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Kavita L. Kendre
Department of Chemistry, Yeshwant College, Nanded, Maharashtra, India

Girish Pande
Department of Chemistry, N.S.B. College, Nanded, Maharashtra, India

Madar Jahagirdar
Department of Chemistry, S.K.M, Gunjoti, Maharashtra, India

D. R. Kulkarni
Department of Chemistry, S.K.M, Gunjoti, Maharashtra, India

Correspondence:
Kavita L. Kendre
Department of Chemistry, Yeshwant College, Nanded, Maharashtra, India

Synthesis and physicochemical studies of newly formed complexes of inner transition metals with2,2'- Dipyridyldisulfide

Kavita L. Kendre, Girish Pande, Madar Jahagirdar, D. R. Kulkarni

Abstract
The La(III) and Sm(III) complexes of 2,2'-dipyridyldisulphide have been synthesized in alcohol and refluxed in the reaction medium (1:2, M: L ratio).The yield percentage of formed complex is ranging from 80-90%. The complexes are colored solids. The complexes were synthesized and characterized by elemental analysis, IR, electronic spectra, molar conductance, TGA, and powder XRD. An IR spectrum indicates that the ligand behaves as bidentate ligand. Molar conductance studies indicates the electrolytic behaviour of these complexes. Thermal decomposition profiles are consistent with the proposed formulations. The powder XRD studies show that all the complexes are amorphous in nature. The antimicrobial activities of the ligand and their metal complexes were screened by agar diffusion method and found that the metal complexes have higher antimicrobial activity than the free ligand.

Keywords: 2,2'-dipyridyldisulphide, inner transition metals, antimicrobial activity.

1. Introduction
Metal ions affect the well-being of human in various ways. Several of these elements are indispensable for life and nature governs their uptake metabolism, and excretion consequently their concentrations in a human body are compartmentalized and well defined. The Inner transition metal ions are known to have the Small radii and variable coordination number ranging from 6 to 12, which make them excellent spacers in assembling fascinating metal organic frameworks. Inner transition metal complexes are of continuing interest mainly due to their structural and properties and their application in diagnostic pharmaceutical and laser technology [1-6]. The catalytic nature has been found to exhibit anticancer and fungicidal properties [7-8]. Synthesis, characterization and antimicrobial studies of inner transition metal complexes have been an active field of research [9-10]. Lanthanide complexes attract considerable interest in bioinorganic and coordination chemistry. [11] Some of the lanthanide complexes are used in biomedical analysis as MRI contrast agents [12]. Because of special, photophysical and biological properties, lanthanide complexes can be used as biological probes in the areas of clinical chemistry and molecular biology [13]. Due to their special electronic configuration, lanthanide complexes have inspired many efforts on the design and synthesis as potential anticancer and antibacterial agents. [14] In the present communication, we report the synthesis, spectroscopic and biocidal studies of La (III) complex and Sm(III) with DPDS ligand.

2. Materials and Methods
The electronic absorption spectra of the complexes in DMSO were recorded on a Shimadzu double beam UV-visible spectrophotometer model UV 150-02. The infrared spectra of the solid samples in the 500-4000 cm^{-1} were recorded on a Shimdzu FTIR spectrophotometer and Brueker FTIR spectrophotometer using KBr pellets. The thermal analyses (TGA) for the complexes were recorded on a perking Elmer STA 6000 under nitrogen atmosphere at room temp to 1000 ^{0}C 5mg of the samples with the heating rate of 10 ^{0}C per min and the platinum cups as sample holders.

3. Analytical Methods
All the chemicals used were of AR/GR grade. Pure sample of DPDS having molecular formula $C_{10}H_8N_2S_2$, molecular weight (222) was obtained from the Alfa Acer company. The rare earth metal chlorides were used as received from S.D. fine chemicals. The solvents were distilled

before use and distilled water was used for the preparation and analyses. The molar conductivity at room temperature was determined in conductivity water using a dip type cell with a smooth platinum electrode. The magnetic susceptibility measurements were made by gouys method at room temperature using powedered samples of complexes.

