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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, ^{1}H-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, Dehydroacticacid, Powder X-raydiffraction, 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

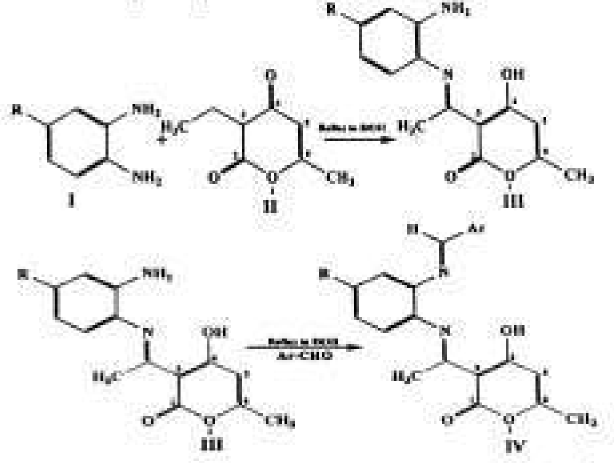
Merck was the supplier for all reagents and solvents. DHA, *o*-phenylenediamine, and 5-bromo Salicylaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were also used for the formation of the complexes.

Instrumentation

The CHN analysis was carried out on Thermo Scientific(FLASH 2000) CHN elemental analyzer. ^{1}H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Brunker) 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%).



Where R=H and Ar= 5-bromo Salicylaldehyde

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-1Indicate 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 [ML(H2O)2] (where M =, La (III), Ce(III) Nd(III)). The study of magnetic properties revels 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}H-NMR spectra of ligand

The ^{1}H NMR spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. 2.07 δ (s, 3H, C_6-CH_3), 2.13 δ (s, 3H, N=C-CH_3), 5.83 δ (s, 1H, C_5-H), 6.73-7.04 δ (m, aromatic protons), 8.96 δ (s, 1H, N=C-H),9.98δ(phenolic (-OH) hydrogen of phenyl ring) and 15.89 δ (s, 1H, enolic OH of DHA moiety) [I,II,III].

IR spectra

The IR data of ligand (H_2L) and its meta lcomplexes are listed in Table 2. It depict prominent bands at 3296, 1689, 1656, 1360 and 1212 cm^{-1} assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), υ C-N (aryl azomethine) and υ 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 υ 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 find 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${}^4I_{9/2} \rightarrow {}^2G_{9/2}, \rightarrow {}^4G_{5/2}, {}^2G_{7/2}, \rightarrow {}^2S_{3/2}, {}^4F_{7/2}$ 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. ^0C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated)			
					C	H	N	M
(H_2L) $C_{25}H_{17}N_2O_4Br$	442.10	189	Dark Yellow	----	56.71 (56.65)	3.694 (3.65)	6.87 (6.86)	-----
[$LLa(H_2O)_2$]	614.19	>300	Yellow	32.00	41.07 (41.03)	3.12 (3.10)	4.56 (4.53)	22.62 (22.60)
[L $Ce(H_2O)_2$]	615.41	>300	Brown	29.50	40.99 (40.96)	3.11 (3.10)	4.55 (4.51)	22.77 (22.73)
[L $Nd(H_2O)_2$]	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-Al_2O_3 as reference.

In the TG curve of La (III) complex the first weight loss 8.009 % occurred at temperature 190^{0}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 ΔTmax. = 271°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 ΔTmin. = 217.27°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 ΔTmin. = 236.55°C indicates removal of non-coordinated part. In third step from 400-900 °C slow weight loss 19.38 %, confirmed by broad exotherm ΔTmax = 418.28°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 ΔTmin = 240°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

Ea in kJ mol^{-1}, Z in S^{-1}, ΔS in JK^{-1}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 Åin 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 2θ = 23.18° corresponding to d value 3.86254 Å.The unit cell of La(III) complex of L yielded values of lattice constants, a=10.3214 Å, b=9.38521 Å, c = 4.06521 Å and unit cell volume V=345.902 $Å^3$.[XVII]The diffractogram of Ce(III) complex of L shows eleven reflections with maxima at 2θ = 13.654° corresponding to d value 7.45625 Å. The unit cell of Ce(III) complex of L yielded values of lattice constants, a=19.248912 Å, b=8.97364Å, c = 4.068363Å and unit cell volume V=439.7661 $Å^3$.The diffractogram of Nd(III) complex of L had ten reflections with maxima at 2θ = 80.659° corresponding to d value 1.52456 Å. The unit cell parameters of Nd (III) complex of L yielded values of lattice constants, a=11.44839Å, b=8.387201 Å, c = 6.482108 Å and unit cell volume V=320.24919 $Å^3$.In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory in La(III) complex.While $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ 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}forLa (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'snumber 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)**		
	E.Coli	***S. aureus***	***Ps. Aeruginosa***
Ciprofloxacin	25	50	25
L_1	12	15	12
L_1-La	18	16	15
L_1-Ce	19	18	14
L_1-Nd	20	22	17

Table 5 Antifungal Screening of ligand and their metal complexes

Test Compound	Microorganisms		
	Asp. Niger	*Asp. flavus*	*Pen. chrysogenum*
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			

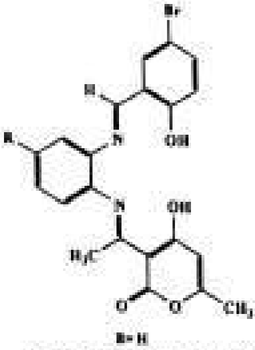


Figure 1. Structure of ligand

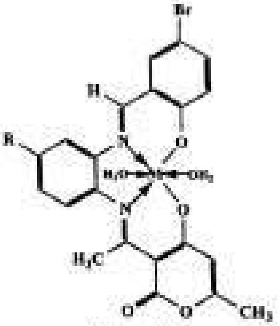


Figure 2(b)

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.

