm ethanol (10ml) and mixed with a solution of the Schiff base H_2L (0.0025 mol) in warm ethanol (20 ml). The mixture was then refluxed on a steam bath for 90 min. The resulting reddish yellow solution was treated with dilute ammonia (pH 4–4.5) with stirring. The complex formed was collected, washed with ethanol and dried over silica gel. The complexes of H_2L^1 were obtained without any pH adjustment. In the cases of heavier lanthanides [Gd(III), Tb(III), Dy(III) and Y(III)] the complexes were immediately formed upon mixing, while in the cases of lighter lanthanides [La(III), Pr(III) and Nd(III)] the products were obtained under refluxing conditions.

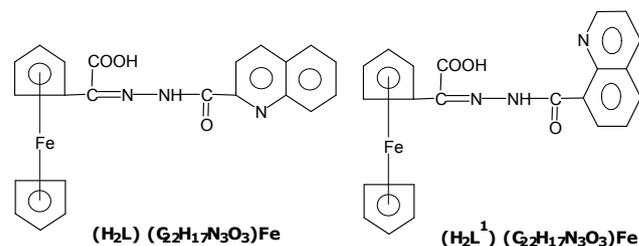
RESULTS AND DISCUSSION

The analytical data presented in Table 1 indicate that the complexes have 1:2 (metal: ligand) stoichiometry. The water molecules associated with these complexes are lost at ~110°C in an oven. Thermograms run for these hydrated complexes also indicate loss of water in the temperature range 60° to 110°C, indicating that water molecules are lattice–held and not coordinated. This is also supported by the presence of a broad

band ~3400 cm^{-1} in the infrared spectra and no new bands in the 600–700 cm^{-1} region, which is almost absent in the anhydrous samples. All these complexes behave as nonelectrolytes in DMF ($\Lambda_M = 12–25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) as compared to 65–90 $ohm^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for 1:1 electrolytes (R.L.Dutta & A.Syamal, 1982) in DMF. The magnetic moment values are normal and follow the trend of the usual double humped curve (Sayed & Iskander, 1971).

Infrared spectra and bonding sites

The ligands H_2L and H_2L^1 are capable of functioning as neutral tridentate (ONO), monobasic tridentate (ONO) (in keto form) or dibasic tridentate (ONO) donor (in enol form). The ligands ferrocenyl keto acid–2–quinolinoyl hydrazine and 8–quinolinoyl hydrazine show characteristic sharp bands at 3300, 3160 (due to νNH); 1690, 1670 (due to $\nu C=O$ amide–I); 1610 (due to $\nu C=N$); and 1265 cm^{-1} due to $\nu(COOH)$ modes respectively. The νOH in the ligands could not be identified with certainty probably due to intramolecular hydrogen bonding with the azomethine nitrogen. On complexation, the νNH band of ferrocene glycolic acid 2–quinolinoyl hydrazine lose both sharpness and intensity and appears at 3240–3200 cm^{-1} , while that of ferrocene glycolic acid 8–quinolinoyl hydrazine complexes appears with diminished intensity at ~3100 cm^{-1} . All these complexes show a broad and medium intensity band in the 3350–3450 cm^{-1} region due to lattice water, which are absent in the anhydrous samples. The sharp strong bands at 1630–1610 cm^{-1} and 1605–1610 cm^{-1} in the complexes have been assigned (D.G. Karrakar, 1967) to the lowered $\nu C=O$ (amide–I) and skeleton $-C=N-N=C-$ vibrations. The band at 1580 cm^{-1} in these complexes may be attributed to the lowered azomethine ($\nu C=N$) group. An upward shift of C–O stretching vibration ~30 cm^{-1} suggests bonding of carboxylic oxygen to the metal ion. This indicates that the ligands are attached to the metal ion in two forms; one as a dibasic ONO donor in the enol form (a) while the other as a monobasic ONO donor in the keto form (b). It has been shown earlier that these ligands cannot function as (NONO) quadridentate donor.



Electronic spectra

The electronic spectra of neodymium(III) complexes (Table 2) of ferrocene glycolic acid 2–quinolinoyl and 8–quinolinoyl hydrazines in DMF and DMSO are identical but are slightly different from the solid state spectra, indicating a substantial influence of the solvents on the symmetry around the central ion. The spectral shape of the hypersensitive transition (${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) of neodymium(III) complexes compare well with the shapes of the bands of 6–coordinated Nd(III) complexes reported by Karakar (N.Rajasekar & S.Soundararajan, 1981) and other authors (S.P.Sinha, 1966). The band due to ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition of Nd(III) at ~23000 cm^{-1} was not resolved possibly due to the strong charge transfer band at 24000 cm^{-1} .

