

Synthesis, Magneto-Spectral and Thermal Characteristics of Some 7-Coordinated Compounds of Lanthanides(III) Chlorides with 4[(Furan-2-ylmethylene)amino]-1,5-dimethyl-2-phenyl pyrazol-3-one and Isonicotinic acid(3',4',5'-trimethoxybenzylidene)hydrazide

Ram K. AGARWAL^{1*}, Surendra PRASAD^{1*} and Neetu GOEL²

¹*Department of Chemistry, School of Pure and Applied Sciences
The University of the South Pacific, P. O. Box 1168 Suva, FIJI ISLAND
e-mail: agarwal_r@usp.ac.fj ; prasad_su@usp.ac.fj*

²*Department of Chemistry, Lajpat Rai College, Sahibabad-201005
(Ghaziabad) U.P., INDIA*

Received 04.12.2003

In the present work, we describe the isolation of some lanthanide(III) chlorides coordination compounds with 4[(furan-2-ylmethylene)amino]-1,5-dimethyl-2-phenyl pyrazol-3-one (FDPPO) and isonicotinic acid(3',4',5'-trimethoxybenzylidene)hydrazide (ITMBH) with the general composition $[\text{Ln}(\text{L})_2\text{Cl}_3]$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho; L = FDPPO or ITMBH). All the isolated compounds were characterized through various physico-chemical studies. The coordinating ligands FDPPO or ITMBH act as neutral bidentate N and O-donors in the present compounds. The central metal ion displays the coordination number 7 in these complexes. Thermal stabilities of these complexes were also studied through thermogravimetric analysis.

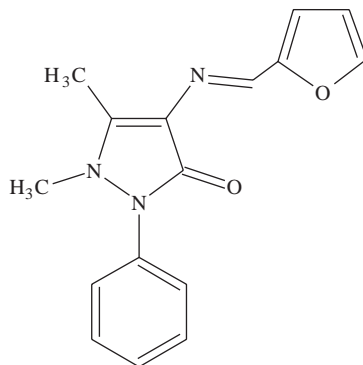
Key Words: Lanthanide(III) complexes, 4[(Furan-2-ylmethylene)amino]-1,5-dimethyl-2-phenyl pyrazol-3-one, Isonicotinic acid(3',4',5'-trimethoxybenzylidene)hydrazide, Coordination number 7.

Introduction

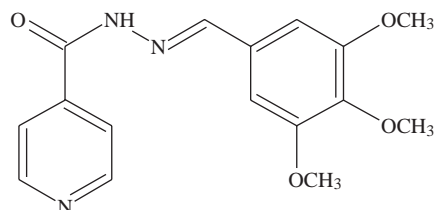
Some of the studies¹⁻⁶ indicate a wide interest in complexes with high coordination numbers. For a metal ion to achieve a higher coordination number, 2 conditions to be satisfied are: an effective size of the metal ion and a high positive formal charge^{7,8}. A high positive charge of the central metal atom is necessary in order to prevent the excess amount of negative charge from accumulating on the metal atom as a result of the association with the electrons contributed by a large number of bonding atoms. Lanthanides(III)

*Corresponding authors

with ionic radii of 1.06–0.85 Å and a + 3 charge fulfill the optimum conditions for high coordination⁹. The coordination number exhibited by the lanthanide ions generally varies from 6 to 10¹, but the crystal structure of hexakis(1,8-naphthyridine)praseodymium perchlorate has been reported to involve a 12 coordinated praseodymium ion^{10,11}. Recently, a number of researchers have isolated high coordination compounds of lanthanide(III) with Schiff bases^{11–14}. We describe the 7-coordinated complexes of lanthanide(III) chlorides with 4[(furan-2-ylmethylene)amino]-1,5-dimethyl-2-phenyl pyrazol-3-one (FDPPPO) (**I**) and isonicotinic acid(3',4',5'-trimethoxybenzylidene)hydrazide (ITMBH) (**II**).



4[(Furan-2-ylmethylene)amino]-1,5-dimethyl-2-phenyl pyrazol-3-one (FDPPPO) (**I**).



Isonicotinic acid(3',4',5'-trimethoxybenzylidene)hydrazide (ITMBH) (**II**).

Experimental

The lanthanide(III) chlorides were obtained from Rare Earth Products Ltd. (India) and were used without further purification. The ligands FDPPPO and ITMBH were synthesized by reported methods^{13,15}.