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RESEARCH ARTICLE

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Multiwalled Carbon Nanotube Based Solid- Phase Extraction Cartridges and its Application in Waste Water Analysis

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ABSTRACT

Isolation of different organic impurity from industrial waste water was carried out using solid phase extraction (SPE) cartridges and analyzed by reverse phase high performance liquid chromatography.

Kalonji oil-a rich source of carbon, easily available in nature and cheap is used as a naturally occurring precursor for the synthesis of Multiwalled Carbon Nanotubes (MWCNTs) in laboratory by chemical oil vapor deposition technique (COVD) by direct pyrolysis at 800°C in an inert gas (Hydrogen) atmosphere. The obtained MWCNTs were purified by acid treatment and characterized by different analytical tools such as XRD (X-ray diffraction), SEM (Scanning Electron Microscope) and FTIR (Fourier Transform Infra-Red Spectroscopy), BET surface area analyser.These MWCNTs used directly to prepare solid phase extraction cartridges in laboratory and studied its application in isolation of organic impurities (Aniline and Phenol) from industrial waste water followed its identification by RP-HPLC (Reverse phase High performance liquid chromatography analysis).

Keywords: Solid-Phase Extraction, Multiwalled Carbon Nanotubes, Water Analysis, Organic Impurities.

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INTRODUCTION

Industrial waste water quality determination before directly pouring it to natural resources is very important now days which is directly or indirectly affecting health of human being and aquatic environment [1]. Different organic and inorganic impurities are the outputs of different chemical and pharmaceutical industries. Industrial effluent quality is determined by physical, chemical and biological parameters [2] Use of naturally occurring precursor for the manufacturing carbon nanotubes by in-house, simple and efficient method is utmost important to get multiwalled carbon nanotubes in laboratory [3]. Aniline is aromatic amine widely used in many chemicals, pharmaceutical, rubber and dye industries as chemical feedstock [4]. Aniline and phenols are carcinogens and are highly toxic to aquatic life even in trace amount [5]. Presence of Aniline in concentration of Synthesizing metallic ppm range will kill 50 % of exposed organisms within 96Hrs [6]

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Traditional methods of water purification such as liquid extraction, distillation, adsorption can be used for removal of many organic and inorganic impurities [7]. Now a day many chemical, dye making and pharmaceuticals industries are looking for alternative and reusable cheap material technologies for the purpose which can be used to overcome the disadvantages. As multiwalled carbon nanotubes having highest surface area as compared to that of activated charcoal which is currently used in many industries for removal of organic and colored impurities from industrial effluents, the multiwalled carbon nanotubes have better performance abilities and advantages over the conventional methods. Functionalization of MWCNTs carried out with different functional groups and with different API's (Active Pharmaceutical Ingredients) [8] [9], is also found to be useful in separation. Carbon Nano beads are also synthesized from naturally occurring oil [10] and can be used for multiple applications. The research objectives of this research is to execute the chepest, simple and reusable technology for treatment of industrial waste of chemical, dye making, pharmaceutical industries before pouring it to natural resources.

The adequate column sizes of such multiwalled carbon nanotubes once used till its loading capacity and can be reused after unloading the separated contaminants using some special treatments which will be found suitable over a conventional method of treating industrial effulents.

MATERIALS AND METHODS

Materials used for research work

Kalonji oil : Purchased from local market
Aniline : LR Grade (ACS chemicals)
Phenol : AR Grade (Rankem)
Sodium dihydrogen orthophosphate : AR Grade (Merck)
Formic acid : AR Grade (Loba Chemie)
Water : Deionized Milli Q
Methanol : HPLC Grade (Rankem)
Industrial waste water : Collected from MIDC Area

Synthesis Methodologies

Synthesis of Multiwalled Carbon Nanotubes: The MWCNTs was synthesized from Kalonji oil using a nickel catalyst, (detail method of synthesis of nickel catalyst is discussed elsewhere [11].) by COVD method by direct pyrolysis at 800°C in an inert atmosphere. In COVD synthesis [12], as represented herewith schematically in figure:1 where 'A' and 'B' are two electric furnaces (vaporizing furnace and pyrolysing furnace respectively). 10 g of Kalonji oil placed in quartz boat 'C' and 200 mg of nickel catalyst in other quartz boat 'D' and both the boats are kept e boats in furnance 'A' and furnace 'B' respectively. The inert gas hydrogen is allowed to pass through quartz tube 'Q' for 5 min with constant flow rate of 10cc/min so as to remove oxygen from the tube. The temperature of pyrolysing furnace 'B' was set to 800°C. Once the furnace 'B' reaches the desired temperature. The furnace 'A' was turned on and temperature was set to boiling point of Kalonji oil. The heating of furnance 'A' was continued till all oil gets vaporized. The heating of furnance 'B' was continued for one hour. The furnance 'B' is allowed to cool at room temperature and material was collected from boat 'D'.

