

An experimental study of Selective Lanthanide complexes and their applications

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Abstract The design and development of lanthanide complexes namely with ligands like ter-pyridine-N-oxide, Schiff base and 2,3-dihydroxy-1,4-naphthoquinone which give thermodynamically stable complexes find use as fluorophors, photodiodes and sensors etc. Gd(III), and Sm(III) complexes of the identified ligands have been synthesized and characterized for their physico-chemical, antimicrobial and luminescence properties. The solid samples on investigation show some interesting topologies of the ligands. Luminescence studies of the N-oxide complexes in acetonitrile show typical emission spectra. Lanthanides bind strongly with the external pyridine rings of the ter-pyridine ligands to improve complex stability. The complexes of Schiff base as a ligand have been developed with acetoacetanilide and 1,3-diaminopropane, $[MX_3(LH_2)]$, where X= Cl, NO_3^- , NCS, have been synthesized in ethyl alcohol and characterized using tools like electrical conductance, spectral and magnetic susceptibility measurements. In these complexes, ligand LH_2 acts as a tetradentate ligand bonded through two azomethine nitrogen atoms and the two enolizable carbonyl group of acetoacetanilide organic moiety. The molar conductance of the complexes in DMF and DMSO is in close agreement with that of non-electrolytes. The IR spectral study, TG & DTA confirms the formation of complex and the thermal behavior as expected. The antimicrobial activity of the ligand and synthesized metal complexes was investigated by agar based disc diffusion method and found that the synthesized metal complexes possess reasonably higher antimicrobial activity than the free ligand. Synthesis of Binuclear octa coordinated lanthanide(III) complexes of 2,3-dihydroxy-1,4-naphthoquinone derivative by conventional and ultrasound assisted methods has been reported. The ultrasound assisted synthesis give the highest yield as against the conventional heating method. The resultant complex was characterized by UV-Vis, FT-IR, 1H NMR spectroscopy which too give the results in harmony with that reported in the literature.

Keywords: Analytical tools, , Decomplexation, labeling, Ligands, , Schiff base, Luminescent, ter-pyridine, TG, DTA

I. INTRODUCTION

Derivatives from 2,2':6',2''-terpyridine (TPy) have dragged much wider attention as they can work as functional templates or basic building blocks in the area like supramolecular and coordination chemistry as well as material science^{1,2}. They find applications in light-harvesting devices, moreover due to their strong complexation tendency with many transition metal ions they form diverse metal complexes and metallo-supramolecular architectures. The so synthesized organometallic complexes have amazing redox, photophysical and catalytic properties exhibited during many organic reactions. These properties have resulted into potential applications in the fields like light-to-electricity conversion, organic light-emitting diodes, sensors and non-linear optical devices^{3,4}. They can also be very well used as building blocks in the development of well-defined two- or three-dimensional multilayers on the solid substrates of

nanoscale materials and devices⁵. A silylated TPy derivative (SiTPy) based on an addition reaction of 4-(chloromethyl) phenyltrimethoxysilane with a polydentate ligand of 4'-(4-pyridyl)-2,2':6',2''-terpyridine (Pyterpy) that contains another pyridyl coordination site at the 4'-position of TPy was newly synthesized⁶. Further, after the addition reaction, the SiTPy was found to contain a substituent trimethoxysilane at the 4'-position of TPy, holding a potential to form organic-inorganic hybrid nanomaterials or composites⁷, as well as holding a promise as a potential candidate to fabricate self-assembled monolayers (SAMs) on the hydrophilic solid supports⁸. In the present work, the luminescent properties of Lanthanide ions with 2,2':6',2''-terpyridine Ligands were investigated in the solutions⁹. Our results revealed that the resulting complexes of Eu^{+3} and Tb^{+3} lanthanide ions with 2,2':6',2''-terpyridine exhibit excellent luminescent emission. The Eu^{3+} chelates coupled to proteins gave luminescence intensities almost identical to the parent complexes,

whereas Tb^{+3} chelates coupled to proteins behaved unpredictably with regard to decay times and luminescence intensities^{10,11}.

