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Research Article

SYNTHESIS AND SPECTRAL (IR, NMR, FAB-MS AND XRD) CHARACTERIZATION OF LANTHANIDE COMPLEXES CONTAINING BIDENTATE SCHIFF BASE DERIVED FROM SULPHADIAZINE AND *O*-VANILLIN

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ABSTRACT

A series of new rare earth complexes of lanthanide(III) of the type;$[(Cl)_2Ln(L)(H_2O)_4]$ [where Ln=La(III), Ce(III), Nd(III), Sm(III), Gd(III) & Y(III), L=Schiff base ligand; o-vanillidene-sulphadiazine (vsdH)] were synthesized by the reactions of $MCl_3.xH_2O$ with KOH and Schiff base in equimolar ratio. These complexes have been characterized on the basis of elemental analysis (Ln, C, H, N, & Cl), melting point, IR, ^{1}H-NMR and ^{13}C-NMR spectral data, whereas the structural composition of the complexes have been determined by FAB-MS spectral studies. X-ray powder diffraction study of one of the complex $[(Cl)_2Gd(vsd)(H_2O)_4]$ was found to be on Phillips powder diffraction PW 3040/60 with Cu-Kα_1 radiation (λ = 1.5406 Å) showing amorphous nature. The complexes were found to be coloured solid and were soluble only in DMF & DMSO.

Key Words: *La(III), Ce(III), Nd(III), Sm(III), Gd(III), Y(III) chloride(s) and Schiff base complexes, FAB-MS, IR studies, ^{1}H-NMR, ^{13}C-NMR, XRD analysis*

INTRODUCTION

Schiff base and their transition (Dubey *et al.*, 2011) and inner-transition metal complexes containing nitrogen and oxygen donor atoms play an important role in biological and inorganic research and have been studied extensively due to their unique coordination and biological properties (Yamada1999, Gao and Xu 2008). Lanthanide complexes with Schiff base ligands have been widely investigated due to their versatile structure interesting coordination and wide pharmacological applications (Nair and Radhakrishanan 1996, Song *et al.*, 2007, Niua *et al.*, 2009). The literature survey indicated that metal complexes derived from sulpha drug have been prepared and used in various physical, biological and pharmacological fields (McNamara 1990, Sabers and Gram 2000, Britton and So 1995). Schiff bases are among the most studied sulpha drug derivatives which have been used for numerous biological applications (Loscher 1998, Dimmock and Baker 1994). However the complex containing sulpha drugs are limited. In this paper, we therefore, present the synthesis and characterization of La(III), Ce(III), Nd(III), Sm(III), Gd(III) and Y(III) complexes of sulphadiazine.

RESULTS AND DISCUSSION

Infrared Spectra

In the spectra of the ligand, (vsd***H***) exhibited characteristic bands in the region 3425 cm^{-1} assignable to –OH stretching frequency, due to presence of –OH group of ligand. Schiff base showed absorption band in the range ~1650 cm^{-1} due to $\upsilon_{C=N,}$ which get shifted to lower frequency around 1630-1590 cm^{-1} on complexation, may be taken as evident for coordination of azomethine nitrogen (Dubey and Baranwal 2009, Atiken *et al.*, 1971) to lanthanide. In the complexes the peak observed due to υ_{C-O} (phenolic) bands appeared in the range 1290-1270 cm^{-1} indicates that the bonding takes place through phenolic oxygen after deprotonation of –OH group. The appearance of new bands in the range 322-318 cm^{-1}and 478-420 cm^{-1} assigned to υ_{Ln-Cl} (Agrawal *et al.*, 2009) and υ_{Ln-N} (Belwal *et al.*, 1998) respectively (Table 2).

^{1}H-NMR spectra

One of the representative complex of Gadolinium (III) was studied for ^{1}H and ^{13}C NMR. The ^{1}H-NMR spectrum of the ligand (vsd***H***) exhibited sharp signal at around δ12.25 ppm due to phenolic proton, whereas this signal was disappeared in its corresponding Gadolinium (III) complex which is the indicative of coordination to Gadolinium metal through phenolic oxygen after deprotonation of phenolic proton.