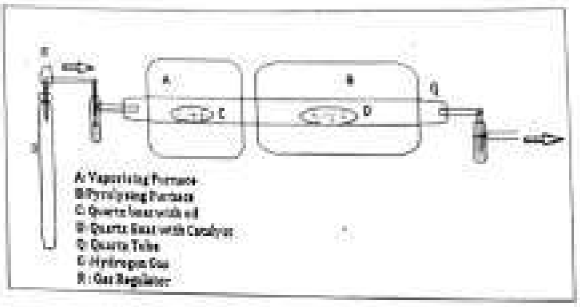

Figure 1: Schematic Diagram of Lenton's Split Tube Furnace

Purification of Multi Walled Carbon Nanotubes

As obtained MWCNTs from boat 'D' was soaked in Hydrochloric acid (50%) followed by Nitric acid (50%) solution for 24Hrs and sonicated for about 2.0 Hrs. The material is filtered using whatmann filter paper, collected and dried at 200°C for 3Hrs in drying air oven.

Characterization of Multi walled Carbon Nanotubes

Purified MWCNTs were characterized by ATR method of Shimadzu Spectrometer with IR Affinity model. X-ray diffraction (XRD) analysis was performed using Phillips analytical X-ray diffractometer with Cu Kα radiation running at 45 KV/40 mA in the 2θ range 2°–100° with step size of 0.02. Specific surface areas were measured using SmartSorb-92/93 model of Smart Instruments Co. Pvt. Ltd. by low temperature nitrogen adsorption using the Brunauer-Emmett-Teller (BET) single point method. The samples were degassed at 150°C for 2 hours prior to analysis. The morphological analysis was performed with a Phillips SEM 505 scanning electron microscope.

Fabrication of Solid-phase Extraction Cartridges

Figure 2 represents as prepared solid phase extraction cartridge in laboratory and it is prepared by handmade method. Weighed accurately about 0.5 g of purified MWCNTs and transferred to a plastic syringe of 5.0 cm length and 5.7 mm diameter containing cotton plug at the bottom. This syringe containing MWCNTs was tapped for 10 minutes and vortexed for 10 minutes later. Once this material is packed, washed it with milli Q grade water followed by methanol and henceforth referred as MWCNTs based SPE cartridge.

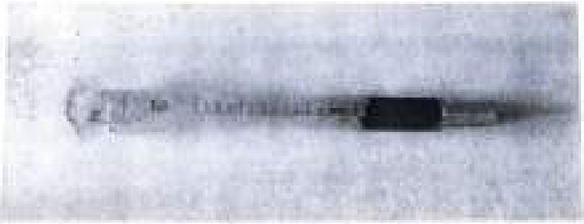

Figure 2: Handmade MWCNTs based SPE cartridge

Application of MWCNTs based SPE cartridge in waste water sample

Industrial waste water sample (1 L; 5.8 pH) were collected from MIDC area dombivali, Kalyan MS, India. This sample is centrifuged for 10 minutes to remove any solid suspended particles. The blank sample is analyzed for identifying the presence of any Aniline and phenol using RP-HPLC with photo Diode Array detector (PDA). The water sample was spiked with Aniline and phenol to get the concentration of each compound as 100 mg/L. The prepared sample was kept for overnight. On next day sample is sonicated and shake well before use, taken 10 ml of this sample and allowed to pass through the conditioned cartridge and allow to adsorb the added impurities on the surface of MWCNTs. Later the impurities were desorbed using Methanol (0.1 % Formic acid) The eluent was collected and concentrated using rotary evaporator and injected 20ul volume to HPLC, identified against standard solution chromatograms.

RP-HPLC Methodologies for Peak Identification

Thermoscientific RP-HPLC model 'Ultimate 3000' was used for the identification of isolated impurities. HPLC equipped with Quaternary low pressure gradient pump, PDA detector, column oven and autosampler is used for this analysis with HPLC column (Inertsil ODS 3V, 250mmX4.6mm and 5.0um particle size). Gradient elution was performed with 0.01M sodium dihydrogen orthophosphate buffer in water as mobile phase 'A' and Methanol as an organic eluent and constant flow rate 1.0 ml/min.

The gradient programme is maintained throughout the run as mentioned in below table1.

Table-1: HPLC Gradient Programme

Time (min)	Flow Rate (ml)	% Mobile Phase A (Buffer)	% Mobile Phase B (MeOH)
0	1.0	70	30
15	1.0	30	70
20	1.0	70	30
25	1.0	70	30

Aniline and phenol individual standard solutions are prepared in methanol (200 ppm each) and injected 20ul volume of each compound along with neat Blank and spiked samples and monitored using PDA detector at 230 nm wavelength.

RESULTS AND DISCUSSIONS

Multiwalled Carbon Nanotubes

Figure 3(a) shows FTIR spectrum of as obtained MWCNTs. Spectra which shows significant band at 2870cm^{-1},2881cm^{-1}, 2924cm^{-1}and moisture related bands 3436 cm^{-1}.

Figure 3 (b) represents FTIR spectra after treatment with acid mixture i.e. after purification, significant increase in peak at 2924 cm-1 and peak related to –OH group at 3436 cm-1 is observed.