A Schiff base ligand is one of the most widely used classes of polydentate ligands in coordination chemistry. Synthesis of tetradentate Schiff base ligands from diamines and corresponding salicylaldehyde derivative is a reaction of importance in organic chemistry, due to the thermodynamic stability of these polydentate ligands with various lanthanide cations. The earlier literature reveals that Schiff base ligands are excellent coordinating ligands due to the high thermodynamic stability of the coordination compounds they form, excellent solubility in common conventional solvents and provides flexibility in the chemical environment about the C=N group. The extended conjugation in a Schiff base often imposes a geometrical constraint and affects the electronic structure as well^{11,35,36}.

Microwaves assisted synthesis has become a prominent and well established technique in chemistry that has found widespread applications in the laboratory as well as in industries. These days number of complexation reactions have been brought about in the field of microwave Chemistry¹². It is extensively employed for the synthesis of new drug moieties and other pharmaceutical intermediates¹³. It has the comparative advantage of enhanced yield of product and rapid reaction rates over conventional techniques¹⁴, because of the shorter time span required for chemical transformations[14]. Quinone and its derivatives are known function as photo and electro chemically active molecules. They find extensive applications in the areas of fabrication of chemical transducers, molecular switch systems¹⁵. Fluorescent heterocyclic compounds are widely used in the making of emitters in electroluminescence devices, probes in biochemical research, photo-conductive materials^{16,17,18}. In this communication, we report the green synthesis of 1,4-quinone derivatives by conventional heating methods using water and ethanol as solvents. The same compounds were also synthesized with the help of ultrasound. All the compounds were characterized by UV-Vis, FT-IR, NMR spectroscopy. The structure of 2,3-dihydroxy-1,4-naphthoquinone as ligand is as shown in fig.1.

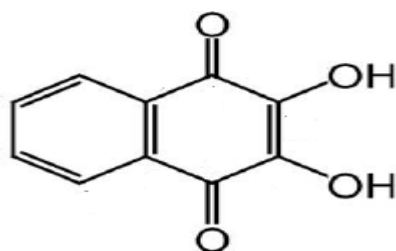
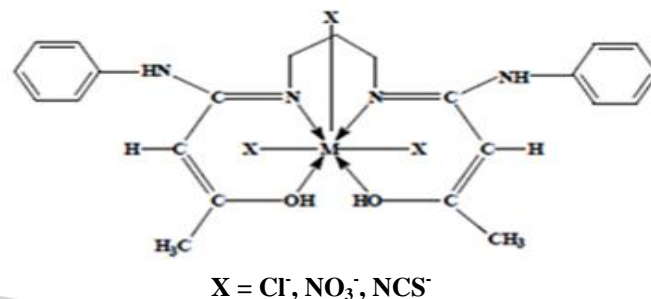


Fig.1. Structure of 2,3-dihydroxy-1,4-naphthoquinone

The work presented here is the synthesis followed by the study of physico-chemical and antimicrobial and luminescence activity of selected lanthanide ions like Gd(III), Dy(III) and Sm(III) with the Schiff base and ter-pyridine-N-oxide ligand with the proposed structure as shown in fig.2.^{19,20,21}



M = Sm(III), Gd(III), Dy(III)

Fig.2. Structure for the lanthanide complexes with and ter-pyridine-N-oxide ligand

