



SPECTRAL, THERMAL, XRD STUDY OF NEW LA(III), CE(III), ND(III), METAL COMPLEXES OF ASYMMETRICAL LIGAND DERIVED FROM DEHYDROACETIC ACID

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Abstract: Solid numerous colored complexes of La(III), Ce(III), Nd(III) from tetradentate Schiff bases are synthesized from o-phenylenediamine, 3-Acetyl-6-methyl-pyran-2,4-dione and 5-bromo Salicylaldehyde. The structures of ligand and complexes are characterized by elemental analysis, magnetic susceptibility, thermal analysis, X-ray diffraction, ¹H-NMR, mass, IR, UV-visible spectra, and conductometry. TGA/DSC spectral and kinetic parameter of the complexes was observed keenly. The x-ray diffraction data proposes Monoclinic crystal system for La (III) complexes and orthorhombic for Ce (III) and Nd (III) complexes. The ligand and their metal complexes were subjected for antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, *Pseudomonas Aeruginosa* and antifungal activity is observed by poison plate method against *Aspergillus Niger*, *Aspergillus flavus*, *Penicilliumchrysogenum*.

Keywords: Tetradentate Schiff Base, Dehydroacetic acid, Powder X-ray diffraction, Thermal analysis Antimicrobial activity.

Introduction

In this paper we are pronouncing our earlier work in the series of lanthanides of tetradentate Schiff bases formed by the reaction of o-phenylenediamine, DHA, and 5-bromo Salicylaldehyde (Fig.1). The complexes of various color, of La (III), Ce(III), and Nd(III) with this tetradentate ligands were synthesized and characterized.

Experimental

Materials

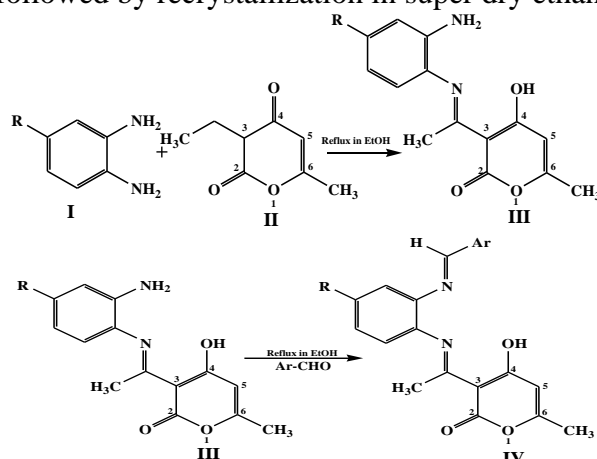
Merck was the supplier for all reagents and solvents. DHA, o-phenylenediamine, and 5-bromo Salicylaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were also used for the formation of the complexes.

Instrumentation

The CHN analysis was carried out on Thermo Scientific(FLASH 2000) CHN elemental analyzer. $^1\text{H-NMR}$ spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Bruker) in CDCl_3 as a solvent using tetra methylsilane as internal Standard. IR study has been carried out on Perkin Elmer-Spectrum RX-I FTIR spectrometer using KBr pellets. The TGA/DSC and XRD were recorded on TA Inc. SDT-2790 and Pan analyticalX'Pert Pro respectively. All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer. Molar conductance of complexes was probed on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

Synthesis of ligand

It's a two-step synthesis; in the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of (10 mmol) of DHA and (10mmol)*o*-phenylenediamine in absolute ethanol for about 3 hr. The progress of reaction was monitored via thin layer chromatography. The resulting mono-Schiff base thus formed was then refluxed with 10mmol of 5-bromo Salicylaldehyde to synthesis final product. Product was then cooled at room temperature and collected by filtration, followed by recrystallization in super dry ethanol. (Yield: 76%).



Synthesis of metal complexes

Metal complexes were prepared by mixing a stoichiometric ratio (1:1) by dissolving in methanol. The ligand (0.01 mol) and metal chloride (0.01 mol) are mixed in hot condition with continuous stirring. The mixture was heated at reflux for about 3-4 h. On cooling, the volume of reaction mixture is reduced to half, then colored solid metal complex is appeared. Thus obtained solid metal complex was purified by petroleum ether and dried over vacuum desiccator (yield: 78%).

Results and discussion

Table-1 Indicate physical characteristics, as CHN, mp. Color and molar conductance data of ligand and metal complexes. The data shows equimolar stoichiometry (metal: ligand) and satisfying general formula $[\text{ML}(\text{H}_2\text{O})_2]$ (where M =, La (III), Ce(III) Nd(III)). The study of magnetic properties reveals octahedral geometry for La (III), Ce (III) Nd (III) at room temperature with two water molecules coordinated to metal ion. Existence of two coordinated water molecules was further confirmed by weight loss before 270°C in TGA-DSC analysis.