Table 1. Characterisation data of lanthanide complexes of aroyl hydrazines

Compound	Colour	Found (Calc.)%		μ_{eff} B.M.
		N	Metal	
Fe ₂ [La(HL)L]H ₂ O	Deep yellow	8.17 (8.33)	13.69 (13.78)	Diamagnetic
Fe ₂ [Ce(HL)L]H ₂ O	Brown	8.20 (8.32)	13.68 (13.88)	2.3
Fe ₂ [Pr(HL)L]1.5H ₂ O	Light yellow	8.10 (8.24)	13.80 (13.83)	3.2
Fe ₂ [Nd(HL)L]2H ₂ O	Greenish light yellow	8.14 (8.34)	13.73 (13.99)	3.3
Fe ₂ [Sm(HL)L]H ₂ O	Deep yellow	8.20 (8.31)	14.70 (14.88)	1.84
Fe ₂ [Gd(HL)L]H ₂ O	Light yellow	8.10 (8.25)	15.28 (15.45)	7.85
Fe ₂ [Tb(HL)L]H ₂ O	Deep yellow	8.00 (8.24)	15.42 (15.59)	9.3
Fe ₂ [Dy(HL)L]H ₂ O	Pale yellow	8.05 (8.21)	15.71 (15.89)	10.32
Fe ₂ [Y(HL)L]H ₂ O	Light yellow	8.0 (8.13)	16.57 (16.75)	Diamagnetic
Fe ₂ [La(HL ¹)L ¹]H ₂ O	Deep yellow	8.17 (8.33)	13.69 (13.78)	Diamagnetic
Fe ₂ [Pr(HL ¹)L ¹]H ₂ O	Deep yellow	8.21 (8.39)	13.79 (14.07)	3.25
Fe ₂ [Nd(HL ¹)L ¹]	Greenish light yellow	8.30 (8.44)	14.32 (14.49)	3.35
Fe ₂ [Sm(HL ¹)L ¹]1.5H ₂ O	Deep yellow	8.0 (8.17)	14.50 (14.62)	1.9
Fe ₂ [Gd(HL ¹)L ¹]	Deep yellow	8.21 (8.33)	15.0 (15.60)	–
Fe ₂ [Tb(HL ¹)L ¹]	Deep yellow	8.13 (8.31)	15.59 (15.74)	9.4
Fe ₂ [Dy(HL ¹)L ¹]H ₂ O	Deep yellow	8.05 (8.21)	15.71 (15.89)	10.2
Fe ₂ [Y(HL ¹)L ¹]H ₂ O	Light yellow	8.06 (8.13)	16.57 (16.75)	Diamagnetic

H₂L = Ferrocene glycolic acid 2–quinolinyl hydrazine.

H₂L¹ = Ferrocene glycolic acid 8–quinolinoyl hydrazine.

Table 2. Electronic absorption data for nd³⁺ complexes

[Nd(HL)L]2H ₂ O		[Nd(HL ¹)L ¹]	
J level	Energy (cm ⁻¹)	J level	Energy (cm ⁻¹)
⁴ G _{9/2}	19493 (3.12)	⁴ G _{9/2}	19531 (2.92)
⁴ G _{7/2}	18939 (7.84)	⁴ G _{7/2}	18939 (6.92)
⁴ G _{5/2}	17006 (17.81)	⁴ G _{5/2}	17064 (16.25)
² G _{7/2}	17211 (18.12)	² G _{7/2}	17182 (16.62)

Compared to the spectra of the aquoneodymium(III) complex, the hypersensitive band mentioned above shows a significant red shift ($\Delta\nu = 200\text{--}250\text{ cm}^{-1}$). For other important bands (e.g. ⁴I_{9/2}→²H_{9/2}, ⁴F_{5/2}; ⁴I_{9/2}→⁴S_{3/2}, ⁴F_{7/2}; ⁴I_{9/2}→⁴G_{7/2}, ²K_{13/2}) the red shift is much less. The nephelauxetic ratio β , ($\beta = \text{average value of } \nu \text{ complex} / \nu \text{ aquo}$) (Henrie & Chopin, 1968), the covalent factor $b^{1/2}$ ($b^{1/2} = [1/2(1-\beta)]^{1/2}$) (D.E.Henrie, (1976) and Sinha parameter δ (metal–ligand covalency per cent) δ (per cent) = $[(1-\beta)/\beta] \times 100$ (D.E.Henrie, 1976) were calculated from the hypersensitive transition of the neodymium(III) spectra (Table 2). The values obtained are close to those calculated for similar other neodymium(III) chelates. The β values in both the complexes are close to unity showing only a slight covalent character of the Nd(III)→ligand interaction; the $b^{1/2}$ values suggest a small participation of 4f orbitals in bonding and along with δ values indicate relatively low covalent character of the bond.