II. MATERIALS & METHODS

Lanthanide complexes with 2,2':6',2''-terpyridine Ligand

Synthesis of 2,2':6',2''-terpyridine Ligands : The step wise procedure followed for the synthesis of ligands is as follows : A flame dried 1L 2-neck flask was purged with Nitrogen to create inert environment in the reactor. Anhydrous Tetrahydrofuran, THF (400 ml) and potassium t-butoxide (20g, 0.179 mol) was added followed by 2-acetylpyridine (10.34 g, 85.4 mmol). The solution was subjected to stirring at room temperature for an hour followed by sonication for 15-20 minutes following which a white solid was found to be formed. The [3-(dimethyl-amino)vinyl 2-pyridyl ketone (15.03 g, 85.4 mmol) was added and the solution colour intensity slowly turned to a very deep red, was further subjected to continuous stirring at room temperature for 48 hours on a magnetic stirrer . The reaction mixture was then cooled in ice and ammonium acetate solution (64.g, 0.833 mol) in acetic acid (200 ml) was added with stirring underway. Methanol (40 ml) was added, the flask fitted with a distillation column, the mixture heated to reflux and the THF gradually removed by distillation over a three hour period. The distillation continued until the temperature attained 115°C. The mixture was poured into water (400 ml) and the excess acetic acid was neutralized with sodium carbonate (~300 g). Toluene (120 ml) and celite (20 g) was added and the mixture was stirred and heated at 80°C. The mixture was cooled to room temperature and filtered through whatmann filter paper no. 41. The solid was powdered and washed with toluene (3 x75 ml). The organic layer of the filtrate was separated and the aqueous layer extracted with (2 x 100 ml) of toluene. The organic layers was agitated with 25 g of alumina and then filtered. The powder was evaporated till we get a brown coloured oil

which was dissolved in 80 ml of chloroform and 40 g of alumina. The powder was then poured onto the top of alumina column and eluted with 20:1 cyclohexane/ethyl acetate as a eluent composition for separation of the product as a light yellow fraction which was further washed and dried to get the pure product. Yield: 63%.

The structure of unsubstituted terpyridine is as shown in

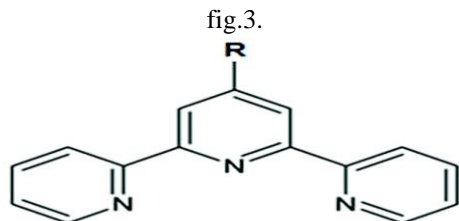


Fig.3. structure of unsubstituted terpyridine

In a similar fashion Mukkala and co-workers went on to report the synthesis of 20 different 2,2':6',2''-terpyridine derivatives with (methylenenitrilo)bis(acetic acid) groups as the stable complex forming moieties and applied them to protein labelling. The different ligands synthesised included the ligands A,B,C and D as shown in fig.4 which are meant for the structure of the substituted terpyridine^{22,23,24}.

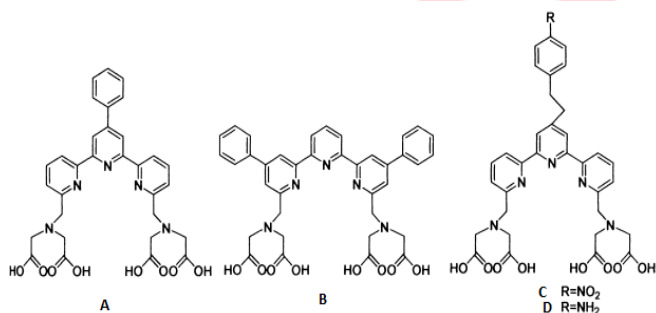


Fig. 4. Structure of the of substituted terpyridine

Lanthanide complexes with Schiff base

Metal salts, acetoacetanilide, 1,3-diaminopropane and other reagents were AR grade. Solvents such as ethanol, methanol and acetone were subjected to purification. C,H and N elemental contribution was estimated for the complexes synthesized,. The metal estimations were carried out by oxalate-oxide method. The IR spectra of the Schiff base and corresponding metal complexes were recorded using FTIR in the 4000-400 cm^{-1} region by preparing pellets of samples with KBr powder. The UV absorption spectrum of the synthesized complexes were recorded in HPLC grade solvents namely, DMF and DMSO in the spectral region of 800-200 nm. Further, molar conductivity measurements were recorded using a conductivity meter. Magnetic measurements of the complexes were done a susceptibility balance at ambient temperature. Thermal Gravimetric and Differential Thermal analysis too was also undertaken in a inert atmosphere with a heating rate of 1000 $^{\circ}\text{C}/\text{min}$.

Synthesis of the ligand

The Ligand(LH₂) was synthesized by making the condensation(LH₂) reaction to take place between acetoacetanilide and 1,3-diaminopropane in 2:1 molar ratio by refluxing in acetone as a solvent.