Another signal was observed at δ8.47 ppm due to azomethine proton, which gets deshielded δ9.90 at ppm it is suggested that coordination takes place through azomethine nitrogen to the metal ion. Chemical shift for aromatic hydrogen was observed at lower field δ7.62-6.55 ppm in the complex.

^{13}C-NMR spectra

^{13}C-NMR spectra of ligand vsdH exhibited signal in the range δ154.04-153.42 ppm due to azomethine carbon, which indicates the coordination of azomethine nitrogen to the Gadolinium metal. Signals were observed at δ161.12-150.43 ppm in the Gadolinium (III) complex due to phenolic carbon, which assigned bonding (Dubey and Mariya 2011, Dubey and Mariya 2010, Dubey *et al.*, 2010, Dubey and Mariya 2012) of phenolic oxygen to the metal.

FAB-mass spectra

FAB-MS spectrum and the fragmentation pattern (Nair and Lalitha, 2011) of the ligand (vsd***H***) are shown in (Fig. 1) and (Scheme 1). The spectrum of the complex $[(Cl)_2Gd(vsd)(H_2O)_4]$ showed molecular ion peak at m/z=685 as shown in (Fig. 2) which supports the molecular mass of the complex. The fragmentation pattern is shown in (Scheme 2). Several peaks were observed in mass spectrum at m/z 667, 613, 533, 519, 455, 378, 347, 243, 173 and 159.The most prominent peak observed at m/z= 159 correspond to $[Gd^+]$.

X-Ray powder diffraction (PXRD)

XRD study of the complex $[(Cl)_2Gd(vsd)(H_2O)_4]$ were made on Phillips powder diffraction PW 3040/60 with Cu-Kα_1 radiation (λ = 1.5406 Å). The powder XRD patterns were recorded in the 2θ range between 15.01 and 60.01with a step size of 0.0167. The X-ray powder diffractogram of Gadolinium (III) complex exhibits amorphous in nature. The X-ray powder diffractogram of Gadolinium (III) complex $[(Cl)_2Gd(vsd)(H_2O)_4]$ are given in (Fig. 3). The parameters of prepared material are calculated for the Gadolinium (III) complex**,** which is summarized in (Table 3).

MATERIALS AND METHODS

Chemical and Reagents

The metal chlorides ($LnCl_3.6H_2O$) were obtained from Loba and used as such. The solvents were purified using standard procedure (Kagon *et al.*, 1993). The metals were estimated, after destroying the organic matter by successive treatment of fuming nitric acid/aquaregia were precipitated as carbonate and determined, as La_2O_3. Chloride was determined by Volhard's method (Vogel 1969) and sulphur was estimated gravimetrically as $BaSO_4$ (Vogel 1969).

Physical Measurements

The infrared spectra of ligand and the complexes, in the range 4000-200 cm^{-1}, were recorded on a KBr discs on a Jasco FT-IR-5300 spectrophotometer. Elemental analysis for C, H, N and S were performed on a Heroceous Carlo Erba 1108 elemental analysis. The NMR spectrum was recorded on a JEOL-AL-300 FT-NMR spectrometer in DMSO-d$_6$ using TMS as the internal standard. FAB-MS spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer /data system using argon /xenon (6kV, 10mA) as the FAB gas. The X-ray powder diffraction was carried out at ambient temperature using Phillips Powder of the PW 3040/60 with Cu-Kα_1 radiation (λ = 1.5406 Å).

Preparation of Ligand

The Schiff base ligand; *o*-vanillidene-sulphadiazine (vsd**H**) was synthesized by the condensation of equimolar ratio of *o*-vanillin (4.934g; 19.71 mmol.) and sulphadiazine (3 g; 19.71 mmol.) in ethanol (30 cm^3); resulting reaction mixture was stirred (~1 h.) and refluxed on a water bath for ~5 h and then allowed to cool at room temperature . The separated compound was purified by recrystallization from the same solvent, (vsd**H**) 65% yield, m.p. 245 ^{0}C.

