Synthesis and Spectral Characterization of Lanthanide Complexes Containing Bidentate Schiff Base Derived From Pyridine-2-Carbaldehyde and 2-Hydrazinylquinoline

V. R. Rajewar¹, M. K. Dharmale^{2,*}, and S. R. Pingalkar^{1,2}

¹Department of Chemistry N.E.S.Science College, Nanded (M.S) ²Department of Chemistry Yeshwant Mahavidyalaya, Nanded (M.S)

*Corresponding email: dharmalevaishu@rediffmail.com

Received 24 September 2014; Accepted 23 April 2015

ABSTRACT

A series of new rare earth complexes of La(III) of the type $[Ln(L)_2(H_2O)_2]Cl_3$ where Ln= La(III), Pr(III), Nd(III), Sm(III) and Tb(III) and L=Schiff base ligand, 2-[2-(pyridin-2ylmethylidene)hydrazinyl]quinoline (PCQH). These complexes have been characterized on the basis of elemental analysis (Ln, C, H, N, and Cl), melting point, IR, ¹H-NMR and UV-Vis spectral data. X-ray powder diffraction study of two of the complex $[Nd(L)_2(H_2O)_2]Cl_3$ and $Pr(L)_2(H_2O)_2]Cl_3$ was found to be on powder diffraction with Cu-K α 1 radiation (λ = 1.5406 Å) showing monoclinic crystal system . The complexes were found to be colored solid and were soluble only in DMF and DMSO.

Key word: Schiff base complexes, IR studies, ¹H-NMR, UV-Vis, XRD analysis

INTRODUCTION

Compounds which contain pyridine and its derivatives or Schiff bases as ligands have occupied a central role in the development of coordination chemistry and biochemistry. Schiff base ligands form a stable complex with different transition metal ions. Schiff bases having multidentate coordination sites are known to form complexes with transition metal ions readily [1-6]. In particular, the transition metal complexes have been the subject for thorough investigation because of their extensive application in wide ranging areas from material science to biological sciences [7-9]. The formation of Schiff base and their metal complexes have a variety of applications in biological, clinical and analytical fields. Many potent antibacterial and antifungal Schiff base compounds of heterocyclic compounds were reported [11-14]. Some heterocyclic Schiff bases can act as antibacterial agent and antifungal agent [15-16].

Chemical properties of quinoline and its derivatives are of interest due to their biological Activity [17], coordination capacity [18], and their use as metal extracting agents [19]. The coordination chemistry, novel structural features and biological activity of the Schiff bases have also attracted attention. The quinoline skeleton is often used for the design of many synthetic compounds with diverse pharmacological properties such as, anti-inflammatory [20], antimicrobial agents [21], cytotoxic activity [22], antidotal and antibacterial [23], antitumor activity [24], antimalarial [25]. Additionally, quinoline derivatives find use in the synthesis of fungicides [2], virucides, biocides, alkaloids, rubber

The journal homepage www.jpacr.ub.ac.id p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

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chemicals and flavoring agents [26]. They are also used as polymers, catalysts, corrosion inhibitors, preservatives, and as solvent for resins and terpenes. Furthermore, these compounds find applications in chemistry of transition metal catalyst for uniform polymerization and luminescence chemistry [27]. Quinoline derivatives also act as antifoaming agent in refineries [28]. Owing to the mentioned significance, the synthesis of substituted quinolines has been a subject of great interest in organic chemistry.

The synthesis of quinolines and their derivatives has been of considerable interest because a large number of natural products and drugs contain this heterocyclic unit [29].Quinolines and their derivatives are receiving increasing importance due to their wide range of biological activities as anti-malarial, anti-bacterial, antiasthmatic, antihypertensive, anti-inflammatory, anti-platelet activity and as tyro-kinase PDGF-RTK inhibiting activity [30-32]. In addition, quinolines have also been employed in the study of bioorganic and bioorganometallic processes [33]. Due to such a wide range of applicability in medicinal, bioorganic, industrial as well as in the fields of synthetic organic chemistry, there has been increasing interest in the development of efficient methodologies for the synthesis of quinolones [34-37].

