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Synthesis, Characterization and Antibacterial Activities of Some Mixed Ligand Complexes of Lanthanide(III) Ions

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Eight new complexes of lanthanide(III) ions with Schiff bases of *p*-anisidine as primary ligand and diphenyl sulphoxide as secondary ligand in the presence of any one of the three anions, *viz.*, nitrate, perchlorate or thiocyanate were synthesized and characterized by infrared spectra, elemental analysis, molecular mass determination, thermal studies and electrical conductance measurements. All the complexes were screened for their antibacterial activities against *S. aureus*, *E. coli*, *K. pneumoniae* and *Ps. aeruginosa*. We have arrived at the composition of complexes by infrared spectral analysis, elemental analysis and conductance measurements as

1. $[Nd(HDDA)_2(DPSO)(NO_3)_3]$
5. $[Nd(DDA)_4(DPSO)(NO_3)_3]$
2. $[Eu(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$
6. $[Sm(DDA)_4(DPSO)(NO_3)_3]$
3. $[Gd(MDDA)_3(DPSO)(NO_3)_3]$
7. $[Sm(DDA)_4(DPSO)(ClO_4)_3]$
4. $[Pr(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$
8. $[Nd(MNDA)_4(DPSO)(NCS)_3]$

Key Words: Synthesis, Lanthanide(III), Complexes, Schiff bases, Diphenyl sulphoxide

INTRODUCTION

We report here the synthesis, characterization and antibacterial screening of solid mixed ligand complexes of nitrates, perchlorates or thiocyanates of certain lanthanide(III) ions, with Schiff bases of *p*-anisidine derived from different aldehydes, *viz.*, vanillin (HDDA-4-hydroxy-3-4-dimethoxydiphenylazomethine), N,N-dimethylamino benzaldehyde (MDDA-4-methoxy-4-(N,N-dimethylamino) diphenylazomethine), *p*-anisaldehyde (DDA-4,4-dimethoxydiphenylazomethine) and 3-nitrobenzaldehyde (MNDA-4-methoxy-3′-nitrodiphenylazomethine) along with diphenylsulphoxide (DPSO). All the Schiff bases were found to be monodentate coordinating through azomethine nitrogen. DPSO is also monodentate coordinating through oxygen atom.

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EXPERIMENTAL

The reagents and solvents were of analytical grade. The nitrates and perchlorates of lanthanide(III) ions were prepared from their oxides by dissolving in hot 50% (v/v) aqueous nitric or perchloric acid. The undissolved oxides were filtered off and the lanthanide nitrates or perchlorates were crystallized by concentrating and cooling the filtrate.

The ligands were prepared by refluxing equimolar methanolic or acetonic solutions of *p*-anisidine with the respective aldehydes and evaporating the solution. The complexes were prepared by refluxing the required methanolic or acetonic solutions of lanthanide nitrate or perchlorate and the ligands for 6 h and evaporating the solution. The complexes formed were purified and dried *in vacuo* over phosphorus(V) oxide. From the nitrato complexes thus formed the thiocyanato complexes were prepared by substitution method. The particular methanolic solution of lanthanide nitrato complex and the required ammonium thiocyanate were refluxed and evaporated to get the thiocyanato complex.

The compositions of all these complexes were determined by metal estimation by oxalate-oxide method[1], the nitrate content using nitron reagent[2], perchlorate content by Kurz[3] method and the thiocyanate gravimetrically as AgSCN[2]. Molar conductances were determined at room temperature using an Elico conductivity bridge CM82T with a dip type conductivity cell having platinum electrodes. IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer 1650 FTIR spectrophotometer. Molar mass was determined by Rast method using biphenyl as solvent. Using these analytical data the compositions of the complexes were determined.

The complexes were screened for their antibacterial activity against *S. aureus*, *E. coli*, *K. pneumoniae* and *Ps. aeruginosa* by disc diffusion method[4] at different concentrations, viz., 10 μg/disc, 25 μg/disc and 50 μg/disc.

RESULTS AND DISCUSSION

Analytical data and electrolytic behaviour of all the complexes are given in Table-1. The IR spectra of the ligands exhibit a strong band around 1600 cm^{-1} which is assigned to the stretching vibration of C=N. The band undergoes a downward shift by 25–20 cm^{-1} in the spectra of the complexes. This clearly indicates the coordination of azomethine nitrogen to metal atom. The lowering in the stretching frequency of 80–70 cm^{-1} found in the complex at 1030–1020 cm^{-1} is indicative of the bonding from the oxygen atom of the sulphoxide of DPSO[5].