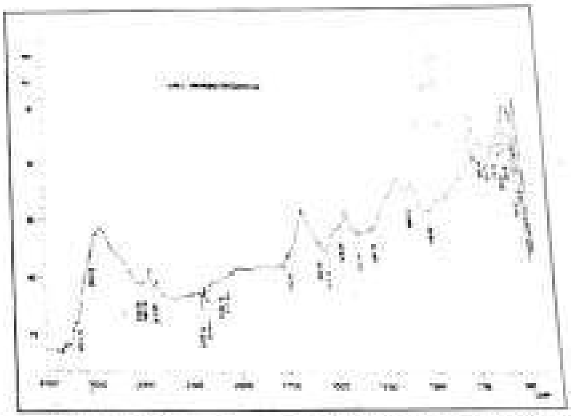

Figure 3(a): FTIR Spectrum of MWCNTs before Purification

Figure 3(b): FTIR Spectrum of MWCNTs after purification

Characterization by Powder XRD Technique: Figure 4 X-Ray Diffractogram of purified MWCNTs shows crystalline pattern which itself indicates the characteristic peaks one at about 2θ value 26° is a characteristic peak of MWCNTs and other represents the presence of trace level metallic impurities present in it.

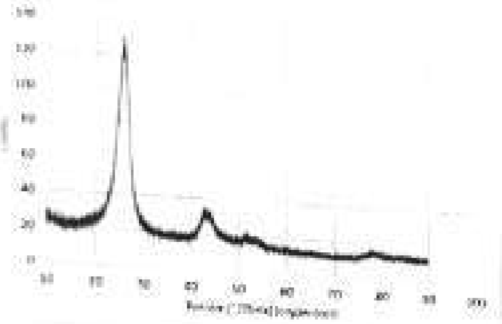

Figure 4: X-Ray Diffractogram of MWCNTs

Surface Area Measurement by BET Technique: Figure 5 indicates the surface area of purified MWCNTs. The higher surface area value was 102.42m²/g which also proves the formation of nanosize.

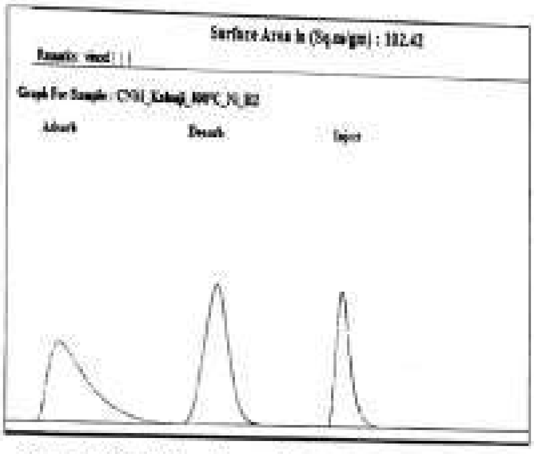

Figure 5: BET Surface Area of MWCNTs obtained from Kalonji oil

Morphology by Scanning Electron Microscopy : Figure 6 shows SEM image of purified MWCNTs obtained from Kalonji oil by COVD method. The SEM image shows the formation of MWCNTs with diameter in the range of 28-82nm.

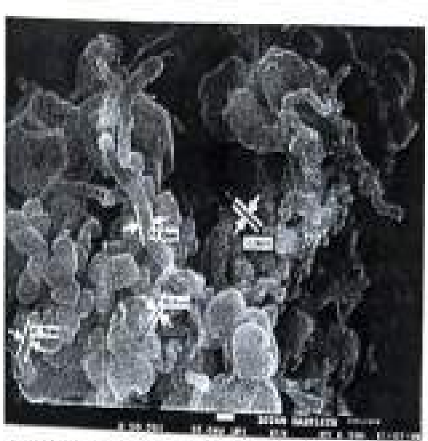

Figure 6: Scanning Electron Microscope Image of MWCNTs

Identification by using RP-HPLC: The obtained chromatograms of HPLC shows the presence of Aniline and phenol peaks collected post MWCNTs based SPE cartridge and confirms the proper isolation capacity of respective analyte as shown in figure 7.

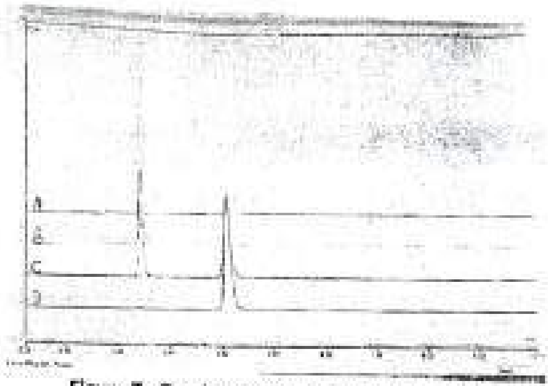

Figure 7: Overlay chromatograms by RP-HPLC

Where A: HPLC chromatogram of Blank (Neat water),
B: HPLC Chromatogram of Aniline
C: HPLC chromatogram of mixture of aniline and Phenol isolated from SPE Cartridges.
D: HPLC chromatogram of Phenol

Values on X axis of chromatogram represents Retention time of respective analyte in minutes while Y axis values represents absorbance in mAU.

CONCLUSION

MWCNTs based SPE cartridges prepared at lab scale are simple, reusable and cost effective as it is synthesized from natural precursor which is cheapest and easily available source. These MWCNTs based

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SPE cartridges can be modified to industrial scale which will be a best alternative material for chemical, dye making and pharmaceutical industries to separate different aromatic compounds like aniline and Phenol from industrial effluent before pouring it to natural resources.