$^1\text{H-NMR}$ spectra of ligand

The ^1H NMR spectra of free ligand in CDCl_3 at room temperature shows the following signals. 2.07δ (s, 3H, $\text{C}_6\text{-CH}_3$), 2.13δ (s, 3H, N=C-CH_3), 5.83δ (s, 1H, $\text{C}_5\text{-H}$), $6.73\text{-}7.04 \delta$ (m, aromatic protons), 8.96δ (s, 1H, N=C-H), 9.98δ (phenolic (-OH) hydrogen of phenyl ring) and 15.89δ (s, 1H, enolic OH of DHA moiety) [I,II,III].

IR spectra

The IR data of ligand (H₂L) and its metal complexes are listed in Table 2. It depicts prominent bands at 3296, 1689, 1656, 1360 and 1212 cm⁻¹ assignable to ν OH, ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively [IV]. The presence of a strong broad band in the 3296 cm⁻¹ region, in the spectra of the ligand, which is not observed in complexes elucidates coordination of phenolic oxygen to the metal ion by deprotonation [V]. Resulting upswing to an extent of 40-60 cm⁻¹ in the ν C-O (phenolic) band [VI]. This shift further confirms the involvement of the enolic oxygen in C-O-M bond. Chelation by nitrogen of azomethine (C=N) is confirmed by observing band at 1656 cm⁻¹ in the spectra of ligand, which found at lower frequency 1603-1632 cm⁻¹ when complex formed [VII]. This change can be supported by transfer of electrons from nitrogen to the vacant d-orbitals of the metal. Finding new bands in the 526-565 and 464-480 cm⁻¹ regions confirms the M-O and M-N bonding respectively [VIII]. No any change in skeletal vibrations (C=C) upon complexation. The presence of coordinated water is confirmed by the appearance of strong band in the 3027-3096 cm⁻¹ region in case of La(III), Ce(III) and Nd(III), which is also supported by appearance of non-ligand band in 825-846 cm⁻¹ region, quoted for rocking mode of water [IX].

Magnetic susceptibility and electronic absorption spectra

The electronic absorption spectrum of La (III) complex contains three bands at 30120, 34482 and 27100 cm⁻¹ assignable to the transitions $\eta \rightarrow \pi$, $\pi \rightarrow \pi^*$ and charge transfer respectively. Magnetic moment of the complexes showed that the La (III) complex is diamagnetic. The electronic absorption spectra of Ce(III) complex show three strong bands at 19801, 24390 and 26666 cm⁻¹ which may be assigned to the transitions $^2F_{5/2} \rightarrow ^2D_{3/2}$, $^2F_{5/2} \rightarrow ^2D_{5/2}$ and charge transfer respectively. Electronic transitions together with magnetic moment value 2.58 BM. Nd(III) complex show three bands at 19230, 17223 and 13262 cm⁻¹ which may be attributed to the transitions $^4I_{9/2} \rightarrow ^2G_{9/2}$, $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2} \rightarrow ^2S_{3/2}$, $^4F_{7/2}$ respectively. Electronic transitions along with magnetic moment value 3.58 B.M suggest high spin octahedral geometry for Nd (III) complex [X, XI].

Table-1 Physical characterization, analytical and molar conductance data of compounds

Compound Molecular formula	Mol.Wt.	M.P /Decomp Temp. °C	Color	Molar conduc. Mho cm ² mol ⁻¹	Found (calculated)			
					C	H	N	M
(H ₂ L) C ₂₅ H ₁₇ N ₂ O ₄ Br	442.10	189	Dark Yellow	----	56.71 (56.65)	3.694 (3.65)	6.87 (6.86)	-----
[LLa(H ₂ O) ₂]	614.19	>300	Yellow	32.00	41.07 (41.03)	3.12 (3.10)	4.56 (4.53)	22.62 (22.60)
[L Ce(H ₂ O) ₂]	615.41	>300	Brown	29.50	40.99 (40.96)	3.11 (3.10)	4.55 (4.51)	22.77 (22.73)
[L Nd(H ₂ O) ₂]	614.40	>300	Yellow	31.80	40.99 (40.90)	3.11 (3.09)	4.55 (4.51)	22.75 (22.71)

Table-2 IR data of ligand and metal complexes

Compound	IR band frequency (cm ⁻¹)							
	ν (OH)	ν (C=O)	ν (C=N)	C=C	C-N	C-O	M-O	M-N
L	3296	1689.3	1656.7	1566	1360	1212	-	-
La-L	3027	1682	1603	1563	1385	1245	526	480

Ce-L	3096	1681	1625	1561	1385	1253	565	478
Nd-L	3088	1682	1632	1562	1384	1216	560	464

Thermal analysis

The TG/DSC analysis of all La (III), Ce (III), and Nd (III) complexes was done from ambient temperature to 1000°C in nitrogen atmosphere using α -Al₂O₃ as reference.