Synthesis of the complexes

[Ln(FDPPPO)₂Cl₃] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho)

A methanolic solution of FDPPPO was refluxed for 1 h, and then a methanolic solution of the trivalent lanthanide chloride was added (metal:ligand in a 1:2.2 mole ratio) to it. The reaction mixture was refluxed for ~1 h, and then kept on a hot plate for slow heating until a thick layer of the precipitate had settled. The supernatant liquid was decanted off and the product was separated. It was then washed several times with methanol to remove any excess metal chloride and/or ligand. Finally, it was washed with anhydrous diethyl-ether and dried in vacuo over P₄O₁₀.

Ln(ITMBH)₂C₃] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho)

The ligand (2.2 mmol) in hot methanol (20 mL) was added dropwise with constant stirring to a solution of appropriate lanthanide(III) chloride (1 mmol) in methanol (10 mL). The reaction was continued for 2 h. The volume of the solution was then reduced to 10 mL by evaporation and a precipitate formed on the addition of a small amount of anhydrous diethyl-ether. This was filtered off, washed with ether and dried in vacuo over P₄O₁₀.

Analyses

The metal content was estimated as its oxide by direct combustion in a platinum crucible. The nitrogen was determined by the Kjeldahl method. The chloride content was determined by Volhard's method. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of ± 0.01 °C accuracy. The conductivity measurements were carried out using a Toshniwal conductivity bridge (type Cl01/0) and a dip type cell operated at 220 V AC mains. The magnetic measurements were carried out at room temperature on a Gouy balance with [HgCo(SCN)₄] as a calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model 521 in CsI in the range 4000-200 cm⁻¹. A Hilger Uvspek Spectrophotometer with a 1cm quartz cell was used for recording the visible spectra of Pr³⁺, Nd³⁺ and Sm³⁺ complexes. Thermogravimetric analysis of the lanthanide(III) complexes was carried out in static air, with open sample holders and a small platinum boat, at a heating rate of 6 °C/min.

Results and Discussion

The reaction of the non-aqueous solution of lanthanide(III) chlorides with FDPPO or ITMBH resulted in the formation of coordination compounds of the composition LnCl₃.2L (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho; L = FDPPO or ITMBH). The analytical data of the present complexes are given in Table 1. The analytical data indicate that the complexes are generally pure and need no further purification. The coordination compounds are generally stable and did not undergo any apparent change in color when kept for a long time. The pyrolysis curves indicate no change up to 135 °C suggesting the absence of either a coordinated or uncoordinated aquo-ligand in these coordination compounds. The molar conductance values in nitrobenzene (Table 1) are too low to account for any dissociation. Therefore, these coordination compounds are considered to be non-electrolytes. The cryoscopic molecular weight determination in nitrobenzene also supports the non-electrolytic behavior as well as the monomeric nature of these complexes. The magnetic moment values of the present complexes are given in Table 1. Lanthanum complexes are diamagnetic in nature, as expected from their closed shell electronic configurations and the absence of unpaired electrons. All other tripositive lanthanide ions are paramagnetic due to the presence of 4*f*-electrons, which are effectively shielded by 5*s*²5*p*⁶ electrons. A comparison of these observed values with those observed for 8-hydrated sulfates¹⁶ and those calculated for uncomplexed ions indicates that the 4*f*-electrons do not participate in any bond formation in these complexes. The compounds discussed here show a little deviation from the Van-Vleck values¹⁷, although the simple Curie equation has been used. This was expected as the crystal field splitting of the *f*-orbitals was of the order of 100 cm⁻¹, a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to the thermal population of excited states whose degenerate levels have been

split by the crystal field. It was just possible that the splitting of the lowest excited state of Sm (${}^6\text{H}_{7/2}$) might have given an altered value of the magnetic moment, but this effect was not observed. Thus the magnetic moments of the new complexes reported here are within the range predicted and observed in the compounds of paramagnetic ions as reported earlier¹⁸⁻²⁰.