EXPERIMENT

Chemicals and instrumentation

All chemicals and solvents are used AR grade. All the metals were used as their chloride salts. UV spectra recorded on UV-vis spectrophotometer 119. Conductance or metal complex was determined in DMSO on conductivity meter quiptronics model NOEQ665. Melting points were recorded on in recorded by open capillary method and are uncorreded. ¹H-NMR spectra or a Schiff base and its metal complex recorded on Brucker 300 MHz spectrometer in DMSO. Elemental analysis was carried out on Eager 350 analyser. Magnetic measurements were done on solid complexes using Guoy method. Powder XRD pattern of complexes are recorded Philips Analytical XRD B.V. at CFC Shivaji University Kolhapur.

Preparation of 2-[2-(pyridin-2-ylmethylidene)hydrazinyl]quinoline (PCQH) Schiff base

The Schiff base ligand was synthesized by condensation of pyridine-2-carbaldehyde (0.01 M) and 2-hydrazinylquinoline (0.01 M) in 50 mL ethanol was refluxed on water bath for 4-5 hours in presence of 2-3 drops of glacial acetic acid. The reaction mixture was kept overnight, and faint pink precipitate was obtained. Then, Schiff base was filtered, washed with ethanol. It is dried in vacuum desiccator and recrystallized from ethanol. The purity of Schiff base was checked by TLC.



Figure 1. Reaction scheme for preparation the Schifs base

Preparation of metal complexes, [La(L)₂.2H₂O]Cl₃ Complex

The warm ethanolic solution of (PCQH) complexing agent (0.02 M) and ethanolic metal chloride (0.01 M) was added in the ratio (1:2) drop wise with constant stirring. The pH of the reaction solution was maintained in the range of 6.8 to 7.1 by adding alcoholic ammonia. Resulting reaction mixture was refluxed for four to five hours. The blackish yellow

complex was allowed to settle and collected by filtration, washed with warm ethanol. Then dried in vacuum dessicator and recorded the yield.

Preparation of metal complex, [Pr(L)₂.2H₂O]Cl₃ complex

The aqueous solution of $PrC1_3$ (0.01 M) in hot ethanolic. Also, ligand (PCQH) 0.02 M was dissolved in hot ethanolic solution. The aqueous solution of metal chloride was added to the ligand drop wise with constant stirring. The pH of reaction mixture was adjusted about 6.8 to 7.0 by putting alcoholic ammonia drop by drop. The resulted reaction solution was refluxed for four to five hours on water bath. The dull yellow precipitate was allowed to settle down. It is filtered through Whatmann filter paper. The complex was purified in warm ethanol. The metal complex was dried in a vacuum dessicator and the yield were recorded and stored in the glass sample bottle.

Preparation of metal complex, [Nd(L)₂.2H₂O]Cl₃ complex

A molar solution of neodymium chloride and ligand (PCQH) were prepared by dissolving weighed amounts in ethanol. These solutions were then mixed each other in 1:2 ratios with constant stirring. By adding alcoholic ammonia PH of the reaction mixture was adjusted to 7.0 and refluxed on water bath for four to five hours. Coffee color precipitate appears. The precipitate of complex were filtered and purified by washing with warm ethanol. Then complex is dried in dessicator and record the yield.

Preparation of metal complex, [Tb(L)2.2H2O]Cl3 complex

Weight amount of TbC1_3 0.01 M were prepared in ethanol. Also ligand (PCQH) 0.02 M were dissolved in hot ethanolic solution. The metal chloride solution was added to the ligand drop by drop with constant stirring. The reaction pH was maintained at 6.9 to 7.1 by adding alcoholic ammonia. The resulting reaction mixture was refluxing on water bath for 4 to 5 hours. The dull brown precipitate of complex was digested, separated by filtration and then washed with warm ethanol and dried in vacuum at room temperature.

Preparation of metal complex, [Sm(L)₂.2H₂O]Cl₃ complex

A molar solution of samarium chloride and ligand (PCQH) were prepared dissolving weighed amounts in ethanol. These solutions were then mixed each other in 1:2 ratios with constant stirring. By adding alcoholic ammonia, pH of the reaction mixture was adjusted to 7.0 and refluxed on water bath for 4 to 5 hours. Dark brown color precipitate appears. The precipitate of complex were filtered and purified by washing with warm ethanol. Then complex is dried in desiccators and record the yield.