In the TG curve of La (III) complex the first weight loss 8.009 % occurred at temperature 190°C, indicates the removal of two molecules of coordinated water, an endothermic peak at corresponding temperature in DSC corresponds to dehydration step.

The second step slow decomposition from 200-490 °C with 26.95 % mass loss. This can be further confirmed by observing broad exotherm in DSC with $\Delta T_{max.} = 271^\circ\text{C}$ indicates that the complex is thermally quite stable.[XII,XIII]. The TG-DSC curve of Ce (III) complex show first mass loss 3.114 % (calcd.4.01%) in the range 150-250°C and an endothermic peak in this region $\Delta T_{min.} = 217.27^\circ\text{C}$, indicate removal of two coordinated water molecules. The second step slow decomposition from 250-400 °C with 15.98 % mass loss. This can be further confirmed by observing endotherm in DSC with $\Delta T_{min.} = 236.55^\circ\text{C}$ indicates removal of non-coordinated part. In third step from 400-900 °C slow weight loss 19.38 %, confirmed by broad exotherm $\Delta T_{max} = 418.28^\circ\text{C}$ indicate loss of coordinated part. The TGA

DSC curve of Nd (III) complex shows a first weight loss 6.196 % (calcd.6.8%) in the range 160-240°C and an endothermic peak in this region $\Delta T_{min} = 240^\circ\text{C}$, indicating the

Presence of two coordinated water molecules. The anhydrous complex first show fast decomposition in 240-350°C range with 13.11% mass loss (calcd.13.01%) may be attributed to removal of non-coordinated part of ligand. The second step decomposition at 350-600°C, with mass loss of 9.89 % (calcd.9.80%) corresponds to decomposition of coordinated part of ligand. A broad endotherm in DSC is observed for this step.[XIV]

Kinetic calculations

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS , z (pre-exponential factor), E_a and n (order of reaction), together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method and Coats-Redfern integral method The data is arranged in Table 3. The results show that the values obtained by two methods are analogous. Low values of E_a of the complexes are indicating the autocatalytic effect of metal ion after thermal decomposition[XV].

Table-3. The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient(r)
La(III)	I	1.35	HM	35.14	58320	-159.28	41.63	0.9997
			CR	34.08	172113	-111.99	41.93	0.9986
	II	1.35	HM	24.08	61868	-132.69	36.73	0.9989
			CR	23.99	362280	-89.69	32.50	0.9980
Ce(III)	I	0.55	HM	33.99	44568	-103.76	42.20	0.9999
			CR	31.54	47183215	-104.61	39.81	0.9987
	II	0.55	HM	40.47	73267	-120.17	55.32	0.9999
			CR	38.83	35088264	-91.63	50.16	0.9999
Nd(III)	I	0.51	HM	32.42	53248	-129.69	47.98	0.9980
			CR	31.88	75580	-85.00	42.08	0.9989

E_a in kJ mol^{-1} , Z in S^{-1} , ΔS in $\text{JK}^{-1}\text{mol}^{-1}$ and ΔG in kJ mol^{-1}

Powder x-ray diffraction

Scanning of x-ray diffractogram of La(III), Ce (III), Nd(III)metal complexes of L is done at wavelength 1.543 Å in the range 5-100°. The x-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using computer program[XVI]. The diffractogram of La(III) complex of L had ten reflections with maxima at $2\theta = 23.18^\circ$ corresponding to d value 3.86254 Å. The unit cell of La(III) complex of L yielded values of lattice constants, $a=10.3214 \text{ \AA}$, $b=9.38521 \text{ \AA}$, $c = 4.06521 \text{ \AA}$ and unit cell volume $V=345.902 \text{ \AA}^3$. [XVII] The diffractogram of Ce(III) complex of L shows eleven reflections with maxima at $2\theta = 13.654^\circ$ corresponding to d value 7.45625 Å. The unit cell of Ce(III) complex of L yielded values of lattice constants, $a=19.248912 \text{ \AA}$, $b=8.97364 \text{ \AA}$, $c = 4.068363 \text{ \AA}$ and unit cell volume $V=439.7661 \text{ \AA}^3$. The diffractogram of Nd(III) complex of L had ten reflections with maxima at $2\theta = 80.659^\circ$ corresponding to d value 1.52456 Å. The unit cell parameters of Nd (III) complex of L yielded values of lattice constants, $a=11.44839 \text{ \AA}$, $b=8.387201 \text{ \AA}$, $c = 6.482108 \text{ \AA}$ and unit cell volume $V=320.24919 \text{ \AA}^3$. In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory in La(III) complex. While $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ for sample to be orthorhombic were tested and found to be satisfactory for Ce (III) and Nd (III).