Infrared spectra

FDPPO complexes

Infrared absorptions of FDPPO have been assigned by a comparison of its spectra with those of the 5-membered pyrazole ring system²¹, the monosubstituted benzene ring system²², antipyrine and 4-aminoantipyrine^{23,24}, substituted 4-aminoantipyrine²⁵ and other Schiff bases of 4-aminoantipyrine^{26,27}. The infrared spectra of all the complexes show a considerable negative shift in carbonyl (pyrazolone) absorption $\Delta\nu$ (C=O) 45-50 cm^{-1} indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the oxygen atom of the free base. The (C=O) stretching frequency occurring at 1650 cm^{-1} in free ligands has been observed in the region of 1605-1600 cm^{-1} in all the present complexes. Another important band occurs at 1590 cm^{-1} , attributed to $\nu(\text{C}=\text{N})$ mode^{28,29}. In the spectra of all the complexes this band is shifted to a lower wave number (Table 2), indicating the involvement of the N-atom of the azomethine group in coordination^{28,29}. The strong band in the 1510-1490 cm^{-1} range has been assigned to the ring stretching of the 5-membered ring in the present complexes, and several other absorptions associated with C-H out-of-plane deformation modes appear in 920-720 cm^{-1} in the present ligand. Such absorption associated with the pyrazolone ring undergoes a slight positive shift due to a decrease in electron density on the aromatic ring on complexation. In the far infrared region the bands in the 460-360 cm^{-1} range are assigned to ν (Ln-O) and ν (Ln-N) modes^{28,29}.

ITMBH Complexes

The key IR bands of lanthanide(III) chloride complexes of ITMBH are shown in Table 3. The ligand ITMBH is expected to act as a tridentate with possible coordination sites being pyridinic-nitrogen, azomethinic-nitrogen and the amide group. The IR frequencies in the present ligand associated with the amide group (carbonyl-oxygen), azomethinic-nitrogen ($>\text{C}=\text{N}$) and heterocyclic-nitrogen ($\equiv\text{N}$) are expected to be influenced in complex formation with lanthanide(III) metal ions. Generally all amides show 2 absorption bands: (i) the carbonyl absorption band near 1640 cm^{-1} , known as the amide-I band, and (ii) a strong band in the 1600-1500 cm^{-1} region, known as the amide-II band. The origin of these bands in hydrazides, the carbonyl absorption, responsible for the amide-I band, is likely to be lowered³⁰ frequently by the NH group as in normal amides. The amide-I band in ITMBH appears at 1660-1640 cm^{-1} . In the IR spectra of the complexes a considerable negative shift in ν (C=O) is observed, indicating a decrease in the stretching force constant of (C=O) as a consequence of coordination through the carbonyl oxygen atom of the free base³¹.

The absorption at 1565-1560 cm^{-1} has been assigned to amide-II absorption. The NH-stretching absorption in the free ligand occurs at 3290-3220 cm^{-1} , which remains unaffected after complexation. This precludes the possibility of coordination through an imine nitrogen atom. Another important band occurs at 1590 cm^{-1} , attributed to ν (C=N) azomethine mode^{32,33}. In the spectra of all the complexes this band

Table 1. Analytical, conductivity and molecular weight data of lanthanide(III) chloride complexes of FDPPO and ITMBH.