RESULT AND DISCUSSION

Physical and analytical parameters

Physical parameters of the complexes such as molar conductance, decomposition point, chloride percentage, metal ligand ratio are listed in the Table 1. Complexes are intensively colored, insoluble in water and common organic solvents but soluble in DMSO and DMF. They decompose above 2700 °C, and suggesting good thermal stability at normal condition [38]. Molar conductance of La(III), Pr(III), Nd(III), Tb(III) and Sm(III) complexes (λ m 114 and 120 Ω^{-1} .cm².mol⁻¹) reveals their electrolytic natures [39-40]. Magnetic moments values indicates that Pr(III), Nd(III), Tb(III) and Sm(III) metal complexes were paramagnetic in nature. La(III) metal complex is diamagnetic in nature. On the basis of elemental analysis (C,

H, N), metal ion (Table 1.2) and thermal measurements empirical formula of the complexes was deduced.

Compound	F.W.	Yield	ML ratio	MP decomposition temperature	Color	Mole conductance (Ω ⁻¹ cm ² mol ⁻¹)	% of Cl cal. (obs)	Magnetic moment
PCQH(L)	248.28	65%	-	203 °C	Faint pink	-	-	-
$[La(L)_2.2H_2O]Cl_3$	778.06	54%	1:2	>270 °C	Blackish yellow	114	13.64 (13.70)	diamagnetic
[Pr(L)2.2H2O]Cl3	781.88	61%	1:2	>270 °C	Dull yeloow	120	13.60 (13.65)	Paramagnetic
$[Nd(L)_2.2H_2O]Cl_3$	785.21	58%	1:2	>270 °C	Coffee color	118	13.55 (13.49)	Paramagnetic
[Tb(L)2.2H2O]Cl3	798.08	50%	1:2	>270 °C	Dull brown	117	13.30 (13.27)	Paramagnetic
$[Sm(L)_2.2H_2O]Cl_3$	791.33	53%	1:2	>270 °C	Dark brown	115	13.55 (13.51)	Paramagnetic

Table 1. Physical and analytical data of PCQH metal complexes.

Table 2. Percent of C, H, N,O and metal ion in PCQH metal complexes

Compound	Empirical	%С	%Н	%N	%O	%M
Compound	formula	(calcd.)	(calcd.)	(calcd.)	(calcd.)	(calcd.)
PCQH(L)	$C_{15}H_{12}N_4$	72.56	4.87	22.57	-	-
$[La(L)_2.2H_2O]Cl_3$	C30H30Cl3LaN8O2	46.20	3.88	13.64	4.10	14.37
$[Pr(L)_2.2H_2O]Cl_3$	$C_{30}H_{30}Cl_3N_8O_2Pr$	46.08	3.87	14.33	4.09	18.02
$[Nd(L)_2.2H_2O]Cl_3$	C ₃₀ H ₃₀ Cl ₃ N ₈ O ₂ Nd	45.89	3.85	14.27	4.08	18.37
$[Tb(L)_2.2H_2O]Cl_3$	C ₃₀ H ₃₀ Cl ₃ N ₈ O ₂ Tb	45.05	3.78	14.01	4.00	19.87
$[Sm(L)_2.2H_2O]Cl_3$	$C_{30}H_{30}Cl_3N_8O_2Sm$	45.89	3.85	14.27	4.08	18.37

Electronic Spectra

The electronic spectra of ligand and complexes are recorded in the range 200 to 1000 nm with UV-Visible spectrophotometer 119-PC based instrument in DMSO solvent from Department of Microbiology, Pharmacy College Nanded. The ligand (PCQH) shows strong absorption band at 37453 cm⁻¹ assigned for $\pi \rightarrow \pi *$ transition. Absorption bands and corresponding transition are given in the Table 3.

