International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2019): 7.583

Synthesis and Antibacterial Activity of Complexes of 2, 2'- Dipyridyldisulphide with ND(III) and TB(III) Metals

Kavita L. Kendre[1], Girish Pande[2]

[1]Assistant Professor, Department of Chemistry, Yeshwant College, Nanded, India

[2]Assistant Professor,, Department of Chemistry, N.S.B. College, Nanded, India

Abstract: ***The Nd(III) and Tb(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 ligands behaves as bidentate ligand. Molar conductance studies indicates an electrolytic behavior 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 also [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 Nd (III) complex and Tb(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 1000^0C 5mg of the samples with the heating rate of 10^0C 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 an 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. Experimental

Preparation of Neodymium (III) Chloride– 2,2'-Dipyridyldisulphide complex

To a hot methanolic solution of the2,2'-Dipyridyldisulphide (20 ml), a methanolic solution of Neodymium (III) Chloride (10 ml) was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 4hr. The precipitated solid metal complex was cooled, filtered off and washed with methanol, petroleum ether and dried in vaccum desiccator (yield=70 %).

Preparation of Terbium (III) Chloride–2,2'-Dipyridyldisulphide Complex

2,2'-Dipyridyldisulphide (0.02M) was dissolved in ethanol (20ml) by little warming and to this was added Terbium (III) Chloride hexahydrate (10 ml) in methanol (0.01M). The mixture was refluxed on a steam bath for 4 hours, cooled at

room temperature and then left overnight by adding 1:1 alcoholic ammonia. The resulting crystals were filtered and washed several times with warm ethanol to remove excess of the metal Chloride or ligand. Finally, the complex was dried in air. (yield 70%)

5. Result and Discussion

Physical and analytical parameters

On the basis of elemental analysis, metal ligand ratio and thermo gravimetric analysis molecular formulae of the complexes are assigned in table no 1. Complexes possess different colors than ligand, insoluble in ethanol, chloroform and acetone where as they are sparingly soluble in DMSO/DMF. They decompose at relatively higher temperature (>270^{0}C) indicating good thermal stability at normal conditions[37].

Table 1: Physical and analytical data

Compound	Molecular Formula	Formula Wt	Yield (%)	Color	M.P. ^{0}C	M : L ratio
DPS	$C_{10}H_8N_2S_2$	220.31	70	White	58^{0}C	-
[Nd(DPS)$_2$2H$_2$O]3Cl	$C_{20}H_{20}N_4O_2S_4Cl_3Nd$	731.21	70	pista	>270^{0}C	1:2
[Tb(DPS)$_2$2H$_2$O]3.Cl	$C_{20}H_{20}N_4O_2S_4Cl_3Tb$	741.90	70	Faint yellow	>270^{0}C	1 : 2

Table 2: Elemental analysis data

Compound	M.F.	Elemental Analysis % found (calculated)						
		C	H	N	O	S	Cl	M
DPS	$C_{10}H_8N_2S_2$	55.02 (54.52)	4.15 (3.66)	13.21 (12.72)	- -	30.12 (29.11)	- -	- -
Nd-DPS	$C_{20}H_{20}N_4O_2S_4Cl_3Nd$	33.60 (32.82)	3.8 (3.28)	8.23 (7.65)	4.98 (4.37)	17.91 (17.15)	15.11 (14.54)	20.20 (19.70)
Tb-DPS	$C_{20}H_{20}N_4O_2S_4Cl_3Tb$	33.78 (33.18)	2.99 (2.51)	8.24 (7.74)	2.87 (2.21)	18.32 (17.72)	15.15 (14.69	22.15 (21.95)

Infrared Spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal[38]. The IR spectra of ligand 2,2'-Dipyridyldisulphide (Fig. 3) in which the presence of 1602 cm^{-1} band due to –CH=N group which is changed in all complexes by rising to higher frequencies i.e. 1620-1633 cm^{-1} [39-40] indicating coordination of ligand with metal. The IR spectrum of the ligand showed a band at 1082 cm^{-1} due to the C-S group and 426 cm^{-1} band due to S-S bond. The presence of these band in all the spectra of all metal complexes indicates that there is no coordination of sulphur atom with central metal ion. Presence of water molecules in the complexes is also indicated by appearance of υ OH vibrations in the range of 3045 to 3137 cm^{-1} [41-43].

Thus ligand 2,2'-Dipyridyldisulphide can coordinates to metal through azomethine nitrogen and with involvement of water molecules reflecting its bidentate nature in the formation of new complexes. The appearance of the M–N bands at 464 cm^{-1} and 458 cm^{-1} and the M–O bands at 518 cm^{-1}and 516 cm^{-1} [44-45] in the of 2,2'-Dipyridyldisulphide lanthanide complexes indicates that coordinated through O atom in Nd and Tb complexes respectively. The IR spectral data and their tentative assignments are given in Table 3.

Table 3: FTIR spectral data

Compound	ν C-S	ν C = N	νS -S	ν Rock -OH	ν M – O	ν M-N	H_2O
DPS	1082	1602	428	-	-	-	-
[Nd(D PS)$_2$2H$_2$O]3Cl	1082	1620	428	844	518	464	3045
[Tb(DPS)$_2$2H$_2$O]3Cl	1083	1652	431	885	516	458	3045

Electronic Spectra

UV-visible spectra of ligand and complexes recorded in the range of 200 to 800 nm. The ligand 2,2'-Dipyridyldisulphide exhibits absorption band near 35587 cm^{-1} due to π→π* transition, resulting from intra molecular charge transfer within the ligand molecule. Complexes exhibit new absorption bands that are not seen in free ligand..Appearance of new transition bands on complexation are assignable to electronic transitions from one energy level to other and ligand to metal change transfer are the supportive evidences and suggest involvement of metal orbital and ligand orbital in the formation of new coordination linkage.