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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, ^{1}H-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, Dehydroacticacid, Powder X-raydiffraction, 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.

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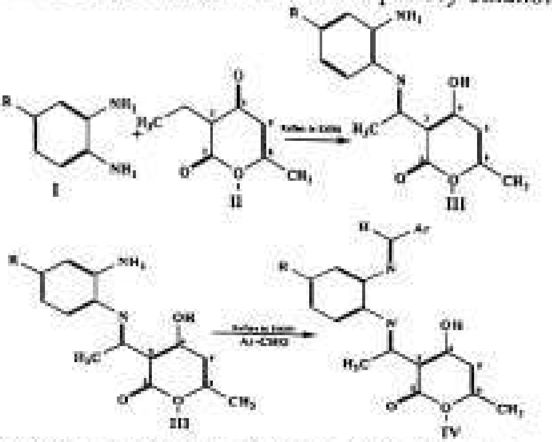
Instrumentation

The CHN analysis was carried out on Thermo Scientific(FLASH 2000) CHN elemental analyzer. ^{1}H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Bruuker) 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%).



Where R=H and Ar= 5-bromo Salicylaldehyde

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-1Indicate 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 [ML(H2O)2] (where M =, La (III), Ce(III) Nd(III)). The study of magnetic properties revels 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}H-NMR spectra of ligand

The ^{1}H NMR spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. 2.07 δ (s, 3H, C_6-CH_3), 2.13 δ (s, 3H, N=C-CH_3), 5.83 δ (s, 1H, C_5-H), 6.73-7.04 δ (m, aromatic protons), 8.96 δ (s, 1H, N=C-H),9.98δ(phenolic (-OH) hydrogen of phenyl ring) and 15.89 δ (s, 1H, enolic OH of DHA moiety) [I,II,III].

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IR spectra

The IR data of ligand (H_2L) and its meta lcomplexes are listed in Table 2. It depict prominent bands at 3296, 1689, 1656, 1360 and 1212 cm^{-1} assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), υ C-N (aryl azomethine) and υ 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 υ 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 find 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$^4I_{9/2}\rightarrow {}^2G_{9/2},\rightarrow {}^4G_{5/2},{}^2G_{7/2},\rightarrow {}^2S_{3/2},{}^4F_{7/2}$ 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. ^0C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated)			
					C	H	N	M
(H_2L) $C_{25}H_{17}N_2O_4Br$	442.10	189	Dark Yellow	----	56.71 (56.65)	3.694 (3.65)	6.87 (6.86)	-----
[$LLa(H_2O)_2$]	614.19	>300	Yellow	32.00	41.07 (41.03)	3.12 (3.10)	4.56 (4.53)	22.62 (22.60)
[L $Ce(H_2O)_2$]	615.41	>300	Brown	29.50	40.99 (40.96)	3.11 (3.10)	4.55 (4.51)	22.77 (22.73)
[L $Nd(H_2O)_2$]	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-Al_2O_3 as reference.

In the TG curve of La (III) complex the first weight loss 8.009 % occurred at temperature 190^{0}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 ΔTmax. = 271°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 ΔTmin. = 217.27°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 ΔTmin. = 236.55°C indicates removal of non-coordinated part. In third step from 400-900 °C slow weight loss 19.38 %, confirmed by broad exotherm ΔTmax = 418.28°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 ΔTmin = 240°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

Ea in kJ mol^{-1}, Z in S^{-1}, ΔS in JK^{-1}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 Åin 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 $2\theta = 23.18°$ corresponding to d value 3.86254 Å.The unit cell of La(III) complex of L yielded values of lattice constants, a=10.3214 Å, b=9.38521 Å, c = 4.06521 Å and unit cell volume V=345.902 Å^3.[XVII]The diffractogram of Ce(III) complex of L shows eleven reflections with maxima at $2\theta = 13.654°$ corresponding to d value 7.45625 Å. The unit cell of Ce(III) complex of L yielded values of lattice constants, a=19.248912 Å, b=8.97364Å, c = 4.068363Å and unit cell volume V=439.7661 Å^3.The diffractogram of Nd(III) complex of L had ten reflections with maxima at $2\theta = 80.659°$ corresponding to d value 1.52456 Å. The unit cell parameters of Nd (III) complex of L yielded values of lattice constants, a=11.44839Å, b=8.387201 Å, c = 6.482108 Å and unit cell volume V=320.24919 Å^3.In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory in La(III) complex.While $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ 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}forLa (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'snumber and volume of the unit cell were computed [XVIII].