Synthesis of the lanthanide complexes with 2,3-dichloro-1,4-naphthaquinone

The lanthanide(III) complexes were synthesized using methanolic solution of the ligand LH₂ (0.001 mol), Ln(III) salt (0.001 mol) in a dropwise manner with constant stirring on a magnetic stirrer. The pH of the reaction mixture was maintained between 7- 8 by adding requisite amount of 10% liquor ammonia which is then followed by refluxing the reaction mixture for 10 hours. The resulting solution was pre-concentrated to one third of its original volume and kept on standing overnight. The precipitated metal complex was then filtered with Whatmann filter paper no. 41, washed with methanol (3X) and dried in a vacuum desiccators.

Experimental

All the chemicals used are AR grade including Lanthanide chlorides and solvents used are of high purity. The procedure followed in both conventional and microwave assisted synthesis is as follows :

Conventional heating method

A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was added to ethanol (100 mL) and the solution was refluxed for 5 h at 60 $^{\circ}\text{C}$. The resulting solution was cooled and the precipitate was filtered, dried at room temperature and purified.

Ultrasound assisted method

A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was ground together and irradiated in a domestic microwave oven for 10 s/cycle (1350 W). The duration of irradiation varied depending on the degree of completion of the reaction (40-110 s), as confirmed by thin layer chromatography. After the completion of the reaction, the product was set aside to cool and then ice cold water (100 mL) was added. The solid product was filtered, dried at room temperature and recrystallized from ethanol^{25,37,38}.

III. RESULTS & DISCUSSION

Lanthanide complexes with 2,2':6',2''-terpyridine Ligand

The luminescence property exhibited by Eu⁺³ and Tb⁺³ metal ions as core complexed with ligands A, B, C, D in terms of intensity is tabulated in table 1 below :

Table 1. Luminescence intensity for metal ions, Eu^{+3} and Tb^{+3} with substituted terpyridine ligands

Ligand	Luminescence intensity ($\epsilon\phi$)	
	Sm^{+3}	Gd^{+3}
A	1950	1800
B	3700	1450
C	570	30
D	210	54

The ligand A showed high luminescence intensities comparatively for both Sm^{3+} and Gd^{3+} while ligand B almost doubled the relative luminescence of the Sm^{3+} complex ($\epsilon\phi = 3700$). Conversely, it decreased the relative luminescence of the Gd^{3+} complex ($\epsilon\phi = 1450$). Ligands C and D gave very poor relative luminescence intensities for both which indicate that the substituents in the aromatic part caused lowering of the ligand triplet state causing an

Table 2 : Physico chemical data for the LH_2 ligands with selected Lanthanide cations

Complex	M.P. ($^\circ\text{C}$)	Color	% contribution					M_{eff} B.M.
			M	C	H	N	C/S	
$[\text{Sm}(\text{LH}_2)(\text{Cl})_3]$	285	Greenish white	24.06	40.45	4.42	8.37	15.30	1.50
$[\text{Sm}(\text{LH}_2)(\text{NCS})_3]$	279	Murky White	21.24	43.30	4.11	13.40	12.95	1.63
$[\text{Gd}(\text{LH}_2)(\text{Cl})_3]$	295	Reddish yellow	24.44	42.15	4.50	8.45	15.15	7.29
$[\text{Gd}(\text{LH}_2)(\text{NO}_3)_3]$	294	Reddish yellow	21.35	36.65	3.60	13.45	--	7.84

Electrical conductivity

The molar conductance values of 10^{-3}M solutions of the complexes of gadolinium, and samarium in two non aqueous solvents, DMF and DMSO were found to lie in the range of 12.5-15.4 and 7.3-9.6 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. These experimentally found values for the given complexes show their behavior like non-electrolytes^{17,26,34}.

Magnetic behaviour

The magnetic moment values of the complexes are tabulated in Table 2. All the lanthanide complexes synthesized were paramagnetic due to the presence of unpaired electrons in their electronic configuration and the experimental magnetic moment values of Gd(III) and Sm(III) complexes are in tune with the calculated ones which indicates that the 4f electrons are not much influenced by the strength of ligand field generated by the Schiff base. The little deviation of the magnetic moment values of Sm(III) complexes could be attributed to low J-J separation, which leads to the thermal excitation and thereby increase in population density of higher energy levels^{19,29,30}.

energy leakage back to the ligand triplet state. Further, the binding of these ligands to proteins gave variations in the results.