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Ligand/complex	Absorbance (nm)	v/cm^{-1}	Transition				
PCQH(L)	267	37453	$\pi \rightarrow \pi^*$				
$[La(L)_2.2H_2O]Cl_3$	354	28248	$n \rightarrow \pi^*$				
$[Pr(L)_2.2H_2O]Cl_3$	498	20080	LCMT				
	249	40160	$\pi \rightarrow \pi^*$				
$[Nd(L)_2.2H_2O]Cl_3$	323	30959	$n \rightarrow \pi^*$				
$[Tb(L)_2.2H_2O]Cl_3$	264	37878	$\pi \rightarrow \pi^*$				
$[Sm(L)_2.2H_2O]Cl_3$	261	38314	$\pi \rightarrow \pi^*$				

Table 3. Electronic spectral data of PCQH complexes

The UV electronic spectra of La(III), Pr(III), Nd(III), Tb(III) and Sm(III) metal ion complexes indicates the transition is shifted towards higher or lower frequencies which confirm the coordination of the ligand to the metal ions. La(III) metal complex shows absorption bands 20080 cm⁻¹ assigned as LMCT transition [41-43].

Infrared spectra of metal complex

The Infrared spectra of ligand and metal complexes provide some information regarding the bonding in the compounds. Important absorption frequencies of ligand and complexes along with their assignments are presented in the Table 4.

IR spectra of PCQH (L) Ligand shows strong band in the region of 3165 cm⁻¹ which is assigned to v (O-H) stretching vibration of phenolic group. A band due to v (N=CH) stretching vibrations in ligand appears at 1618 cm⁻¹. A band due to v (N=CH) of pyridine stretching vibrations in ligand appears at 1570 cm⁻¹.

The IR,spectra of complexes compared with ligand, the strong band at 3134 to 3424 cm⁻¹ observed in complex due v (O-H) of water molecule [44]. The water molecule is also confirmed the band present at 1012 to 1133 cm⁻¹ due to v (H₂O) rocking vibration. Band present in ligand at 1618 cm⁻¹ due to v (CH=N) vibration shifted to frequency at 1508 to 1643 cm⁻¹ indicating the involvement of azomethine group in coordination [45,46]. Band present in ligand at 1570 cm⁻¹ due to v (CH=N) vibration of pyridine shifted to frequency at 1400 to 1537 cm⁻¹ indicating the involvement of this group in coordination. The new bands observed in complex in the region 400-600 cm⁻¹ attributable to v (M-N) and v (M-O) band stretching respectively [47,48].

Table 4. Infrared spectral data of PCQH ligand and their metal ion complexes

Compound	v(C=N) Azomethine	v(C=N) Pyridine	ν(H ₂ O)	ν(H ₂ O)	v(M-O)	ν(M-N)
PCQH(L)	1618	1570	-	-	-	-
$[La(L)_2.2H_2O]Cl_3$	1631	1481	3344	1014	513	443
$[Pr(L)_2.2H_2O]Cl_3$	1643	1537	3402	1012	555	462
$[Nd(L)_2.2H_2O]Cl_3$	1593	1400	3134	1111	526	457
$[Tb(L)_2.2H_2O]Cl_3$	1579	1484	3424	1124	605	514
$[Sm(L)_2.2H_2O]Cl_3$	1508	1428	3392	1133	605	499





Proton-NMR spectra

The ¹H-NMR spectral studies of ligand PCQH indicated signals at the aromatic and pyridine protons. The Ar-H was recorded as chemical shifts in the regions 7.1-8.4 ppm, 8.7 ppm (s, 1H) for azomethine proton (Figure 2-above) [49]. A signal corresponding to

azomethine in free ligand at δ 8.7 ppm is shifted to down field region [50] at δ 11.8 ppm in metal complex (Figure 2-bottom). A new peak observed at δ 2.2-4.2 ppm in complex due to corresponding water molecule [51]. Thus, DPMDI molecule seems to be coordinated to the metal ions through azomethine and water molecule.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA and DSC) of metal complexes are used to i) get information about the thermal stability of new complexes, ii) decide whether the water molecules are inside or outside the inner co-ordination sphere of the central metal ion and iii) suggest a general scheme for thermal decomposition of chelates. In the present investigation, heating rates were suitably controlled at 10°C min-1 under nitrogen atmosphere and the weight loss was measured from the ambient temperature upto 1000°C. The TGA data are presented in Table 5. The TGA curve of the Nd(III) complexes (Figure 3A) showed a rapid first step decomposition around 80°C with 4.6 % mass loss (calculated 4.6%) indicating the loss of two lattice water molecules [52]. The complex %.[Nd(L)₂.2H₂O]Cl₃ shows a weight loss of 32.26% at a temperature range 360 °C which corresponds to the removal of two pyridine ring and three chloride molecule. A weight loss of 29.17% is observed in the temperature range 360-610 °C, 7.23% metal oxide is removed [49]. In the Nd-complex the amount of residue is 21.60% [53].