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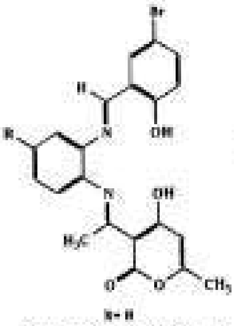
Ligand and metal complexes are subjected for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus, Pseudomonas Aeruginosa* by Agar Cup Method [XIX,XX]. The compounds were tested at the concentration of 1 % in DMSO, considering Ciproflaxin as standard (Table-4). 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)**		
	E.Coli	***S. aureus***	***Ps. Aeruginosa***
Ciprofloxacin	25	50	25
L_1	12	15	12
L_1-La	18	16	15
L_1-Ce	19	18	14
L_1-Nd	20	22	17

Table 5 Antifungal Screening of ligand and their metal complexes

Test Compound	Microorganisms		
	Asp. Niger	*Asp. flavus*	*Pen. chrysogenum*
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			



R= H

Figure 1. Structure of ligand

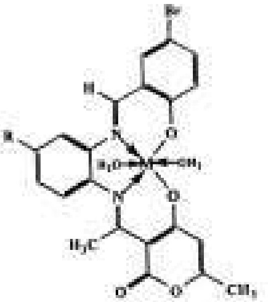


Figure 2(b)

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

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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, ^{1}H-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, Dehydroacticacid, Powder X-raydiffraction, 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.

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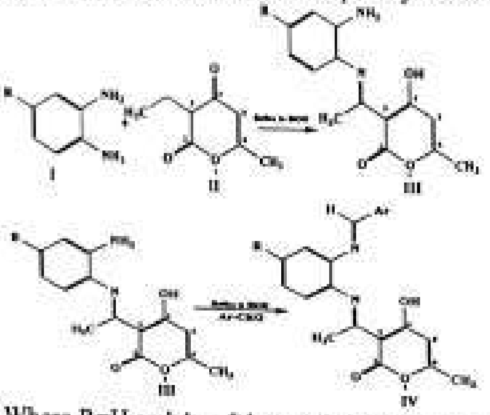
Instrumentation

The CHN analysis was carried out on Thermo Scientific(FLASH 2000) CHN elemental analyzer. ^{1}H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Bruuker) 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%).



Where R=H and Ar= 5-bromo Salicylaldehyde

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-I 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 [ML(H2O)2] (where M =, La (III), Ce(III) Nd(III)). The study of magnetic properties revels 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}H-NMR spectra of ligand

The ^{1}H NMR spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. 2.07 δ (s, 3H, C_6-CH_3), 2.13 δ (s, 3H, N=C-CH_3), 5.83 δ (s, 1H, C_5-H), 6.73-7.04 δ (m, aromatic protons), 8.96 δ (s, 1H, N=C-H),9.98δ(phenolic (-OH) hydrogen of phenyl ring) and 15.89 δ (s, 1H, enolic OH of DHA moiety) [I,II,III].

IR spectra

The IR data of ligand (H_2L) and its meta lcomplexes are listed in Table 2. It depict prominent bands at 3296, 1689, 1656, 1360 and 1212 cm^{-1} assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), υ C-N (aryl azomethine) and υ 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 υ 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 find 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$^4I_{9/2} \rightarrow {}^2G_{9/2}, \rightarrow {}^4G_{5/2}, {}^2G_{7/2}, \rightarrow {}^2S_{3/2}, {}^4F_{7/2}$ 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. ^0C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated)			
					C	H	N	M
(H_2L) $C_{25}H_{17}N_2O_4Br$	442.10	189	Dark Yellow	----	56.71 (56.65)	3.694 (3.65)	6.87 (6.86)	-----
$[LLa(H_2O)_2]$	614.19	>300	Yellow	32.00	41.07 (41.03)	3.12 (3.10)	4.56 (4.53)	22.62 (22.60)
$[L Ce(H_2O)_2]$	615.41	>300	Brown	29.50	40.99 (40.96)	3.11 (3.10)	4.55 (4.51)	22.77 (22.73)
$[L Nd(H_2O)_2]$	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-Al_2O_3 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 ΔTmax. = 271°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 ΔTmin. = 217.27°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 ΔTmin. = 236.55°C indicates removal of non-coordinated part. In third step from 400-900 °C slow weight loss 19.38 %, confirmed by broad exotherm ΔTmax = 418.28°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 ΔTmin = 240°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

Ea in kJ mol^{-1}, Z in S^{-1}, ΔS in JK^{-1}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 Åin 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 2θ = 23.18° corresponding to d value 3.86254 Å.The unit cell of La(III) complex of L yielded values of lattice constants, a=10.3214 Å, b=9.38521 Å, c = 4.06521 Å and unit cell volume V=345.902 $Å^3$.[XVII]The diffractogram of Ce(III) complex of L shows eleven reflections with maxima at 2θ = 13.654° corresponding to d value 7.45625 Å. The unit cell of Ce(III) complex of L yielded values of lattice constants, a=19.248912 Å, b=8.97364Å, c = 4.068363Å and unit cell volume V=439.7661 $Å^3$.The diffractogram of Nd(III) complex of L had ten reflections with maxima at 2θ = 80.659° corresponding to d value 1.52456 Å. The unit cell parameters of Nd (III) complex of L yielded values of lattice constants, a=11.44839Å, b=8.387201 Å, c = 6.482108 Å and unit cell volume V=320.24919 $Å^3$.In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory in La(III) complex.While $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ for sample to be orthorhombic were tested and found to be satisfactory for Ce (III) and Nd (III).