Complex	% Analysis: Found (Calcd.)			Λ_m Ohm ⁻¹ cm ² mole ⁻¹	Average m.w.	Formula weight	μ_{eff} (B.M.)
	Ln	N	Cl				
[La(FDPPO) ₂ Cl ₃]	17.62 (17.74)	10.64 (10.72)	13.48 (13.59)	2.7	779	783.5	Diamag
[Pr(FDPPO) ₂ Cl ₃]	17.84 (17.95)	10.60 (10.69)	13.45 (13.55)	3.1	788	785.5	3.57
[Nd(FDPPO) ₂ Cl ₃]	18.13 (18.26)	10.58 (10.65)	13.37 (13.50)	2.8	781	788.5	3.53
[Sm(FDPPO) ₂ Cl ₃]	18.58 (18.71)	10.49 (10.57)	13.29 (13.40)	2.6	786	794.5	1.61
[Gd(FDPPO) ₂ Cl ₃]	19.42 (19.58)	10.40 (10.48)	13.17 (13.28)	2.1	795	801.5	7.84
[Tb(FDPPO) ₂ Cl ₃]	19.60 (19.78)	10.38 (10.45)	13.15 (13.25)	1.9	798	803.5	9.39
[Dy(FDPPO) ₂ Cl ₃]	19.98 (20.16)	10.35 (10.42)	13.10 (13.21)	2.3	800	806.0	10.57
[Ho(FDPPO) ₂ Cl ₃]	20.24 (20.40)	10.31 (10.38)	13.08 (13.17)	2.1	802	808.5	10.39
[La(ITMBH) ₂ Cl ₃]	15.70 (15.87)	9.48 (9.59)	12.06 (12.16)	2.1	870	875.5	Diamag
[Pr(ITMBH) ₂ Cl ₃]	15.86 (16.06)	9.38 (9.57)	12.02 (12.13)	1.9	872	877.5	3.63
[Nd(ITMBH) ₂ Cl ₃]	16.18 (16.35)	9.43 (9.54)	11.98 (12.09)	2.3	874	880.5	3.50
[Sm(ITMBH) ₂ Cl ₃]	16.81 (16.92)	9.38 (9.47)	11.90 (12.01)	2.4 2.4	879	886.5	1.64
[Gd(ITMBH) ₂ Cl ₃]	17.40 (17.57)	9.31 (9.40)	11.80 (11.91)	1.8	885	893.5	7.80
[Tb(ITMBH) ₂ Cl ₃]	17.62 (17.75)	9.29 (9.38)	11.78 (11.89)	2.7	887	895.5	9.52
[Dy(ITMBH) ₂ Cl ₃]	17.89 (18.09)	9.26 (9.35)	11.75 (11.85)	3.0	891	898.0	10.61
[Ho(ITMBH) ₂ Cl ₃]	18.15 (18.32)	9.23 (9.32)	11.72 (11.82)	2.9	893	900.5	10.21

Table 2. Key IR bands (cm⁻¹) of lanthanide(III) chloride complexes of FDPPO.

Compound	ν (C=O)(pyrazolone)	ν (C=N) (azomethine)	ν (Ln-O)/ ν (Ln-N)
FDPPO	1650 vs	1590 s	-
[La(FDPPO) ₂ Cl ₃]	1602 s,br	1550 m	455 m, 392 w
[Pr(FDPPO) ₂ Cl ₃]	1600 s,br	1552 m	450 m, 382 w
[Nd(FDPPO) ₂ Cl ₃]	1600 s	1565 sh, 1545 s	455 m, 390 w
[Sm(FDPPO) ₂ Cl ₃]	1600 s	1562 s, 1545 s	472 m, 365 w
[Gd(FDPPO) ₂ Cl ₃]	1600 s,br	1550 sh	460 m, 360 w
[Tb(FDPPO) ₂ Cl ₃]	1600 s,br	1550 s	465 m, 365 w
[Dy(FDPPO) ₂ Cl ₃]	1602 s	1552 s	445 m, 350 w
[Ho(FDPPO) ₂ Cl ₃]	1605 s	1550 s	462 m, 380 w

Table 3. Key IR bands (cm^{-1}) of lanthanide(III) chloride complexes of ITMBH.

Compound	ν (NH) asym & sym	Amide-I	ν (C=N) azomethine	Amide-II + δ (NH)	ν (Ln-O) ν (Ln-N)
ITMBH	3290 m 3220 m	1660 v 1640 s	1590 s	1565 s 1560 sh	-
[La(ITMBH) ₂ Cl ₃]	3292m 3220m	1630 s 1610 m	1565 s	1540 s 1520 s	465 m 380 w
[Pr(ITMBH) ₂ Cl ₃]	3290 m 3222 m	1635 m 1610 sh	1560 s	1530 s 1522 m	450 m 382 w
[Nd(ITMBH) ₂ Cl ₃]	3292 m 3225 m	1650 m 1620 m 1600 m	1560 s	1540 s 1515 m	437 m 375 w
[Sm(ITMBH) ₂ Cl ₃]	3290 m 3225 m	1635 s 1615 s	1575 s 1570 sh	1518 s 1505 w	425 m 372 w
[Gd(ITMBH) ₂ Cl ₃]	3295 m 3220 m	1635 m 1618 m	1570 s 1550 sh	1530 s 1520 m	452 m 370 w
[Tb(ITMBH) ₂ Cl ₃]	3290 m 3220 m	1640 m 1610 sh	1570 s	1528 m 1510 m	455 m 372 w
[Dy(ITMBH) ₂ Cl ₃]	3290 m 3225 m	1650 m 1600 vs	1570 vs	1525 s,br	460 m 365 w
[Ho(ITMBH) ₂ Cl ₃]	3292 m 3222 m	1638 s 1615 s	1570 s 1540 sh	1518 s 1505 w	458 m 360 w

is shifted to a lower wave number, and appears in the 1570-1550 cm^{-1} region, indicating the involvement of the N-atom of the azomethine group in coordination^{32,33}.