The spectra of praseodymium(III) complexes in both solid and solution (DMF and DMSO) exhibit two bands ~17120 and 20495 cm⁻¹ in the visible region, which may be due to the hypersensitive ³H₄→¹D₂ and ³H₄→³P₀ transitions respectively (R.Ludwig & A.Appelhaagen, 2005). These bands show some red shift compared to the aquopraseodymium (III) ion. The other important bands in this region are not resolved. The electronic spectra of samarium(III) and dysprosium(III) complexes of the same ligand in both solution and solid state are very nearly the same; [Sm(HL)L]H₂O: 24390, 28901, 39940, 31055; [Dy(HL)L]H₂O: 24630, 28901, 30030, 31010; [Sm (HL¹)L¹]H₂O: 24630, 29761, 31446, 34013; [Dy(HL¹)L¹]H₂O: 24752, 29678, 31446, 33783 cm⁻¹. This is expected because these two ions are hole equivalent of each other.

The molar extinction coefficient (ϵ) values of these complexes over the range 250–460 nm are very high, indicating a charge transfer origin (J.L.Atwood, *et al.*, (2001), S.O.Kang, *et al.*, (2007), M.Yoshizawa, *et al.*(2005).

Thermal analysis

The neodymium (III) complexes were subjected to thermal analysis in nitrogen atmosphere. The DTA curves for complexes with H₂L show an endothermic effect at 110 C due to dehydration of the samples. The water loss of [Nd(HL)(L)2H₂O] corresponds to two molecules of water (Found, 4.7; Calc. 4.7%). At 250°C the DTA curve shows a deep endothermic effect due to incongruent fusion of the complex with H₂L which on subsequent heating begins to decompose followed by highly exothermic two step oxidative loss (250–500°C) of the tridentate ligands. The final solid product remaining is invariably Nd₂O₃ (Found Nd₂O₃. 22.1; Calc. 22.2%). The H₂L¹ complex [Nd(HL¹)(L¹)], however, is found to be stable up to 350°C. The complex is decomposed at ~355°C with a highly exothermic loss over a very narrow temperature range (5–10°C). The total loss over this temperature range corresponds to one mol of the tridentate ligand (Found 40.0, Calc. 40.2%). A two step exothermic loss of the remaining ligand follows, giving Nd₂O₃ at 610 (Found: Nd₂O₃, 23.5; Calc. 23.2%). Based on elemental analysis and ebulliometric molecular weight determination the solid Lanthanion chelates approached 1:2 (metal–ligand) stoichiometry. The room temperature magnetic moment values of the lanthanon chelate correspond to the formula, $\mu_{\text{eff}} = 2[J(J+1)]^{1/2}$ the magnetic moment suggest the presence of 0, 1, 2, 3, 5, 7, 6, 5, 4, 3 unpaired electrons in La, Ce, Pr, Nd, Sm,

Gd, Tb, Dy, Ho and Er complexes, respectively indicating the tripositive oxidation states of the Ln-ion in them. A double humped curve is obtained on plotting μ_{eff} values versus number of unpaired electrons. However La(III) chelates were found to be diamagnetic. The μ_{eff} values also indicated the absence of metal-metal bonding.

¹H-NMR Spectra

To substantiate further the bonding in these compounds ¹H-NMR spectra of H₂L and H₂L¹ and their Lanthanone (III) chelates were recorded in CDCl₃/TMS. The chemical shift values (δ ppm) of different protons are give below. In the ¹H-NMR spectra of H₂L and H₂L¹ signals due to COOH and NH protons appeared at δ 11.8 and 11.4 and 6.64 and 6.61 ppm respectively (Ghosh & Bhardwaj, (2004) Lakshminarayan, Suresh and Ghosh, (2006) Ludwig, (2001) . The signals due to -COOH protons disappeared in the spectra of corresponding metal chelates. The multiplets due to azomethine protons appearing at δ 7.15–87.85 ppm in H₂L and H₂L¹ were shifted towards higher field in the metal chelates (~ 15 ppm) indicating donation of lone pair of electron of >C=N nitrogen to the central metal atom. The position of signals due to -CH₂ (δ 3.07–3.15) (multiplet) in H₂L and ferrocenyl protons (δ 7.12) (multiplet) were found unchanged in the metal chelates. The results obtained conclusively indicate hexa coordinated octahedral geometry for the Lanthanone (III) chelates under study (Lu, *et al.*,(2005); Chi, *et al.*(2007).

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