Lanthanide complexes with Schiff base

The complexes synthesized were thermodynamically stable at room temperature and non-hygroscopic which was verified using TG/DTA analysis. They are insoluble in common organic solvents like ether, acetone, benzene etc. but are soluble in DMF and DMSO. Lanthanide(III) complexes vary in colour ranging from greenish to reddish brown. The analytical data and empirical formula of the complexes is tabulated in Table 2. The data indicates 1:1 molar ratio of the metal and the ligand and the complexes can be represented as $[\text{Ln}(\text{LH}_2) \text{X}_3]$ where Ln means Lanthanides which refer to elements like Sm, Gd or Dy and $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{NCS}^-$ [32].

Infrared spectra

The characteristic IR frequencies of the ligand LH_2 and its complexes along with their assignments are listed in Table 3. Bands due to $-\text{OH}$ and $-\text{C}=\text{N}$ are distinguishable and provide evidence regarding the structure of the ligand and its bonding with metal. A band at 1591cm^{-1} in the ligand is attributed to $-\text{C}=\text{N}$ stretching vibration. On coordination, this band is shifted to lower frequency by 722cm^{-1} . The remarkable shift of this band is a clear indication of the participation of the azomethine nitrogen atoms in complex formation²⁶.

Table 3: Characteristic IR spectral vibrational frequencies of Ln(III) complexes

Compound	ν (C=N) cm^{-1}	ν (C-O) cm^{-1}	ν (M-O) cm^{-1}	ν (M-N) cm^{-1}
$[\text{Sm}(\text{LH}_2)(\text{Cl})_3]$	1574	1258	416	536
$[\text{Sm}(\text{LH}_2)(\text{NO}_3)_3]$	1576	1260	414	535
$[\text{Gd}(\text{LH}_2)\text{Cl}_3]$	1585	1260	424	511
$[\text{Gd}(\text{LH}_2)(\text{NO}_3)_3]$	1584	1257	420	511

The vibrational frequency absorption band between 510-536 cm^{-1} , 414-425 cm^{-1} , 3305 cm^{-1} are assigned to the stretching vibration of M-N, M-O bond and free -OH in ligand respectively. However, the complexes, show blue shift indicating a weakening of -OH bond due to coordination through enolic -OH which is further coordinated to the central metal ion without deprotonation. The stretching vibration of enolic C-O at 1251 cm^{-1} in the ligand shows a red shift by 8-13 cm^{-1} in complexes which confirms the bond formation between metal and ligand. The nitrate complexes of samarium(III), gadolinium(III) show characteristic & distinct vibrational frequencies which are assigned to the coordinated nitrate ions. The infrared spectra of nitrate complexes elicits two strong bands at 1430 cm^{-1} and 1310 cm^{-1} which were absent in the ligand spectrum. These could be attributed to ν_4 and ν_1 vibrations, respectively, of the coordinated nitrate ion. The magnitude of separation of these bands is around 110 cm^{-1} , which indicates that the nitrate ion is coordinated to the metal ion as a monodentate ligand. The combination frequency observed in the region 1700-1800 cm^{-1} of the infrared spectrum corresponds to $(\nu_1 + \nu_4)$ for a monodentate coordinated ligand and is in agreement with the reported value., The medium band around 1073 cm^{-1} due to the ν_2 vibrations of the nitrate is an additional evidence for the coordinated nitrate ion^{27,28}.

Electronic spectra

The f orbitals in Ln^{3+} ions are deep inside the metal; therefore, the crystal field splitting effects are too small in the lanthanide complexes as against the transition metals. The electronic spectra of the complexes in Dimethyl sulfoxide show the two pronounced bands in the spectral regions 250-257 nm and 352-359 nm, which are in agreement with those observed for the ligand. There is a hypsochromic shift (Blue shift) in the absorption spectrum of complex indicating the formation of complexes.