The strong bands observed at 1530-1400 cm^{-1} and 1075-1020 cm^{-1} are tentatively assigned to asymmetric and symmetric ν (C=C) + ν (C=N) of the pyridine ring and pyridine ring breathing³⁴, and deformations remain practically unchanged in frequency and band intensities revealing non-involvement of pyridinic nitrogen in coordination. The overall spectral evidence suggests that ITMBH acts as a bidentate ligand and coordinate through the amide-oxygen and azomethinic nitrogen atom forming a 5-membered chelate ring. The far IR spectral bands of the ligand are practically unchanged in these complexes. However, some new bands with medium to weak intensities appear in the region 460-360 cm^{-1} in the complexes under study, which are tentatively assigned to ν (Ln-O)/ ν (Ln-N) mode^{28,29}. In the present complexes, ν (Ln-Cl) has been assigned in the 290-270 cm^{-1} region.

Electronic Spectra

Electronic spectral data for solutions of some representative complexes investigated in CH_3CN along with aqueous salt solution data are given in Table 4 for comparison. Lanthanum(III) complex has no significant absorption in the visible region. The absorption bands of Pr(III), Nd(III) and Sm(III) complexes in the visible and near infrared region appear due to transitions from the ground levels $^3\text{H}_4$, $^4\text{I}_{9/2}$ and $^6\text{H}_{5/2}$, respectively, to the excited J-levels of 4f-configuration. Some red shift or nephelauxetic effect is observed in the CH_3CN solution of these coordination compounds. This red shift is usually regarded as an evidence of a higher degree of covalency than exists in the aquo compounds^{35,36}. In all the complexes a marked enhancement in the intensity of the bands was observed.

Table 4. Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) chloride complexes of FDPPO.

Complex	LnCl ₃ electronic spectral bands	Complex electronic spectral bands	Energy levels	(1- β)	β	$b^{1/2}$	δ (%)	η
[Pr(FDPPO) ₂ Cl ₃]	22,470	22,320	³ H ₄ → ³ P ₂	0.00667	0.99332	0.04083	0.67148	0.00335
	21,280	21,100	→ ³ P ₁	0.00845	0.99154	0.04596	0.86128	0.00425
	20,830	20,650	→ ³ P ₀	0.00864	0.99135	0.04647	0.87153	0.00435
	16,950	16,750	→ ¹ D ₂	0.01179	0.98820	0.05429	1.19307	0.00591
[Nd(FDPPO) ₂ Cl ₃]	19,420	19,250	⁴ I _{9/2} → ² G _{9/2}	0.00875	0.99124	0.04677	0.88273	0.00440
	17,390	17,200	→ ⁴ G _{5/2} , ² G _{7/2}	0.01092	0.98907	0.05224	1.10406	0.00551
	13,420	13,200	→ ² S _{3/2} , ⁴ F _{7/2}	0.01639	0.98360	0.06401	1.66632	0.00823
	12,500	12,350	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.01200	0.98800	0.05477	1.21457	0.00601
[Sm(FDPPO) ₂ Cl ₃]	24,850	24,720	⁴ H _{5/2} → ⁴ F _{9/2}	0.00523	0.99476	0.03615	0.52575	0.00262
	24,100	23,820	→ ⁶ P _{5/2}	0.01161	0.98838	0.05387	1.17464	0.00586
	21,600	21,450	→ ⁴ I _{13/2}	0.00694	0.99305	0.04165	0.69885	0.00349

The red shift of the hypersensitive bands was utilized to calculate the nephelauxetic effect (β) in these complexes. From the β values the covalence factor ($b^{1/2}$), Sinha parameter ($\delta\%$) (metal-ligand covalency percent) and the covalency angular overlap parameter (η) have been calculated and are shown in Table 4. The positive values for (1- β) and $\delta\%$ in these coordination compounds suggest that the bonding between the metal and the FFAAP is covalent compared with the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were positive, indicating covalent bonding.

