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Synthesis, spectroscopic characterization and thermal studies of some rare earth metal complexes of Tetradentate Schiff Base Ligand

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***Abstract*— The solid complexes of La(III), Ce(III) and Pr(III) with 4-Hydroxy-3-(1-{2-[(2-hydroxy benzylidene)-amino]-4-methyl phenylimino}-ethyl)-6-methyl-pyran-2 one (H_2L) derived from 4-methyl-phenylenediamine, 3-acetyl-6-methyl-(2*H*)pyran,2,4(3*H*)-dione (dehydroacetic acid or DHA) and salicylic aldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-visible, IR,^{1}H-NMR spectra, X-ray diffraction, thermal analysis and screened for antimicrobial activity. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donar atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). The physico-chemical data suggests distorted octahedral geometry for La(III), Ce(III) and Pr(III) complexes. The X-ray diffraction data suggests monoclinic crystal system for La(III) and Ce(III) and orthorombic crystal system for Pr(III) complexes. Thermal behaviour (TGA/DTA) of the complexes was studied and kinetic parameters were determined by Horowitz-Metzger and Coats-Redfern methods. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and *Bacillus Sp*. Fungicidal activity against *Aspergillus Niger*, *Trichoderma* and *Fusarium oxysporum*.**

***Keywords*— Dehydroacetic acid, Unsymmetrical tetradentate Schiff Base, Rare Earth metal complexes, thermal analysis, Powder X-ray diffraction and biological activity.**

I. Introduction

Tetradentate Schiff bases with N_2O_2 donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry[1-5]. Schiff bases of o-phenylenediamine reported to have variety of applications including biological[6], clinical[7] and analytical[8] fields. Many symmetrical tetradentate bis-type Schiff bases of 1, 2-diamines with o-hydroxy aldehyde/ketone have been prepared and studied intensively.

However much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes. In particular those derived from aromatic 1, 2 diamines have been under-investigated[9]. It is worthwhile to mention here that unsymmetrical Schiff bases of this type are difficult to obtain and are not easily isolated [10].

One of the oxygen heterocyclic compounds 3-acetyl–6-methyl-2H-pyran 2,4(3H)-dione (DHA) was reported to be an excellent chelating agent and to possess promising fungicidal, bactericidal, herbicidal and insecticidal activities[11-15]. It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring system[16-20]. A search of the literature reveled that no works has been done on Lanthanide (III) nitrate metal complexes of the asymmetrical Schiff base derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde.

II. Experimental

Dehydroacetic acid purchased from Merck was used as supplied. o-phenylene diamine and salicylic aldehyde of A.R. grade were used for synthesis of ligand. A.R. grade metal nitrate were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. IR spectra were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ^{1}H-NMR spectra of ligand were measured in $CDCl_3$ using TMS as internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701 respectively. The UV-visible spectra of the complex were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10-3 M solution in DMF.

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General procedure for the synthesis of ligand

The ligand was prepared by a reported method21. A typical procedure for synthesis of Schiff bases was as follows a 50mL solution of 0.10mmol (0.168gm) of dehydroacetic acid, 0.10mmol (0.108gm) of 4 methyl-phenylenediamine and 0.10mmol (0.122gm) of salicylic aldehyde in absolute ethanol was refluxed for about 4hrs. The precipitate thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol (Yield: 85%). (Fig. 1)

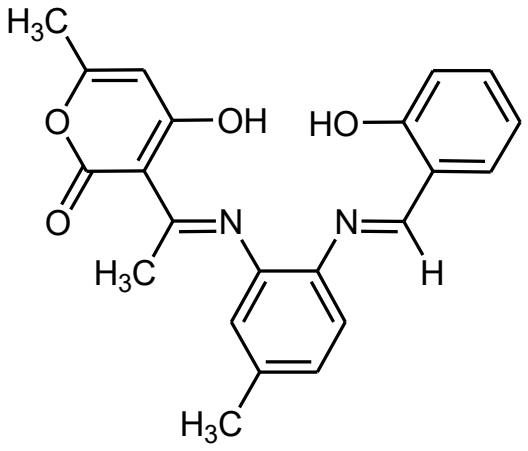

Fig. 1. Structure of ligand

General procedure for the synthesis of Metal complexes

To a hot solution of ligand (0.01 mol) in chloroform, methanolic solution (25mL) of metal nitrate (0.01mol) was added under constant stirring. The pH of reaction mixture was adjusted to 7.5-8.5 by adding 10% alcoholic ammonia solution and refluxed for about 6-7hrs. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether (40:60) and dried over calcium chloride in vacuum desiccators (Yield= 55%).

III. Result And Discussion

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in (Table 1). The analytical data of complexes revels 1:1 molar ratio (metal: ligand) and corresponds well with the general formula $[ML(H_2O)_2.\ NO_3.]$ (Where M=La(III), Ce(III) and Pr(III). The magnetic susceptibilities of La (III), Ce (III), and Pr (III), complexes at room temperature are consistent with distorted octahedral structure.