Table 1: Synthetic physical and analytical data of lanthanide metal complexes

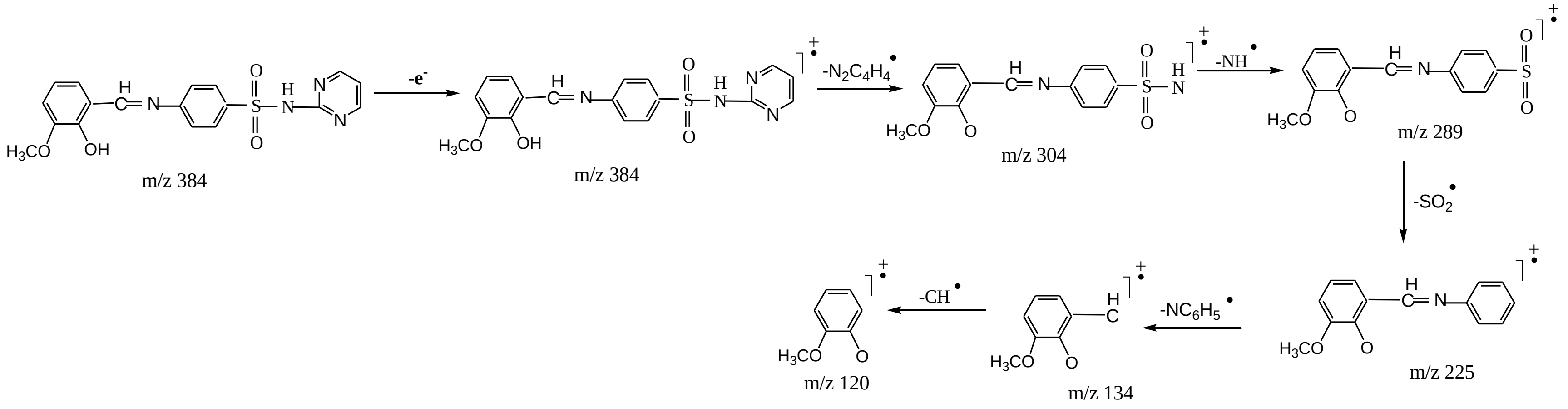
S.No.	Molecular formula of complexes; (% Yield)	Physical state and Colour	M.P/D.P (^{0}C)	Elemental Analysis % : Found (Calcd)						$\mu_{effctive}$ (B.M.)
				Metal	Chlorine	Carbon	Hydrogen	Nitrogen	Sulphur	
1.	[($C_{18}H_{24}N_4O_4S$] 75	Light Yellow	245	-	-	56.30 (56.25)	4.18 (4.17)	15..00 (14.58)	8.40 (8.33)	
2.	[(Cl)$_2$La$C_{18}H_{24}N_4O_8S$] 45	Light Yellow	265	14.35 (14.45)	11.26 (11.36)	35.00 (35.06)	3.79 (3.89)	9.08 (9.09)	5.18 (5.19)	Diamagnetic
3.	[(Cl)$_2$Ce$C_{18}H_{24}N_4O_8S$] 46	Light Yellow	290	14.35 (14.45)	11.26 (11.36)	35.00 (35.06)	3.79 (3.89)	9.08 (9.09)	5.18 (5.19)	Diamagnetic
4.	[(Cl)$_2$Nd$C_{18}H_{16}N_4O_8S$] 40	Light Yellow Powdered Solid	260	21.39 (21.49)	10.35 (10.45)	32.14 (32.24)	3.48 (3.58)	8.26 (8.36)	4.68 (4.78)	-
5.	[(Cl)$_2$Sm$C_{18}H_{24}N_4O_8S$] 37	Light Green Powdered Solid	335	22.16 (22.19)	10.26 (10.36)	31.89 (31.95)	3.45 (3.55)	8.18 (8.28)	4.63 (4.73)	1.59
6.	[(Cl)$_2$Gd$C_{18}H_{24}N_4O_8S$] 34	Yellow Powdered Solid	240	22.89 (22.99)	10.24 (10.25)	31.53 (31.63)	3.41 (3.51)	8.12 (8.19)	4.59 (4.69)	7.54
7.	[(Cl)$_2$Y$C_{18}H_{24}N_4O_8S$] 46	Cream Powdered Solid	280	14.35 (14.45)	11.26 (11.36)	35.00 (35.06)	3.79 (3.89)	9.08 (9.09)	5.18 (5.19)	Diamagnetic