Complex	Decomposition	I a st fue set ant	Weight loss (%)		
Complex	temperature (°C)	Lost fragment	Experimental	Theoretical	
	25-80	Two lattice water molecule	4.656	4.601	
	80-360	Two pyridine ring, three chloride molecule	32.26	33.26	
$[\mathrm{Nd}(\mathrm{L})_2.2\mathrm{H}_2\mathrm{O}]\mathrm{Cl}_3$	360-610	Two quinolone ring	29.17	32.70	
	610-800	Organic moiety	7.12	6.90	
	800-1000	Metal oxide	21.60	21.08	
	25-80	Two lattice water molecule	4.456	4.62	
	80-360	Two pyridine ring, three chloride molecule	33.68	32.91	
$[PI(L)_2.2\Pi_2O]CI_3$	360-610	Two quinolone ring	32.85	27.10	
	610-800	Organic moiety	6.90	7.40	
	800-1000	Metal oxide	21.16	21.10	
	25-80	Two lattice water molecule	4.56	4.45	
	80-360	Two pyridine ring, three chloride molecule	32.38	33.16	
$[Sm(L)_2.2H_2O]Cl_3$	360-610	Two quinolone ring	32.42	33.14	
	610-800	Organic moiety	6.84	7.32	
	800-1000	Metal oxide	22.08	22.67	

 Table 5. Thermal Analysis data for metal complexes

The TGA curve of the Pr(III)-complexes (Figure 3B) showed a rapid first step decomposition around 800 °C with 4.4% mass loss (calculated 4.6%) indicating the loss of two lattice water molecules [54]. The complex $[Pr(L)_2.2H_2O]Cl_3$ shows a weight loss of 33.68 % at a temperature range 350 °C which corresponds to the removal of two pyridine ring ligand and three chloride molecules. A weight loss of 32.85% is observed in the temperature range 360–610 °C which suggests the elimination of two quinoline ring. From 610-8000 °C, 6.9% organic moiety is removed. In the Pr-complex, the amount of metal oxide is 21.16 % [55].

The TGA curve of the Sm(III)-complexes (Figure 3C) showed a rapid first step decomposition around 70 °C with 4.5% mass loss (calculated 4.4%) indicating the loss of two lattice water molecules [56]. The complex $[Sm(L)_2.2H_2O]Cl_3$ shows a weight loss of 32.38% at a temperature range 370 °C which corresponds to the removal of of two pyridine ring ligand and three chloride molecule. A weight loss of 32.42% is observed in the temperature range 370-610 °C which suggests the elimination of two quinoline ring. From 610-8000 °C, 6.8 % organic moiety is removed. In the Sm-complex the amount of metal oxide is 22.08% [57].



Figure 3. The DSC-TGA data of metal complex: (**A**) [Nd(L)₂.2H₂O]Cl₃; (**B**) [Pr(L)₂.2H₂O]Cl₃; and (**C**) [Sm(L)₂.2H₂O]Cl₃



Figure 4. X-ray diffractogram of metalcomplex [Nd(L)₂.2H₂O]Cl₃



Figure 5. X-ray diffractogram of metalcomplex [Pr(L)₂.2H₂O]Cl₃

X-Ray analysis

Powder XRD patterns of the selected complexes recorded in the 20 range from 10 to 900 at wave length 1.5405 A° using Cu K α radiation source. Miller indices and interplanar distances are then determined indexing major diffractograms. Lattice parameter a, b, c, and α , β , γ are computed from program. Data has been summarized in the following Table 6 dan 7, meanwhile the diffractograms are showed in Figure 4 and 5, respectively.