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Table 5 Antifungal Screening of ligand and their metal complexes

Test Compound	Microorganisms		
	Asp. Niger	*Asp. flavus*	*Pen. chrysogenum*
L₁	-ve	-ve	-ve
L₁-La	-ve	-ve	-ve
L₁-Ce	-ve	+ve	-ve
L₁-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

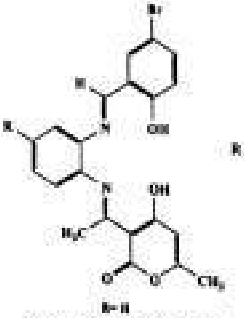
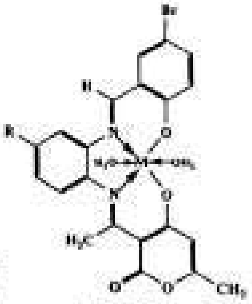


Figure 1. Structure of ligand



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Liquid-Liquid Extraction and Separation of Osmium(VIII) with 4-(4-Methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol in Organic Acid Medium

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ABSTRACT

A novel method is proposed for the extraction of microgram level concentration of osmium (VIII) from malonate medium with 4-(4-Methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant. The osmium (VIII) from the organic phase is stripped with mixture of thiourea and 2M hydrochloric acid and determined by spectrophotometric method. The method affords the binary separation and determination of osmium (VIII) from synthetic mixture. The method is successfully applied for the separation and determination of osmium from the alloys. The method is highly selective, simple and reproducible. The corrosive acids are not used in extraction of Os(VIII) in this method due to this it has green approach.

Keywords: Osmium (VIII), Solvent extraction, Alloys.

INTRODUCTION

0.001mg L^{-1} is the abundance of osmium in the earth crust. Osmium has wide range of applications as catalyst, hardening agent in alloys, polymer staining, buckminster fullerene adducts. Osmium has electronic, industrial and environmental importance. Hence it has paramount importance in the development of separation method to recover osmium to meet the future demands. Solvent extraction has become an effective technique in the recovery and separation of osmium **[1-4]**. The important tendency of osmium is to form chloro complex in chloride medium. Liquid- liquid extraction technique of separation uses the difference in kinetic behavior for the formation of extractable species as well as the strength of electrostatic interactions of their chlorocomplexes with liquid anion exchanger. The inertness of the chlorocomplex of osmium in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported for osmium (VIII) are trioctyl phosphine oxide **[5]**, trioctylamine **[6]**, bis- 2-ethylhexyl phosphoric acid **[7]**, cynex 925 **[8]**, n-octylaniline **[9-10]**. The methods reported are not so reliable for routine application because these methods suffer from the drawbacks such as operating condition (emulsion formation leading to problem for the separation, slow equilibrium) and ionic exchanger, nature of diluents, critical pH range etc.

In present investigation, extraction behavior of osmium (VIII) using 4-(4-methoxybenzylidene imino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant presence of malonate medium. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru(III) and Au(III), Pd(II) and Pt(IV), Ir(III) and Os(VIII) [**11-19**].

MATERIALS AND METHODS

A Shimadzu UV-Visible spectrophotometer (UV-1701) with 1cm quartz cells was used for measurement. pH measurements were carried out with an Elico digital pH meter model LI-120(±0.01) A stock solution of osmium (VIII) was prepared by dissolving 1g of osmium tetraoxide (S. D. Fine, India) in dilute Analytical grade hydrochloric acid (1 mol dm^{-3}) and diluting to 100 mL with distilled water and further standardizing it [**19**]. A working solution 100 μg mL^{-1} was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT is synthesized by known literature method [**11**]. MBIMTT (0.1 mol dm^{-3}) solution was prepared in chloroform.

Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in distilled water. All the chemicals used were of AR grade. Double distilled de-ionized water was invariably used throughout the measurements.

Recommended Method: An aqueous solution containing 100 μg of osmium(VIII) and sufficient quantity of sodium malonate to make its concentration 1 M in total volume of 25 mL, then the pH of solution adjusted to 1.0 using hydrochloric acid and sodium hydroxide. The resulting solution was transferred to 125 mL separating funnel. The aqueous phase was equilibrated once with 10 mL of 0.1 mol/dm^3 MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was back-stripped with mixture of 1ml 10% thiourea and 9 mL 2M hydrochloric acid solution. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Osmium(VIII) was estimated by spectrophotometric method [**20**].

RESULTS AND DISCUSSION

The concentration of MBIMTT in chloroform was varied from the $1 \times 10^{-5} - 2$ M under optimum condition. It was found that 0.1 M reagent in chloroform was needed for quantitative extraction of Os(VIII) from malonate medium.

Effect of equilibration time: Variation of the shaking period from 5 seconds to 5 min showed that a minimum 10 second equilibration time is adequate for quantitative extraction of osmium(VIII) from malonate media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of Os(VIII) malonate medium. Prolonged shaking up to 5 min has no adverse effect on the efficiency of extraction.

Effect of diluents: Keeping all other variable constant, the Os(VIII) was extracted with MBIMTT with various diluents. MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of Os(VIII). The extraction of Os(VIII) was found to be incomplete in isobutyl methyl ketone, isoamylalcohol, while no extraction in n-butanol and 4-methyl-2-pentanol. Chloroform is recommended for further extraction procedure because it offers better phase separation.

Nature of extracted species: The composition of complex was confirmed by using log D- log C plot. The graph log $D_{[Os(VIII)]}$ versus log $C_{[MBIMTT]}$ at sodium malonate concentration was to be found linear and having slope of 1.25. Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Os(VIII): MBIMTT].

Loading capacity of MBIMTT: The concentration of Os(VIII) was varied to determining the loading capacity of MBIMTT. The loading capacity of 10 mL of 0.1 M MBIMTT was found to be 7 mg of Os(VIII).