With two water molecules and one nitrate molecule coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TGA-DTA analysis. The metal chelate solution in DMF shows low conductance and this supports their non-electrolyte nature.

Table .1. Physical characterization, analytical and molar conductance data of compound

Ligand/Complexes	F. W.	M.P. / Decomp. Temp.^{0}C	Magnetc moment μeff (B.M.)	Molar conduc. Mho cm^2 mol^{-1}	Found % (Calculated)			
					C	H	N	M
(HL)	362.39	185	----	----	69.12 (69.60)	4.88 (5.01)	7.50 (7.73)	–
$[LaL(H_2O)_2]NO_3$	597.82	>300	Dia.	33.04	41.60 (42.22)	3.07 (3.37)	6.80 (7.03)	22.40 (23.25)
$[CeL(H_2O)_2]NO_3$	599.03	>300	2.58	29.00	42.01 (42.14)	3.10 (3.36)	7.10 (7.02)	23.05 (23.41)
[PrL (H2O)$_2$]NO_3	599.03	>300	3.50	30.06	42.10 (42.14)	3.01 (3.36)	6.80 (7.02)	23.00 (23.41)

^{1}H-NMR spectra of ligand

The **^{1}H-NM*R*** spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. δ 2.15 (s, 3H, -CH_3), 2.55 (s, 3H, N=C-CH_3), 5.54 (s, 1H, phenolic OH), 5.84 (s, 1H, Ar-H), 6.90-7.40 (m, 8H, Ar-H), 8.60 (s, 1H, N=C-H), 15-80 (s, 1H, enolic OH of DHA moiety)

Mass Spectra of the Ligand

Mass Spectra data confirm the structure of the Ligands HL as indicated by the peaks corresponding to their molecular mass.

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FTIR Spectra

The IR spectrum of free ligand shows characteristic bands at 3060-3300, 1708, 1621, 1340 and 1252 cm^{-1} assignable to intramolecular hydrogen bonded (υ OH), lactone carbonyl (υ C=O), azomethine (υ C=N), aryl azomethine (υ C-N) and phenolic (υ C-O) stretching modes respectively[22,23]. The data is given in Table 3. The absence of a weak broad band in the 3060-3300 cm^{-1} region, noted in the spectra of the metal complexes indicates deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by upward shift in phenolic (υ C-O)[24] to the extent of 30-50 cm^{-1}. On complexation, the υ (C=N) band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of the azomethine group is coordinated to the metal ion. This is supported by upward shift in υ C-N to the extent of 10-50 $cm.^{-1}$ [25] The IR spectra of metal chelates showed new bands in the 425-540 cm^{-1} assigned to (M-N)[26-29] and 350-320 cm^{-1} assigned to (M-O) modes .[30] The I.R spectra show a strong band in the 3150-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. Infrared spectra of the nitrato complexes reveled two additional strong bands around 1486 and 1279cm^{-1}, which were absent in the free ligand[31]. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the 820-835 cm^{-1} region, assignable to the rocking mode of water.[31] The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

Thermal analysis

The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000°C in nitrogen atmosphere using α-Al_2O_3 as reference. The La(III), Ce(III) complexes of ligand H_2L were Chosen for a thermal study. On the TG curve of the La(III) complex, the first step shows a steep slope between 50–280 °C with a mass loss of 5.8%(calculated 6.0%), indicating the removal of two molecules of coordinated water. An exothermic peak in the range 100–300 °C ΔTmax = 271.76°C) on the DTA curve corresponds to the dehydration step. The second step decomposition from 280-450°C, with 13.10% (calcd. 12.81%) mass loss, and a sharp exothermic (ΔTmax = 344°C) in DTA may be attributed to removal of non-coordinate part of ligand.

The third step decomposition is from 450-600°C with 9.4 % (calcd. 10.10%) mass loss and broad exothermic (ΔTmax = 490°C) in DSC may be attributed to removal of coordinate nitrate part of the complexes. The mass of final residue corresponds to stable La_2O_3, The TGA-DSC curve of Ce(III) complex of ligand , shows a first weight loss 5.8 % (calcd. 6.1%) in the range 160-205°C and an endothermic peak in this region, indicate removal of two coordinate water molecules. The first step decomposition is from 200 to 310 °C, with 12.10 % (calcd. 12.81 %) mass loss and may be attributed to removal of non-coordinated part of ligand. The second step decomposition from 310-400°C, with 10.5% (calcd. 10.10 %) mass loss and may be attributed to removal of coordinate nitrate part of the complex. The third step decomposition is from 420 to 900°C with 17.90 % (calcd 18.22 %) mass loss corresponds to decomposition of coordinated part of ligand. The mass of the final residue corresponds to stable Ce2O3, 52.50 % (calcd. 53.58 %).