Thermal Studies

[Ln(FDPPO)₂Cl₃] (Ln = La, Gd or Dy)

The thermogravimetric results of these complexes are summarized in Table 5. The weight loss curves of these complexes suggest that these complexes do not show the presence of water molecules either in or out of the coordination sphere. The analysis of these curves suggests that above 210 °C the compounds start to lose mass with partial evaporation of the organic ligand up to a temperature of 260 °C. The mass loss corresponds to one molecule of FDPPO, and in the temperature range 300-370 °C the second molecule of FDPPO is also lost. The residue obtained after heating up to ~825 °C to constant weight is very close to that expected for lanthanide oxide³⁷.

[Ln(ITMBH)₂Cl₃] (Ln = Pr, Gd or Tb)

The thermogravimetric data on these complexes are presented in Table 6. The pyrolysis curves of [Ln(ITMBH)₂Cl₃] (Ln = Pr, Gd or Tb) indicate that the complexes do not possess water of crystallization. The complexes are stable up to 220 °C, beyond which they start to lose mass up to a temperature of 260 °C, which corresponds to the loss of one molecule of ITMBH. The remaining organic ligand was lost in the 280-350 °C temperature region. The residues obtained at 820 °C are due to the formation of stable lanthanide oxides³⁷.

Table 5. Thermoanalytical results of lanthanide(III) chloride complexes of FDPPO.

Complex	Sample wt (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%)	
			210-260 °C		300-370 °C		825 °C	
			Theor ^a	Exp	Theor ^b	Exp	Theor ^a	Exp
[La(FDPPO) ₂ Cl ₃]	12.90	2.69	34.33	34.16	68.66	68.49	20.80	20.93
[Gd(FDPPO) ₂ Cl ₃]	14.20	3.23	33.56	33.38	67.12	66.93	33.58	22.74
[Dy(FDPPO) ₂ Cl ₃]	16.30	3.80	33.37	33.19	66.74	66.59	23.13	23.33

a – calculated for loss of one molecule of FDPPO

b – calculated for total loss of FDPPO

c – calculated for lanthanide oxides as La₂O₃, Gd₂O₃ or Dy₂O₃

Table 6. Thermoanalytical results of lanthanide(III) chloride complexes of ITMBH.

Complex	Sample wt (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%)	
			220-260 °C		280-350 °C		820 °C	
			Theor ^a	Exp	Theor ^b	Exp	Theor ^c	Exp
[Pr(ITMBH) ₂ Cl ₃]	12.90	2.52	35.97	35.78	71.95	71.98	19.45	19.58
[Gd(ITMBH) ₂ Cl ₃]	14.30	2.91	35.25	35.08	70.50	70.19	20.25	20.38
[Tb(ITMBH) ₂ Cl ₃]	16.10	3.40	35.17	35.03	70.35	70.03	20.88	21.13

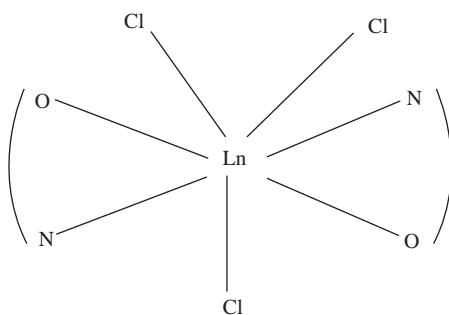
a – calculated for loss of 1mole of ITMBH

b – calculated for total loss of ITMBH.

c – calculated for lanthanide oxides as Pr₆O₁₁, Gd₂O₃ or Tb₄O₇

Stereochemistry

The non-ionic nature of the present complexes and infrared data reveal the bidentate nature (N, O) of both the coordinating ligands, resulting in the coordination number 7 in these complexes³. The tentative structure of the complexes may be represented as



Proposed structure of [Ln(L)₂Cl₃] (L = FDPPO or ITMBH and Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho)

References

1. M.E. Harman, F.A. Hart, M.B. Hursthouse, G.P. Moss and P.R. Raithby, *J. Chem. Soc. Chem. Commun.*, **39**, 66 (1976).
2. B. Erikson, L. Larson and L. Niimisto, *J. Chem. Soc.*, **14**, 616C (1978).