Effect of diverse ions: Various ions were used in order to assess the tolerance of these ions on the extraction of osmium (VIII). Osmium(VIII) was extracted in the presence of different diverse ions (Table 1). The tolerance limit was set as the amount of foreign ions cause ±2 % errors in recovery of osmium. The results showed that in the extraction and determination 100 µg of the osmium, these ions did not interfere at the level tested. The reproducibility of osmium extraction investigated from six replicate measurement was found to be 99.00± 0.95%.

Table 1. Effect of diverse ions on the extractive determination of Os(VIII)

Tolerance limit (mg)	Foreign ion added
100	Fluoride, Citrate, Oxalate, Acetate, EDTA, Malonate, Bromide, Iodide
20	Ca(II), Ba(II), Be(II), Mg(II), Fe(III)
15	Mn(II), Fe(II), Cr(III), Co(II)
10	Mo(VI), Sr(II), Ti(IV), Ce(IV)
5	U(VI), Mn(VII), Sb(III), Zn(II), Pb(II), Hg(II), Ni(II), Sn(II), Cu(II)

Binary separation of osmium(VIII) from base metals: The method allowed separation and determination of osmium(VIII) from a binary mixture containing either iron(III), cobalt(II), nickel(II), and copper(II).

The separation of osmium(VIII) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1 mol dm$^{3-1}$ MBIMTT in chloroform. Under these conditions all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate, 1-nitroso-2 naphthol, DMG [**21**], and pyrimidine-2-thiol [**22**] respectively. Osmium is stripped from the organic phase with mixtures of 1 mL 10% thiourea and 9 mL of 2 M HCl. The extract was evaporated to moist dryness and leached with 1 mol dm$^{3-1}$ hydrochloric acid to form the solution. Osmium(VIII) was estimated by spectrophotometric method [**20**]. The recovery of osmium(VIII) and that added ions was 99.5% and results are reported in table 2.

Table 2. Binary separation of Os(VIII) from Fe(III), Co(II), Ni(II) and Cu(II)

Composition of Metal ions µg^{-1}	Recovery* Os(VIII) %	Relative Standard Deviation %
Os(VIII), 100; Fe(III); 15000	99.5	0.12
Os(VIII), 100; Co(II) 10000	99.5	0.08
Os(VIII), 100; Ni(II) 5000	99.7	0.13
Os(VIII), 100; Cu(II) 5000	99.7	0.14

*-average six determinations

Separation of Osmium(VIII) from multi component synthetic mixture: In its natural occurrence osmium is always associated with the noble and base metals; hence its separation from these metals is of great importance. Under the optimum condition for extraction of osmium(VIII), there is quantitative extraction of Pd(II), Pt(IV) and Rh(III). But the coextracted metal ions cannot be back stripped by mixture of thiourea and 2M hydrochloric acid solution. Thus the MBIMTT reagent is made selective towards osmium(VIII) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of osmium from many metal ions (Table 3).

Analysis of alloys: To ascertain the selectivity of the reagent the proposed method was successfully used in the determination of osmium(VIII) in alloys. The real samples were not available; hence the synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in table 4. The average recovery of osmium(VIII) has been found to be 99.4%.

Table 3. Analysis of Synthetic Mixtures

Composition(μg)	Iridium found(μg)	Recovery (%)*	R.S.D.(%)
Os, 100; Pt,500	99.5	99.7	0.06
Os, 100; Pd,500	99.5	99.7	0.07
Os, 100; Ru,500	99.6	99.8	0.07
Os, 100; Rh,500	99.4	99.6	0.07
Os, 100; Pt,500; Ru,500	99.7	99.8	0.06
Os, 100; Pt,500; Pd,500	99.7	99.6	0.07
Os, 100; Pt,500; Rh,500	99.6	99.4	0.05
Os, 100; Pt,500; Ru,500; Pd, 500	99.5	99.7	0.05
Os, 100; Pt,500; Rh,500; Pd, 500	99.7	99.6	0.06
Os, 100; Pt,200; Ru,200; Pd, 200; Fe,2000; Co,2000; Ni, 2000; Cu, 2000	99.3	99.3	0.06

*- average six determination

Table 4. Analysis of Alloys

Alloys	Composition of Alloys%	Osmium(VIII) taken (μg)	Osmium(VIII) found by proposed method* (μg)	Recovery (%)*	R.S.D.
Siserkite	Os, 80; Ir, 20	100	99.6	99.7	0.06
Irodosmine	Os, 25; Ir, 75	100	99.6	99.5	0.06
Aurosmiridium	Os, 25; Au, 25; Ir, 50	100	99.5	99.7	0.05

* average six determination

APPLICATION

It is used for binary separation of osmium(VIII) from base metals, Separation of Osmium(VIII) from synthetic mixtures and analysis of Alloys.

CONCLUSION

These results underline the potential of the proposed method for the quantitative, selective extraction of osmium(VIII) with MBIMTT containing low concentration of iridium. It is free from interference from the large number of diverse ions which are associated with osmium(VIII) in its natural occurrence. The important features of this method are low reagent concentration is required, and the time required for the equilibrium is very short (30 seconds).The method is effective to determine and separate the osmium content from the alloys. The method is applicable to the analysis of osmium (VIII) in synthetic mixtures. The method is very simple, selective and reproducible.

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