The nitrato complexes are observed around 1460, 1350 and 1300 cm^{-1} due to ν_4, ν_1 and ν_2 modes of coordinated nitrate ions[6]. The difference between ν_4 and ν_1 is 110 cm^{-1} which supports the unidentate coordination of nitrate ion. The perchlorato complexes exhibit bands around 1170, 1023, 620, 525 cm^{-1} and a medium intensity band around 930 cm^{-1} due to ν_4, ν_1, ν_3, ν_5 and ν_2 modes of monodentately coordinated perchlorate ions[7,8]. The thiocyanato complexes exhibit two bands around 2050 and 830 cm^{-1} which are assigned to ν(CN) and ν(CS) modes of coordinated thiocyanate which are not present in the spectra of

the ligand or in other anionic complexes. Since ν(CN) mode is lower than 2100 cm^{-1} and ν(CS) vibration is greater than 774 cm^{-1}, the thiocyanate ions are coordinated to metal through nitrogen in a unidentate fashion[7, 8]

TABLE-1
ANALYTICAL DATA OF LANTHANIDE(III) COMPLEXES

Complex	m.w. Found (Calcd.)	Metal % Found (Calcd.)	Electrolytic nature
$[Nd(HDDA)_2(DPSO)(NO_3)_3]$	1040.00 (1046.24)	13.07 (13.78)	Non-electrolyte
$[Eu(HDDA)_3(DPSO(ClO_4)_2]ClO_4$	1422.50 (1423.40)	9.77 (10.63)	1 : 1 electrolyte
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$	1306.80 (1307.25)	11.68 (12.02)	Non-electrolyte
$[Pr(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$	1655.00 (1657.40)	7.80 (8.50)	1 : 1 electrolyte
$[Nd(DDA)_4(DPSO)(NO_3)_3]$	1495.00 (1496.24)	9.56 (9.64)	Non-electrolyte
$[Sm(DDA)_4(DPSO)(NO_3)_3]$	1499.50 (1502.65)	9.54 (10.01)	Non-electrolyte
$[Sm(DDA)_4(DPSO)(ClO_4)_3]$	1612.25 (1614.85)	9.10 (9.35)	Non-electrolyte
$[Nd(MNDA)_4(DPSO)(NCS)_3]$	1540.90 (1544.24)	9.31 (9.34)	Non-electrolyte

Antimicrobial Activity

All the eight complexes were screened for antibacterial activity and inhibition zone diameters (in mm) of the complexes along with the gentamycin standard are presented in Table-2.

TABLE-2
ANTIMICROBIAL ACTIVITY OF MIXED LIGAND LANTHANIDE(III) COMPLEXES AT DIFFERENT CONCENTRATIONS

Complex	*S. aureus* mm	*E. coli* mm	*K. Pnuemoniae* mm	*Ps.Aeruginosa* mm
	10 25 50	10 25 50	10 25 50	10 25 50
$[Nd(HDDA)_2(DPSO)(NO_3)_3]$	12 12 12	NZ NZ NZ	NZ NZ NZ	NZ NZ NZ
$[Eu(HDDA)_3(DPSO(ClO_4)_2]ClO_4$	12 12 NZ	NZ NZ NZ	12 12 12	NZ NZ NZ
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$	14 18 20	NZ NZ NZ	NZ NZ NZ	NZ NZ NZ
$[Pr(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$	8 10 11	7 10 12	8 12 12	7 10 12
$[Nd(DDA)_4(DPSO)(NO_3)_3]$	20 20 20	NZ NZ NZ	NZ NZ NZ	NZ NZ NZ
$[Sm(DDA)_4(DPSO)(NO_3)_3]$	15 22 22	NZ NZ NZ	NZ NZ NZ	NZ NZ NZ
$[Sm(DDA)_4(DPSO)(ClO_4)_3]$	14 16 16	14 14 16	NZ NZ NZ	NZ NZ NZ
$[Nd(MNDA)_4(DPSO)(NCS)_3]$	12 20 20	NZ NZ NZ	NZ NZ NZ	NZ NZ NZ
Gentamicin Disc	22 mm	20 mm	24 mm	23 mm

NZ: No zone Disc concentration 10 μg, 25 μg and 50 μg Zone size: mm

Four different antibacterial strains, *viz.*, (1) *Staphylococcus aureus* (2) *Escherichia coli* (3) *Klebsiella pneumoniae* and (4) *Pseudomonas aeruginosa* were used in the study. All the complexes were found to be active towards one or the other

bacteria used. *S. aureus* was affected by all the complexes. The complex $[Pr(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$ inhibited the growth of all the four bacterial strains. Again it was found that perchlorato complexes are more effective than the nitrato and thiocyanato complexes. Comparing the activities of the complexes $[Sm(DDA)_4(DPSO)(NO_2)_3]$ and $[Sm(DDA)_4(DPSO)(ClO_4)_3]$, where the difference is only in the anions, the perchlorato complex was found to be active towards *S. aureus* and *E. coli*, but nitrato complex was more active towards *S. aureus* than the perchlorato complex and it was inactive towards *E. coli*. The standard used in the study was gentamycin. It can be seen that not in all cases but in some cases as the concentration increases the activity also increases. Eventhough it cannot be generalized that as the concentration increases the activity also increases, but in most cases the activity increases by increase in concentration. Again it can be seen that *Ps. aeruginosa* became inhibited by $[Pr(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$ only.

Conclusion

All the complexes under study inhibited the growth of one or the other bacteria. All the complexes are active towards *S. aureus*. Perchlorato complexes are more active than the nitrato and thiocyanato complexes. The inhibition diameter increases with increase in concentration in most cases.

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