The cell data and crystal cell parameter for metal complex $[Nd(L)_2.2H_2O]Cl_3$ was showed in Figure 4 and Table 6. This result gives crystal system: monoclinic, lattice type: P, lattice parameter: a= 16.71285 b= 8.19882 c= 2.95567 A°, and lattice parameter: α = 90.000 β = 108.062 γ = 90.000. This result attributed to monoclinic crystal system [58].

h k	1		20 (cal)	20 (Obs)	d(cal)	d (obs)
-2	1	0	7.75909	7.75704	5.70557	5.70773
-2	0	1	15.11849	15.12500	2.95342	2.95235
1	0	1	17.02311	17.02641	2.63119	2.63083
2	0	1	18.53036	18.53169	2.42379	2.42374
-6	1	1	20.18664	20.19542	2.23224	2.23140
-6	2	1	22.42805	22.41373	2.01901	2.02031
-8	1	0	23.51837	23.52289	1.93037	1.93009
-9	2	0	28.36228	28.35563	1.62153	1.62192
-6	4	1	30.09779	30.09859	1.53606	1.53606
-10	3	1	33.65487	33.66373	1.38996	1.38967
-6	2	2	34.53787	34.53521	1.35867	1.35879
-4	6	0	36.59269	36.59507	1.29218	1.29214

Table 6. The lattice parameter of metal complex [Nd(L)₂.2H₂O]Cl₃

Table 7. The lattice parameter of metal-complex [Pr(L)₂.2H₂O]Cl₃

h k l	2θ (cal)	20 (Obs)	d(cal)	d (obs)
-1 0 0	5.54831	5.53873	7.96710	7.96702
-1 0 1	7.28328	7.28169	6.07610	6.06944
-1 1 0	7.91893	7.91549	5.59112	5.58678
0 2 1	13.14968	13.14437	3.38599	3.38490
1 2 1	15.07010	15.04577	2.96268	2.96551
-1 3 1	18.69783	18.69014	2.40285	2.40261
3 1 1	20.83278	20.82923	2.16594	2.16534
0 3 2	21.93854	21.93838	2.06176	2.06092
-4 0 0	22.75180	22.73063	1.99178	1.99273
-3 3 1	23.93230	23.91901	1.89889	1.89917
4 0 1	25.75287	25.74120	1.77288	1.77301
-2 3 3	26.85754	26.85035	1.70505	1.70491
-3 0 4	27.81326	27.80106	1.65091	1.65105
4 3 0	29.08270	29.06866	1.58474	1.58496
-5 2 1	30.19569	30.17782	1.53155	1.53193
1 5 1	31.29968	31.28697	1.48273	1.48286
-3 1 5	34.86908	34.85211	1.34738	1.34762
-2 5 3	36.76413	36.75352	1.28700	1.28703

In addition, the cell data and crystal parameter for metal complex $[Pr(L)_2.2H_2O]Cl_3$ are displayed in Figure 5 and Table 7. It was result that crystal system: monoclinic, lattice type: P, lattice parameter: a= 12.91538 b= 4.54932 c= 6.64278 A°, and lattice parameter: α = 90.000 β = 134.080 γ = 90.000. This result is attributed to monoclinic crystal system [59].

Based on the above results, the probable structure of the metal complexes resulted is proposed as below.







Structure for [Pr(L)₂.2H₂O]Cl₃ complex

 $H_{2}O \longrightarrow Sm^{3+} OH_{2}$

Structure for [Sm(L)₂.2H₂O]Cl₃ complex

CONCLUSION

To summarized, a series of new rare earth complexes of La(III) has been synthesized. They have type $[Ln(L)_2(H_2O)_2]Cl3$ where Ln= La(III), Pr(III), Nd(III), Sm(III) and Tb(III) and L=Schiff base ligand, 2-[2-(pyridin-2-ylmethylidene)hydrazinyl]quinoline (PCQH)]. The resulted metal complex has been characterized their spectral data including the elemental analysis (Ln, C, H, N, and Cl), melting point, IR, ¹H-NMR and UV-Vis spectral data. The X-ray powder diffraction study of two of the complex [Nd(L)_2(H_2O)_2]Cl_3 and Pr(L)_2(H_2O)_2]Cl_3 was found to be on powder diffraction with Cu-K α 1 radiation ($\lambda = 1.5406$ Å) showing monoclinic crystal system.

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