Differential thermal and thermogravimetric analysis

All complexes were examined by thermogravimetric analysis from ambient temperature to 7000 $^{\circ}\text{C}$ in inert atmosphere. Thermograms for complexes show decomposition in a single stage and all of them start to loose mass only at around 240 $^{\circ}\text{C}$, thereby confirm the thermal stability of the complex. The thermodynamic stability of the complex is attributed to the strong bonding between tetradentate ligand and Ln(III) ions. Single stage decomposition is due to the loss of three coordinated ions and ligand molecule leading to the formation of metal oxide, Ln_2O_3 which is confirmed by way of TG analysis.

Antimicrobial assay

In vitro antibacterial activity against two Gram-negative (Escherichia coli and Salmonella typhimurium) and two Gram-positive (Bacillus subtilis and Staphylococcus

aureus) bacterial strains was tested using agar well diffusion method with Imipenem as reference. The data is tabulated in table 4. A comparative study of the ligand and their metal complexes indicates that most of the metal complexes exhibit higher antimicrobial activity than that of the free ligand and the salt of the lanthanides. Hence complexation results into enhancement in antimicrobial activity substantially. The increase in activity of the complexes can be explained based upon overtone effect and Tweedy's Chelation theory^{27,29,30}.

Table .4: Data for antimicrobial testing (Conc. 1mg/mL)

Compound	Gram- Negative		Gram-positive	
	E.coli	S.typhi	B.subtilis	S.aureus
[Gd(LH ₂)(NO ₃) ₃]	18	16	08	13
[Sm(LH ₂)(NO ₃) ₃]	20	19	18	20
[Gd(LH ₂)(NCS) ₃]	22	21	19	19
[Sm(LH ₂)(NCS) ₃]	25	24	21	22
Imipenem (Std.)	32	28	31	33

Lanthanide complexes with 2,3-dihydroxy-1,3-naphthoquinone

UV-Vis absorption overlay spectrum was recorded for the complex in acetone which shows absorption maximum at 466 nm as shown in Fig.5 which exhibited well defined band which may be attributed to the typical intramolecular charge transfer. There has been a rise in absorbance with concentration at 466 nm.

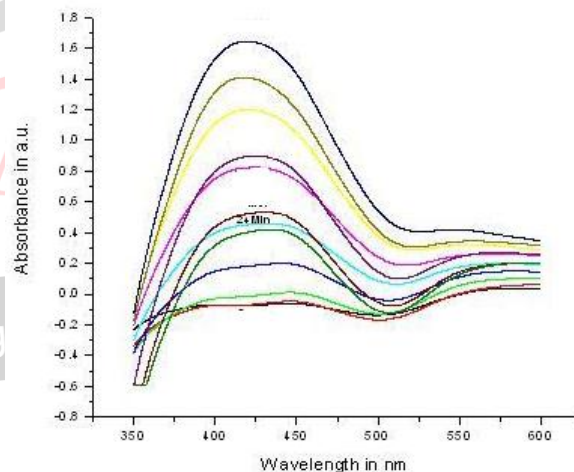


Fig.5. UV-Vis spectra of compounds 1-6 (5 · 10₋₅ M in acetone).

Fluorescence spectrum for the complex obtained on conventional heating is shown in Fig.6 while other one obtained by sonication is shown in fig.7. The compound also exhibited photoluminescence band (Fig. 3). Hence, these quinone

derivatives can be used as effective fluorophores for sensor applications.

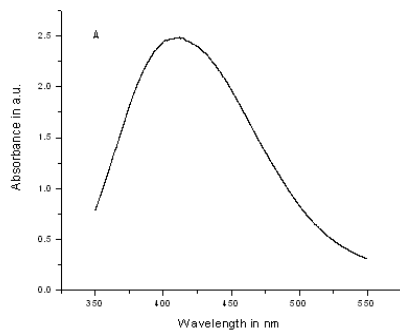


Fig.6. The fluorescence emission spectrum of compound (Conventional heating)