4. Synthesis of Lanthanum (III)-DPDS Complex

To a hot methanolic solution (20ml) of the DPDS ligand (0.02 mol), solution (10ml) of methanolic solution Lanthanum (III) chlorides hydrated[(LaCl3) 7H2O)] (0.01 mol) was added with constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding10% alcoholic ammonia solution and refluxed for about 4-5hr. The precipitated solid metal complex cooled at room temperature and was filtered off and washed with methanol, petroleum ether and dried over calcium chloride in vacuum desiccator. Creamish coloured fine crystals of complex was obtained. Checked the purity by TLC and melting point. (yield= 60 %).

5. Synthesis of Samarium (III)-DPDS Complex

To a hot methanolic solution (20 ml) of the to DPDS ligand (0.02 mol), solution (10ml) of methnolic solution Samarium (III) Chloride hydrated [(SmCl3) 6H2O)] (0.01 mol) was added with constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding10% alcoholic ammonia solution and refluxed for about 4-5h. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether and dried over calcium chloride in vacuum desiccator (yield=65%)

6. Result and Discussion

The colored products were isolated in excellent yields. The elemental analysis and some physical properties for the ligands an d their complexes listed in table no. 1 .Comprise that the found data are in a good agreement with those theoretical ones, and the obtained analytical data indicate the formation of 1 : 2 [M : L] complexes.

These complexes are colored, solid. The values of magnetic moment of complexes are indicating diamagnetic and paramagnetic nature. La(III) complex had not ligand filed stabilization effecting to complete f-sub shell, therefore La(III) complex should be diamagnetic spin free octahedral complex with d^{10} system. The structure of complex was confirmed by its analytical and spectral data. It has been found that the complexes are non-hygroscopic, stable at room temperature, insoluble in common organic solvents, dissolve freely in DMSO/DMF. Empirical formulae of the complexes were deduced on the basis of elemental analysis, metal ligand ratio and thermal analysis (table 1and2) DMSO/DMF. High melting points (above 270^0C) of complexes suggest that complexes are fairly stable at normal temperatures. Molar conductivity (Λ_m [101] to 112 $\Omega^{-1}cm^2$ mol^{-1}) reveals electrolytic nature of the complexes. (table3)

Table 1: The elemental analysis and some physical properties for the ligands an d their complexes

Compound	Empirical Formula	Formula Wt	Yield (%)	Color	M.P. ^{0}C	M : L ratio
DPDS	$C_{10}H_8N_2S_2$	220	75%	White	56-58	-
[La(DPDS)$_2$2H$_2$O]3Cl	$C_{20}H_{20}N_4S_4O_2Cl_3La$	721.92	85%	Cream	>300^{0}C	1 : 2
[Sm(DPDS)$_2$2Cl]H$_2$O.Cl	$C_{20}H_{20}N_4S_4OCl_3Sm$	715.36	75%	Pista	>300^{0}C	1 : 2

Table 2: Empirical formulae of the complexes were deduced on the basis of elemental analysis, metal ligand ratio and thermal analysis

Compound	M.F.	Elemental Analysis % found (calculated)						
		C	H	N	S	O	Cl	M
DPDS	$C_{16}H_{16}N_2O_2$	54.52	3.66	12.72	29.11	-	-	-
La-DPDS	$C_{20}H_{20}N_4S_4O_2Cl_3La$	33.27	2.79	7.76	17.77	4.43	14.73	19.24
Sm-DPDS	$C_{20}H_{20}N_4S_4OCl_3Sm$	33.58	2.54	7.83	17.93	2.51	14.87	21.02

7. Infrared Spectra

The IR spectrum of the ligand showed a sharp band near 1602 cm^{-1}, which may be due to azomethine linkage [15-17] which was shifted to 1633 cm-1 and 1620 cm-1, high frequencies in the metal complexes, indicating co-ordination of the metal ions through the azomethine linkage [18]. The absorption bands at 1082 cm-1shows presence of C-S group in ligand. But there is no change in band value so coordination through S atom is absent here. A similar pattern is observed in case of S-S. The absorption bands at 3186 and3169 cm^{-1}show the presence of coordinated water in the complexes [19].