Density values of the complexes were determined practically by using specific gravity method, and found to be 2.265, 3.6157, 4.8919 gcm^{-3} for La (III), Ce (III), and Nd (III) complexes respectively. Where theoretical density found to be 2.253, 3.62147, 4.6935, gcm^{-3} for respective complexes, and find near to experimental value. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were computed [XVIII].

Antimicrobial activity

Ligand and metal complexes are subjected for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus*, *Pseudomonas Aeruginosa* by Agar Cup Method [XIX,XX]. The compounds were tested at the concentration of 1 % in DMSO, considering Ciproflaxin as standard (Table-4). Poison plate method is used for fungicidal activity, compounds were tested against *Aspergillus Niger*, *Aspergillus flavus*, *Penicillium chrysogenum*. The medium used was Potato Dextrose Agar, and depicted in (Table-5) by comparison with Griseofulvinas standard. Observing Table-4 and 5, conclusion made that the inhibition by metal complexes is more than a ligand. Solubility of metal complexes in organic solvents increase its activity Hydrogenbonding with active center of cell may responsible for enhanced activity [XXI].

Table 4 Antibacterial activity of compounds

Test Compound	Diameter of inhibition zone (mm)		
	<i>E.Coli</i>	<i>S. aureus</i>	<i>Ps. Aeruginosa</i>
<i>Ciprofloxacin</i>	25	50	25
L1	12	15	12
L1-La	18	16	15
L1-Ce	19	18	14
L1-Nd	20	22	17

Table 5 Antifungal Screening of ligand and their metal complexes

Test Compound	Microorganisms		
	<i>Asp. Niger</i>	<i>Asp. flavus</i>	<i>Pen. chrysogenum</i>
L ₁	-ve	-ve	-ve
L ₁ -La	-ve	-ve	-ve
L ₁ -Ce	-ve	+ve	-ve
L ₁ -Nd	-ve	-ve	-ve
DMSO	+ve	+ve	+ve
Griseofulvin	-ve	-ve	-ve
-ve-No growth Antifungal activity present , +ve-Growth Antifungal activity absentRG -Reduced growth			

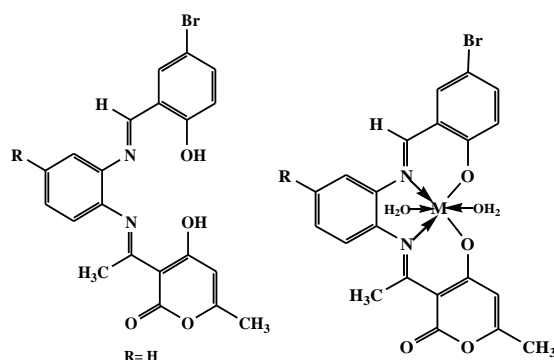


Fig.1 The structure of the Ligand,**Fig.2 b** the proposed structure of the complexes, Where M=La (III), Ce (III), and Nd (III)

Conclusion

In present search we proclaiming synthesis of ligand and its transition metal complexes. Spectral study suggest that azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions (fig.1). Proposing octahedral geometry for La (III), Ce (III), Nd(III)complexes. It is concluded that the ligand is dibasic in nature and ONNO tetradentate metal complexes are biologically active and show enhanced antimicrobial activities compared to its free ligand. The x-ray diffraction data proposes Monoclinic crystal system for La (III) complexes and orthorhombic for Ce (III) and Nd (III) complexes. Thermal study predicts thermal behavior of complexes.

Acknowledgements

The Authors are thankful to chairman People's Education Society Mumbai for providing laboratory facility, and SAIF Punjab University, Chandigarh for providing CHN,IR,¹HNMR,Mass and XRD facility.Also grateful to USIC,Shivaji University, Kolhapur for providing TGA-DSC facility, for biological activity.

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Received on August 15, 2020.