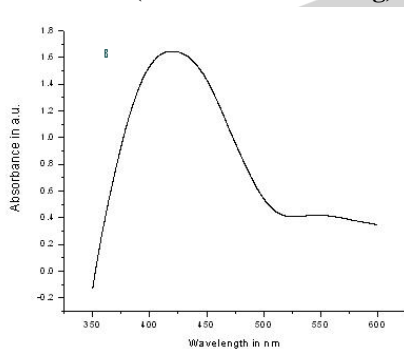


Fig.7. The fluorescence emission spectrum of compound (Ultrasound assisted)

FTIR shows characteristic vibrational frequencies (Cm^{-1}) corresponding to 3240 (NH), 3363 (NH_2 aromatic), 1558, 1643 (C=O), 1141, 1296 (S=O), 833 (C-Cl), 1103, 1141 (C-N) as shown in fig. 8^{26,28}.

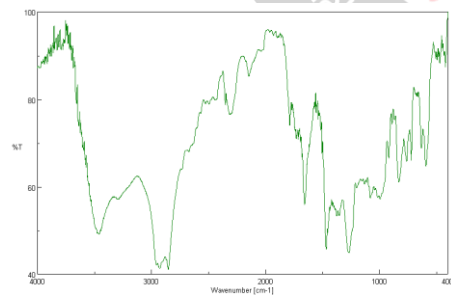


Fig.8. FTIR spectrum of Quinone derivative

The synthesis of the complex was done by a green facile method using water as solvent. The reaction between the 2,3-dichloro-1,4-naphthaquinone and dapsone (4-amino phenyl sulfone) in the presence of ethanol gave 54% yield of the product. However, with water as the solvent, the yield increases substantially to 90%. The said complex was previously synthesized and reported[6]

wherein a equimolar mixture of 2,3-dichloro-1,4-naphthaquinone and dapsone in the presence of phenylene triethylamine as a catalyst with absolute ethanol as solvent was taken. The reaction mixture was subjected to refluxing for 18 h, which gave black precipitate dried subsequently at room temperature, followed by refinement of product.

In the present work the same product was synthesized by sonication i.e. a green facile method which gave better yield of 87%. which was far better than conventional process. Since quinones are known to exhibit photochemical properties, the photochemical properties of the synthesized compounds were studied using UV-Vis and photoluminescence spectroscopy.

IV. CONCLUSION

The thermodynamically stable complexes of the lanthanide ions like Sm, Gd have been synthesized and it is corroborated with the analytical data which show that all the complexes have the empirical formula base in its composition as $[\text{M}(\text{LH}_2)(\text{X})_3]$, where $\text{M} = \text{Sm}(\text{III}), \text{Gd}(\text{III})$ and $\text{X} = \text{Cl}, \text{NO}_3^-, \text{and NCS}$. The molar conductance values in DMF and DMSO and the infrared spectral values predict that all the resulting complexes are nonelectrolytes in nature. The lanthanide ions like Sm^{+3} and Gd^{+3} ions form strong and thermodynamically stable complexes^{11,12}. It was found that these ligands are potential candidates for luminescent devices. The careful consideration must be given to the ligand as slight change in it give quite unpredictable results^{18,19,20}. In the nitro and thiocyanato complexes the anion is coordinated through nitrogen atom. The thermogravimetric studies reveal the absence of coordinated water molecules. Infrared spectra of complexes reveal that LH_2 behaves as a neutral tetradentate ligand linked through two azomethine nitrogen and two enolic oxygen atoms^{21,22,23,24,25}. The infrared spectrum of the nitrate complexes further testifies the monodentate nature of the nitrate group. The magnetic moment values suggest the complexes are paramagnetic due to the presence of unpaired electrons. A coordination number of seven may be assigned to the metal ion in all the complexes in general^{26,27,28,29,30}.

The compound, 2,3-dihydroxy-1,4-naphthaquinone was synthesized by both ultrasound assisted and by conventional heating method and the former method was found to be superior, facile, greener, quicker yielding a higher quantity and purity of the product too. This method can further be employed for synthesizing other derivatives of quinone based complexes as well. Lanthanide complexes with Schiff base as ligands have been successfully synthesized and have been found to possess conductive, magnetic, electronic, antimicrobial etc. properties and

thereby hold lot much of promise in applications as photodiodes, sensors etc^{39,40,41}.

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