The appearance of the M – N band at 464 cm^{-1} and the M–O– band at 542,563 in the complexe indicate that DPDS – metal ions coordinated through an O and a N atom [20-21]. The IR spectral data and their tentative assignments are given in Table 3.

Table 3: The IR spectral data and their tentative assignments

Compound	ν S-S	ν C = N	C-S	ν M – N	ν M – O	ν H$_2$O
Ligand	426	1602	1082	-	-	-
La-DPDS	424	1633	1082	464	542	3186
Sm-DPDS	426	1620	1082	464	563	3169

8. Electronic Spectra

The ultraviolet region band shift and intensity alternation [22-23]. of ligand indicates involvement of ligand in the chelation with metal ion. The ligand DPDS shows strong band at 281 nm. In case of La(III) -DPDS complex the strong band observed at 382 and 282 nm and in Sm(III) at 378 and 294 nm. This shifting in the values of band alternation indicates the involvement of ligand in chelate formation.

Table 4: Result

Complex	Absorbance	ν / cm^{-1}	Assignment	Molar Conductance	Magnetic Moment	Geometry
Ligand	281	35587	π - π*	–	–	–
La – DPDS	382,282	26178, 35460	CT	70	Diamagnetic (–)	Octahedral
Sm – DPDS	378,294	26455, 34013	CT	85	Paramagnetic ()	Octahedral

9. Antimicrobial Activity

Above synthesized complex and the ligand have been screened against bacteria *E. coli* and *Staphylococcus Aureus* and fungi *Aspergillus Niger* and *Alternaria*. Nutrient agar as medium used for bacteria and potato dextrose agar used for fungi. Incubation of plates with complex solution and ligand solution in well done for 48 hrs at 27 ^{0}C temperature.

The zone of inhibition based upon size around the well was measured. Inhibition zone percentage are recorded in Table 5. The percentage inhibition of growth by ligand is less than DPDS metal complex. Thus complex shows greater activity against micro-organisms as compared to ligand DDPDS. This prove that the chelation increases the antimicrobial activity. Results are presented in Table 5.

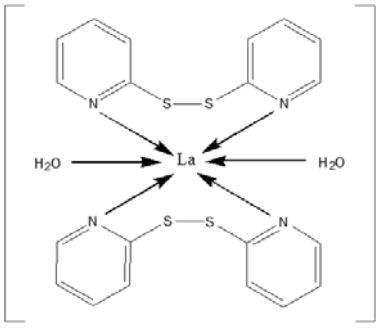
Table 5: Antimicrobial activity of ligand and La(III), Sm(III) complex.

Ligand / Complex	% of Inhibition Zone Inhibition			
	E. Coli	*S. Aureus*	*A. Niger*	*Alternaria*
DPDS	22	-	-	16
La(II)-DPDS	21	21	-	22
Sm(II)-DPDS	19	21	-	22

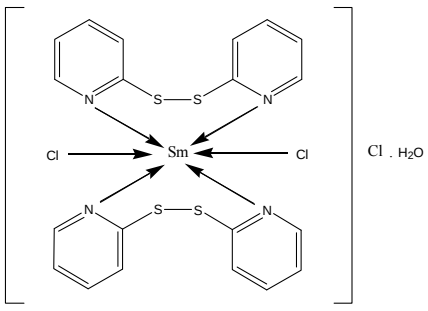
10. XRD

11. Conclusion

Hence on the basis of elemental analysis, IR spectra, UV, spectra, magnetic moment data, conductivity measurement and TGA data, following octahedral structures are proposed for La –DPDS and Sm-DPDS complex.



La-DPDS Complex



Sm-DPDS Complex.

12. Structure of Complexes

13. Acknowledgement

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