The spectra of the ligand and its complexes are tabulated in table No. 4.

The electronic spectra Nd(III) chloride complexes of the ligand DPS are characterized by different absorption bands at 26178, 34482cm^{-1} which can be assigned to n - π* and π - π* transitions. The electronical spectral data and μ_{eff} value suggest a octahedral environment around Nd(III) ion.Molar conductivity 75 – 95 Ω^{-1}cm^2 mol^{-1} indicated electrolytic nature of complexes[46].

Table 4: Electronic spectral data

Complex	Absor bancenm	ν / cm^{-1}	Assignment	Molar Conduc-tance $\Omega^{-1}cm^2$ mol^{-1}	Magnetic Moment (BM)	Geometry
DPS	281	35587	π - π*	–	–	–
$[Nd(DPS)_2 2H_2O]3Cl$	382, 290	26178,34482	n - π* π - π*	75	Paramagnetic 3.69	Octahedral
$[Tb(DPS)_2 2H_2O]3.Cl$	360,	27778,	n - π*	85	Paramagnetic10.12	Octahedral

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 27^0C temperature. The zone of inhibition based upon size around the well was measured. Inhibition zone percentage are recorded in Table5. 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 proves 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.

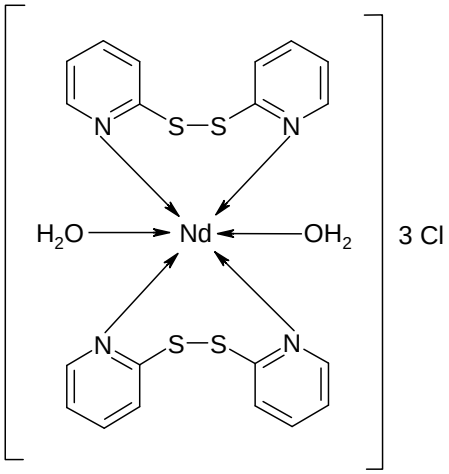
Ligand / Complex	% of Inhibition Zone			
	E.Coli	S.Aureus	A.Niger	Alternaria
DPDS	22	-	-	16
Nd(II)-DPDS Complex	21	21	-	22
Tb(II)-DPDS Complex	19	21	-	22

6. Conclusion

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

Structure

Structure of $[nd(dps)_2 2h_2o]3cl$ complex



References

[1] W. Ramsay, *Ber. Dtsch. Chem. Ges*. 10, 736, **(1877)**.
[2] T. Anderson, *J. Liebigs Ann. Chem*. 60, 86, **(1846)**.
[3] A. E. Chichibabin, *Zh. Russ. Fiz. Khim. O-va*. 37, 1229 **(1905)**.
[4] A. P. Kudchadker and S. A. Kudchadker, Pyridine and Phenylpyridines, API Publication 710, *American Petroleum Institute*, Washington, D.C., **(1979)**.
[5] Technical data, Reilly Industries, Indianapolis, Ind.
[6] R. J. L. Andon and J. D. Cox, *J. Chem. Soc*., 4601, **(1952)**.
[7] R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *Trans. Faraday Soc*. 50, 918, **(1954)**.
[8] L. H. Horsley, Advances in Chemistry Series 116, *American Chemical Society, Washington*, D.C., **(1973)**.
[9] A. O. Fitton and J. Hill, *Selected Derivatives of Organic Compounds*, Chapman Hall, London, **(1970)**.
[10] D. Feitler, W. Schimming, and H. Wetstein (to Nepera Chemical Co.), *Eur. Pat. Appl.* 131, 887, **(1985)**.
[11] *The United States Pharmacopeia XX*, The United States Pharmacopeial Convention, Inc., Rockville, Md., **(1980),** pp. 548−549.
[12] L. D. Markley (to Dow Chemical Co.), *U.S. Pat.* 3, 862, 952, **(1975)**.
[13] V. D. Parker (to Dow Chemical Corp.), *U.S. Pat.* 3,694,332, **(1972)**.
[14] S. Shimizu and co-workers (to Koei Chemical Co.), *Eur. Pat.* 232,182 **(1987).**
[15] Geary W. J.*; Coord. Chem. Rev*. Vol.7, **(1971)** p. 81. - MP
[16] Basawaraja P., Vaidya, V.P., and Vijay Kumar, M.L.; *Ind. J. Heterocyclic. Chem.* Vol. 15. **2005**, p. 169
[17] Latha K P., Vaidya, V.P., and Keshawaya, J.; *J. Ind. Council. Chem*. Vol. 24(2) **(2007)**, p.25.
[18] Thaker B.T., Surati K,R., and Modi, S.R., *; Russian. J, Coord. Chem*. 34. (1), **(2008).** p.25.
[19] R. Rajavel, M. Senthil Vadivu and C. Anitha, July **(2008)**, 5(3), 620-626.
[20] J.T. Makode and A.S. Aswar., *Indian J. Chem.* **(2004),** 43(A), 2120-2125.
[21] M. Ravanasiddappa., T. Sureshg, Syed K., S.C. Radhavendray., C. Basavaraja and S.D. Angadi., *E.J.Chem.*, **(2008)**, 5(2), 395-403.
[22] A. Syamal and M.M. Bari Niazi, *J. Indian Chem., Soc., Sec.-A*. **(1984),** 23, 163.
[23] K.M. Chetan, S.P. Ashwin and Bharat T.T., *E-J. Chem.*, **(2005)**, 2(6), 21.
[24] Dijebbar-Sid, S., Beneli Baitich and Deloume, J .P; *J. Mol. Structure*. vol. 569. **(2001)** p.121.