Table 2: IR spectral data (cm^{-1}) of the lanthanide (III) complexes with vanillidene-sulphadiazine (vsd*H*) Schiff base

S.No.	Complex	υ_{Ln-Cl}	$\upsilon_{Ln=N}$	υ_{OH}	$\upsilon_{C=N}$	$\upsilon_{C=O}$
1.	$[(Cl)_2La(vsd)(H_2O)_4]$	312	430	3415	1620	1270
2.	$[(Cl)_2Ce(vsd)(H_2O)_4]$	315	435	3420	1630	1275
3.	$[(Cl)_2Nd(vsd)(H_2O)_4]$	318	454	3412	1590	1270
4.	$[(Cl)_2Gd(vsd)(H_2O)_4]$	327	420	3412	1626	1277

Table: 3 Parameters of Gadolinium(III) complex

Parameters	**$[(Cl)_2Gd(vsd)(H_2O)_4]$**
Empirical formula	$[(Cl)_2Gd\ C_{18}H_{24}N_4O_8S]$
Formula weight	685
Wave length	1.5406 Å
Powder used	1.6 Kw
Step size	0.0167



Scheme 1. Fragmentation pattern of vanillidene-sulphadiazine (vsd*H*) ligand

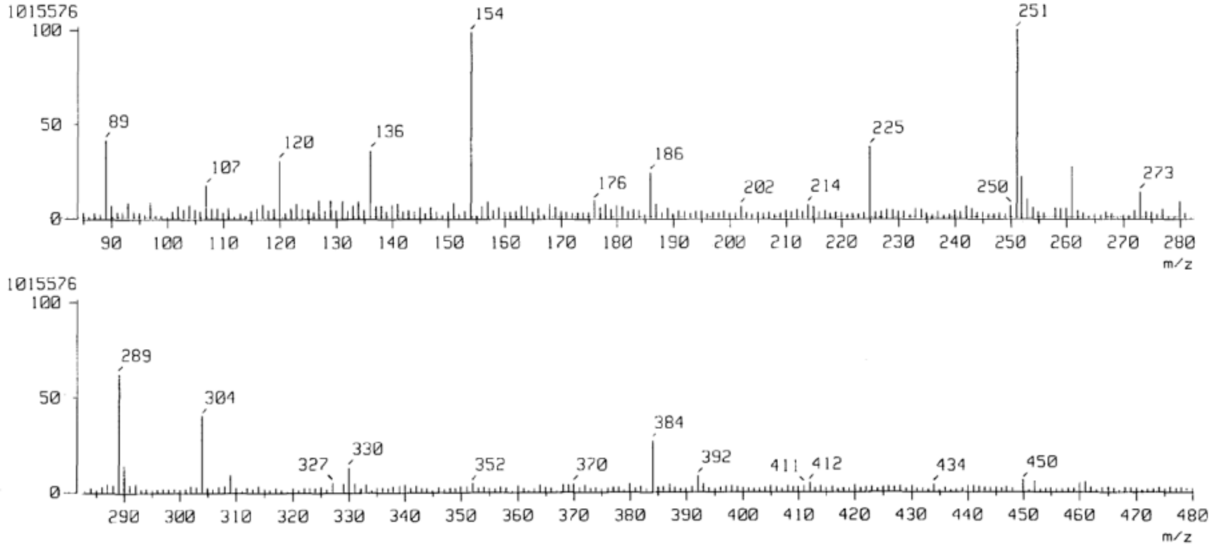
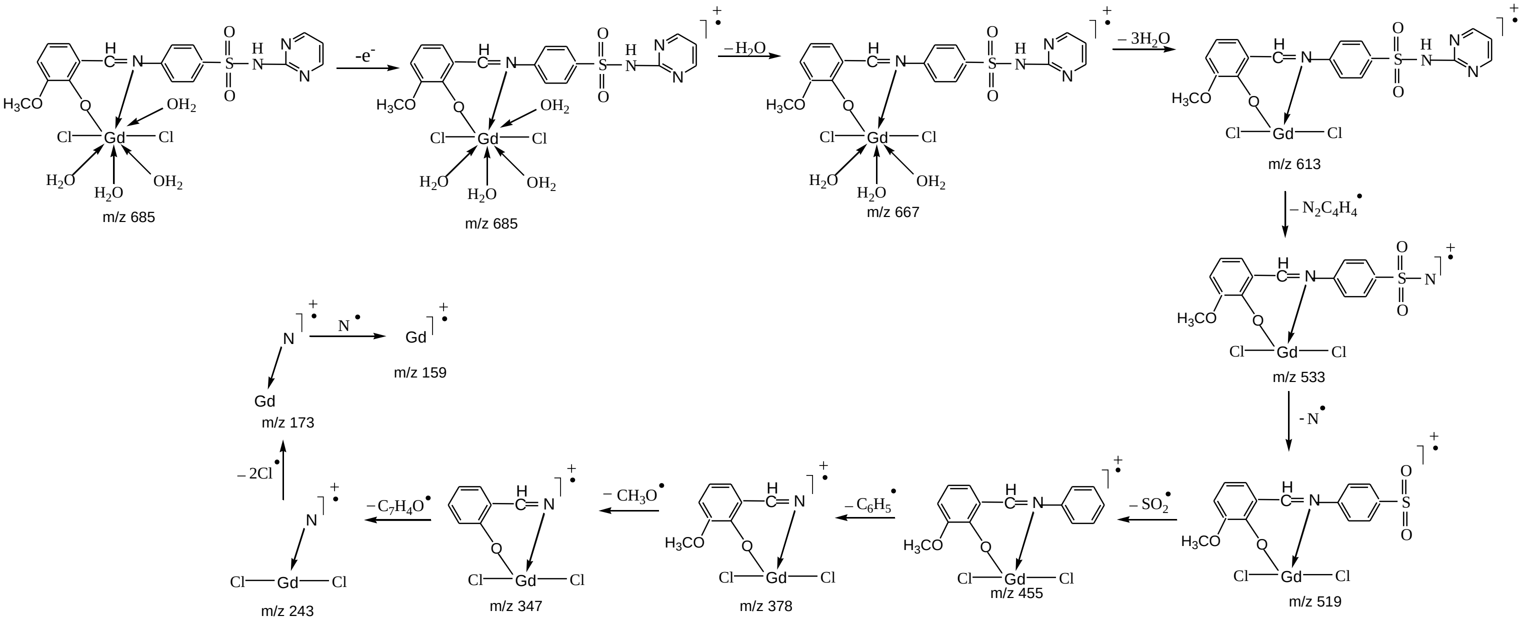