Powder X-ray diffraction

The X-ray diffraction of metal complexes was scanned in the range 5-100° at wave length 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The X- ray diffractograms of La(III) complex shows nine reflections with maxima at 2θ = 27.94° corresponding to d value 3.19 Å. The unit cell values of lattice constants were a = 13.04 Å, b = 9.10 Å, c = 3.66 Å, α = γ = 90° ≠ β. and unit cell volume V = 434.6913 $(Å)^3$. The X- ray diffractograms of Ce(III) complex shows six reflections with maxima at 2θ = 29.03° corresponding to d value 3.04 Å. The unit cell values of lattice constants were a = 8.94 Å, b = 8.94 Å, c = 6.15 Å, α = γ = β= 90° and unit cell volume V = 419.98 (Å)3 .The diffractogram of Pr(III) complex had sixteen reflaction with maxima at 2θ = 23.88° corresponding to d value 3.20Å. The x-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% have been indexed by using computer programme. The above indexing method also yields miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of La (III) complex yielded values of lattice constants a = 13.04 Å, b = 9.10 Å, c = 3.66 Å and unit cell volume V = V = 434.6913 $Å^3$. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = γ = 90° ≠ β. The unit cell of Ce(III) complex yielded values of lattice constants a = 8.94 Å, b = 8.94 Å, c = 6.15 Å, and unit cell volume V = 419.98 (Å)3 required for sample to be monoclinic were tested and found to be satisfactory.

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Hence it can be concluded that La(III) and Ce(III) complex has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [31] and found to be 0.91, 0.97, and 1.94 $g \cdot cm^{-3}$ for La(III), Ce(III), and Pr(III) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number, volume of the unit cell, the number of molecules per unit cell were calculated by using equation $\rho = nM/NV$ and was found to be one, one, and four for La(III), Ce(III), and Pr(III) complexes respectively. With these values, theoretical density were computed and found to be 0.90, 0.96 and 1.93 $g \cdot cm^{-3}$ for respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error.

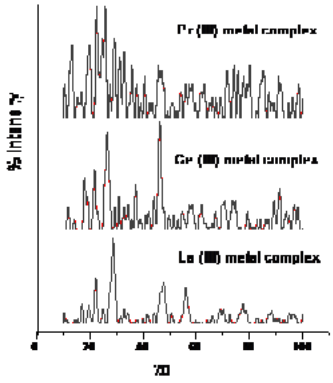

Fig. 2. X-ray diffractograms of La(III), Ce(III) and Pr(III) complexes

Kinetic calculations

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation (E_a), frequency factor (log A), entropy of activation ($\Delta S^{\#}$) and free energy change ($\Delta G^{\#}$) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Coats-Redfern integral method [27] The data is given in Table 2. The results show that the values obtained by two methods are comparable. The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex.[28,29,30] $\Delta S^{\#}$ values were negative, which indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus, Escherichia coli* and *Bacillus Sp* by paper disc plate method.[31,32,33] The compounds were tested at the concentration 0.5 $mg \cdot mL^{-1}$ and 1 $mg \cdot mL^{-1}$ in DMF and compared with known antibiotics *viz* ciproflaxin (*Table* 4). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger*, *Trichoderma, and Fusarium oxysporum* by mycelia dry weight method [24] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (*Table* 6). From *Tables* 4 and 5, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [24-35]. Such enhanced activity of metal chelates is due to lipophilic nature of the metal ions in complexes. The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents, resulting in interference with the normal cell process. [36]

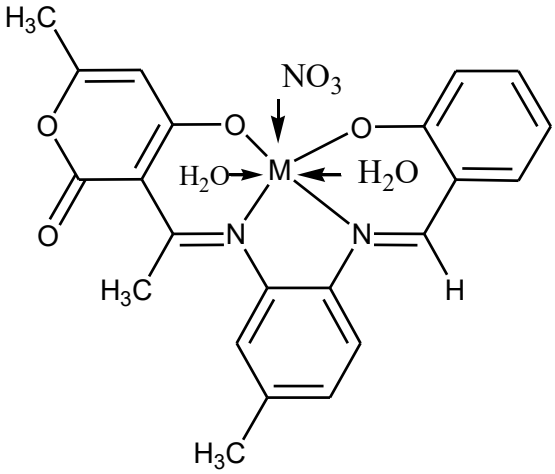

Fig. 3. Structure of Metal Complexes

Where M = La (III), Ce (III) and Pr (III)

IV. Conclusion

In the light of above discussion we have proposed distorted octahedral geometry for La(III), Ce(III) and Pr(III).

Complexes On the basis of the physicochemical and spectral data discussed above, one can assume that the ligand behave as dibasic, ONNO tetradentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig. 3. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests monoclinic crystal system for La(III) and Ce(III) and Orthorombic crystal system for Pr(III) complexes.

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