3. D.K. Koppikar, P.V. Sivapulliah, L. Ramakrishnan and S. Soundararajan, **Structure and Bonding**, **34**, 135 (1978) and references therein.
4. K. Arora, R.C. Goyal, D.D. Agarwal and M.C. Pathak, **J. Indian Chem. Soc.**, **79**, 686 (2002).
5. A. Gupta, K. Arora and D.D. Agarwal, **Asian J. Chem.**, **16**, 489 (2004).
6. A. Gupta, D.D. Agarwal and K. Arora, **Asian J. Chem.**, **16**, 552 (2004).
7. E.L. Muetterties and C.M. Wright, **Quart Rev. (London)**, **21**, 109 (1967).
8. S.J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967).
9. P. Ramamurthy and C.C. Patel, **Canad. J. Chem.**, **42**, 856 (1964).
10. A. Clearfield, R. Gopalan and R.H. Oslen, **Inorg. Chem.**, **16**, 711 (1977).
11. R.L. Dutta and B.R. Das, **J. Scient. Ind. Res.**, **47**, 547 (1988).
12. R.K. Agarwal, H. Agarwal and R.K. Sarin, **Synth. React. Inorg. Met.-Org. Chem.**, **24**, 1681 (1994).
13. R.K. Agarwal and R.K. Sarin, **Polyhedron**, **12**, 2411 (1994).
14. R.K. Agarwal, H. Agarwal and A.K. Manglik, **Synth. React. Inorg. Met.-Org. Chem.**, **26**, 163 (1996).
15. R.K. Agarwal and H. Agarwal, **Synth. React. Inorg. Met.-Org. Chem.**, **31**, 263 (2001).
16. N.K. Dutt and S. Rahut, **J. Inorg. Nucl. Chem.**, **32**, 2105 (1970).
17. R.L. Dutta and A. Syamal, **Elements of Magnetochemistry**, Affiliated East West Press, New Delhi (1993).
18. N.M. Karayannis, C.M. Mikulski, L.L. Pytlewski and M.M. Lales, **J. Less Common Metals**, **20**, 29 (1970).
19. R.K. Agarwal and S.K. Gupta, **Indian J. Chem.**, **25A**, 597 (1986).
20. R.K. Agarwal, M.B.L. Sharma and A.K. Srivastava, **Rev. Roum. Chim.**, **32**, 263 (1987).
21. G. Zerbi and C. Alberti, **Spectrochim. Acta**, **19**, 1261 (1963).
22. L.J. Bellamy, **Infrared Spectra of Complex Molecules**, Methuen, London (1954).
23. R.K. Agarwal and S.C. Rastogi, **Thermochim. Acta**, **95**, 279 (1985).
24. R.K. Agarwal and J. Prakash, **Polyhedron**, **10**, 2399 (1991).
25. R.K. Agarwal, H.K. Rawat and A.K. Srivastava, **Indian J. Chem.**, **27A**, 2277 (1988).
26. R.K. Agarwal, N. Goel, A.K. Sharma, **J. Indian Chem. Soc.**, **78**, 39 (2001).
27. L. Singh, A.K. Sharma and S.K. Sandhu, **Asian J. Chem.**, **11**, 1445 (1999).
28. R.K. Agarwal and H. Agarwal, **Synth. React. Inorg. Met.-Org. Chem.**, **25**, 715 (1995).
29. R.K. Agarwal, B. Bhushan, A. Kumar and R. Prasad, **J. Indian Chem. Soc.**, **72**, 537 (1995).
30. K. Nakamoto, **Infrared Spectra of Inorganic and Coordination Compounds**, Wiley, N.Y. (1970).
31. R.K. Agarwal and K. Arora, **Polish J. Chem.**, **67**, 219 (1993).
32. R.K. Agarwal, J. Prakash and I. Chakraborti, **Polish J. Chem.**, **67**, 1933 (1993).
33. R.K. Agarwal and H. Agarwal, **J. Saudi Chem. Soc.**, **5**, 329 (2001).
34. Y. Kumar, P.D. Sethi and C.L. Jain, **J. Indian Chem. Soc.**, **67**, 796 (1990).
35. C.K. Jorgensen, **Z. Naturforsch.**, **190**, 424 (1964).
36. S.P. Sinha, **Spectrochim. Acta**, **22**, 57 (1966).
37. R.K. Agarwal and S.K. Gupta, **Thermochim. Acta**, **99**, 357 (1986).