Figure 1. FAB mass spectrum of vanillidene-sulphadiazine (vsd*H*) ligand



Scheme 2. **FAB mass fragmentation of complex Gadolinium (III) chloride, $[(Cl)_2Gd(vsd)(H_2O)_4]$**

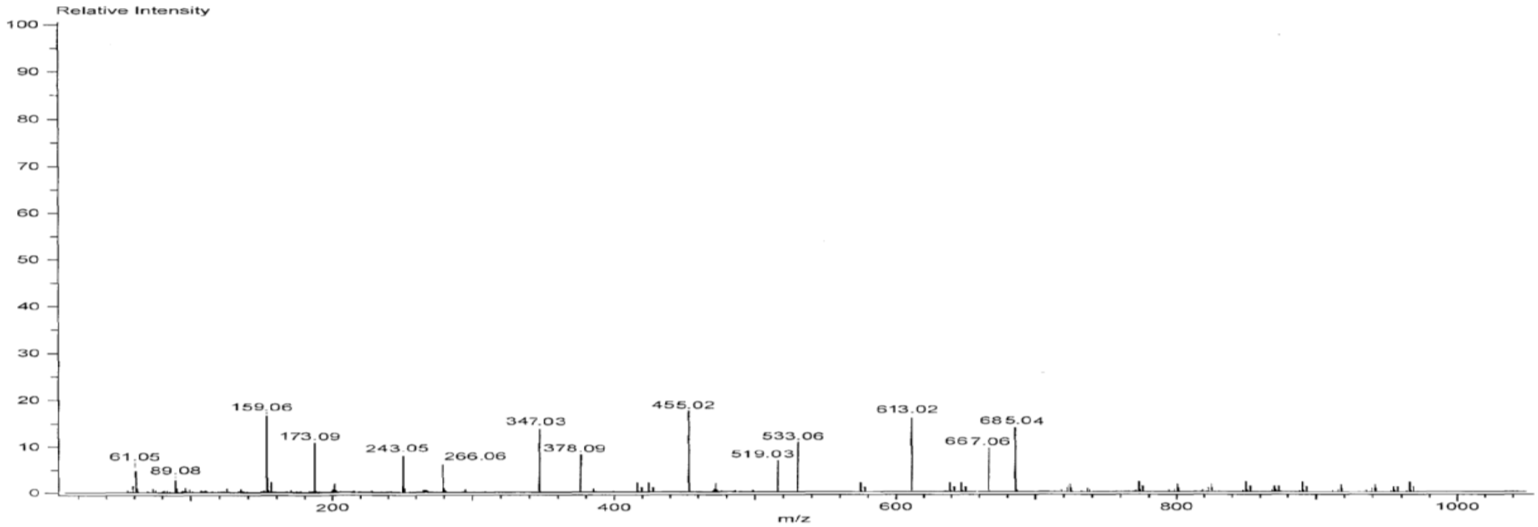


Figure 2. FAB mass spectrum of complex Gadolinium (III) chloride, $[(Cl)_2Gd(vsd)(H_2O)_4]$

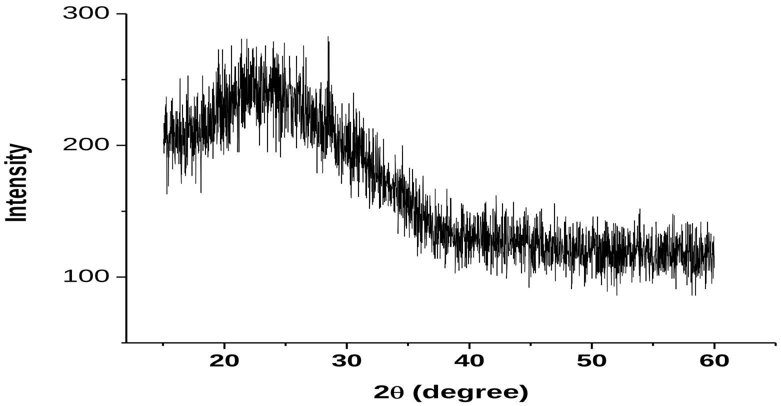


Figure 3: PXRD pattern of the complex $[(Cl)_2Gd(vsd)(H_2O)_4]$

Synthesis of Complexes

The ethanolic solution of hydrated metal chloride, $GdCl_3.6H_2O$ (0.5g; 1.35 mmol.) was added to the ethanolic solution of Schiff base vsd**H** (0.519g; 1.35 mmol.) in 1:1:1 molar ratio(s), followed by the addition of saturated ethanolic solution of KOH (0.076g; 1.36 mmol.) during which time a cream precipitate was obtained. Further, it was refluxed for ~10h. The excess of solvent was removed by distillation, followed by addition of pet-ether (~10 cm^3). The precipitate was filtered off, and dried in vacuo. The crude product was washed with ethanol for several times to remove unreacted metal chloride. It was washed with diethyl ether. The pure product $[(Cl)_2Gd(vsd)(H_2O)_4]$ was dried in vacuo. The compound of the lanthanum chloride (La, Ce, Nd, Gd, Sm & Y) were reacted in equimolar ratio and details of these complexes were collected in (Table 1). The complex $[(Cl)_2Gd(vsd)(H_2O)_4]$ was decomposed at temperature 285 ^{0}C, complex is yellow powdered solid which is soluble in polar solvents such as DMF and DMSO.

Conclusions

The bidentate ligand vsd***H*** was found to be bonded with lanthanide through phenolate oxygen and azomethine nitrogen. The characteristic of the sample have been studied by different physico-chemical techniques IR, NMR and X-ray diffraction analysis. On the basis of above discussion and FAB-MS fragmentation pattern of ligand and their metal complex, A tentative structure was proposed for lanthanide complexes, where the 'Ln' atom surrounded by different atoms showing eight coordination numbers.

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