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Antibacterial Study of Schiff Base Complexes of Some Lanthanide Nitrates

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ABSTRACT

Schiff base complexes of rare earth metals have been an interesting research field for the past few years due to their pharmacological, clinical, analytical and biological applications. Also the chemistry of antipyrine and its derivatives has been extensively investigated due to its physiological properties. The study of the metal complexes of antipyrine in antineoplastic medication, molecular biology and bioengineering has become hotspots in recent years. We report a new Schiff base formed from pyridoxal, a vitamin and 4-aminoantipyrine. Here we explore the antibacterial activity of the newly synthesized Schiff base formed from 4-aminoantipyrine with vitamin B. This Schiff base acts as a tridentate ligand , which form very stable complexes with the lanthanide metals La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Er. The structure of the ligand and complexes were characterized by elemental analysis, IR and UV spectral studies, magnetic susceptibility measurements, electrical conductance and thermo gravimetric analysis. The ligand is found to be chelating with the metal ion in a neutral tridentate manner through the carbonyl oxygen, azomethine nitrogen and the phenolic oxygen. The nitrate ions are monodentately coordinated to the metal ion. All complexes are found to have the formula, $[ML_2(NO_3)_3]$. All the studies reveal a coordination number of nine for the metals in all the complexes.

Keywords: Schiff Base, 2,3-dimethyl-4-(iminopyridoxyl)-1-phenyl-3-pyrazoline-5-one, antibacterial activity, lanthanide complexes.

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INTRODUCTION

Clinical biology is a wide scientific field incorporating biological, chemical as well as physical issues. Lanthanide complexes can be used as diagnostic tools for biology and medicine due to their special, photophysical and biological properties [1]. There are several lanthanide complexes which have been used in various bioanalytical methods such as homogeneous and heterogeneous immunoassays, medical and clinical diagnostics, drug screening, photodynamic therapy, protein-protein interaction, study of ion channels in living cells, DNA hybridization [2]. The Schiff bases derived from 4-aminoantipyrine were known from many years [3-7]. Many studies have highlighted the use of antipyrine derived Schiff base complexes in the field of pharmacology [8]. In recent years the study of metal complexes are interesting because of their antibacterial activity [9]. In the present work, we investigate the antibacterial activity of 2,3-dimethyl-4-(iminopyridoxyl)-1-phenyl-3-pyrazoline-5-one and so lanthanide complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Er(III). The synthesis was carried out at room temperature. The ligand and complexes were screened for activity against the bacteria namely *E.coli* and *B.subtilis.*

MATERIALS AND METHODS

The analar grade 4-aminoantipyrene was obtained from CDH, New Delhi and pyridoxal hydrochloride was supplied by Sigma (99%). The lanthanide nitrates were prepared in laboratory from the corresponding oxides [9].

Experimental

The melting points were determined on a Thoshniwal melting point apparatus. The Schiff base and complexes were analyzed for C, H and N content on a Heracus CHN Analyzer. The metals were analyzed gravimetrically. Molar conductance of the Schiff base and complexes in DMSO were measured at room temperature using Elico CM-180 conductivity meter with a dip type cell of platinum electrode with cell constant 0.986 cm^{-1}. The IR spectra of the complexes were recorded in the range 400-4000 cm^{-1} on a Shimadzu IR 470 spectrophotometer in KBr discs. The electronic spectra in DMSO solution (10^{-3} M) were recorded in the range 200-900 nm on a Shimadzu UV-160A spectrometer. The magnetic susceptibility were measured with a Sherwood Scientific Gouy Balance. Thermogravimetric studies were carried out under nitrogen atmosphere using a Shimadzu thermal analyzer, Model No.3.

Synthesis of Schiff Base: 2,3-dimethyl-4-(iminopyridoxyl)-1-phenyl-3-pyrazoline-5-one

4-aminoantipyrine (0.203g,1mmol) and pyridoxal hydrochloride (0.213g,1mmol) were dissolved separately in about 30 ml ethanol and mixed in 1:1 molar ratio, stirred well and the precipitate formed is filtered, washed in ethanol and then washed with acetone, dried and the melting point was determined (278°C). The new ligand has low solubility in common organic solvents but soluble in hot ethanol.

Synthesis of Complexes

The ligand (0.377g, 1mmol) was dissolved in 30 ml of ethanol and boiled. Lanthanide nitrate (0.5mmol) was dissolved in 25 ml ethanol was poured slowly to it. The mixture was refluxed for 5 hours [10-11]. The solution was concentrated, allowed to cool, then slowly evaporated in air. Brownish yellow complex separated. This complex was repeatedly washed with ethanol and then with acetone, recrystallized from ethanol, dried and kept over P_2O_5. All complexes were synthesized in a similar manner. The formation of the complex may be formulated as

$$Ln(NO_3)_3 + 2L \rightarrow [LnL_2(NO_3)_3]$$
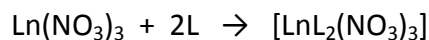
where Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Er.

RESULT AND DISCUSSION

All results indicates that all the complexes have the general formula $[LnL_2(NO_3)_3]$ where Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Er. All the complexes are nonhygroscopic and are partially soluble in DMSO. Analytical data of the ligand and the complexes are presented in Table 1.

Electrical Conductance

The molar conductance of the ligand and complexes were measured using Elico CM 180 conductivity meter with a dip type cell of platinum electrode at a concentration of 10^{-3} molar in DMSO. The electrical conductance measurements suggest a nonelectrolytic nature for all the complexes [12].

IR Spectra

The important infrared spectral data of the Schiff base and the complexes are given in Table 2.

Bands due to –OH and –C=N are distinguishable and provide evidence regarding the structure of the ligand and its bonding with metal. A strong and broad band at 3450 cm^{-1} is attributed to the –OH (both phenolic and alcoholic hydroxyl) present in the ligand. The strong band at 1649 cm^{-1} of the C=O group in the ligand is shifted to 1620 cm^{-1}, in complexes suggesting that the carbonyl oxygen is coordinated [13]. A band at 1603 cm^{-1} in the ligand is attributed to –C=N stretching vibration. On coordination, this band is shifted to 1595 cm^{-1}, which suggests that the ligand is coordinated to metal ion via azomethine nitrogen in all complexes. This change in shift is due to the drift of the lone pair density of azomethine nitrogen towards metal atom [14]. This is supported by the appearance of band at 536–620 cm^{-1} corresponding to the stretching vibration of M–N bond. Bands at 425-500 cm^{-1} correspond to M–O stretching vibrations. A medium band 1098-1174 cm^{-1} is due to pyridyl in-plane vibrations and bands at 760–695 cm^{-1} due to out of plane vibrations of pyridyl ring [15]. Band at 3433 cm^{-1} observed in the ligand is due to stretching vibrations of free –OH. In the ligand, this frequency is downshifted to 3240–3280 cm^{-1} indicating a weakening of –OH

bond due to coordination through phenolic –OH. The coordination by phenolic OH group is in a different manner. The phenolic oxygen was coordinated to the metal ion without deprotonation [16]. It has been reported that the interaction of the lanthanide ion with phenolic oxygen does not increase the acidity to be sufficient for ionization of phenolic proton; consequently the phenolic oxygen is coordinated to the lanthanide ion without deprotonation [17]. As a result of this, in the metal complexes, the OH band becomes less broad, showing a peak at 3200 cm^{-1}. Also υ(C-O) stretching frequency shows a positive shift by 10 cm^{-1} in complexes. The stretching vibration of C-O (phenolic) is observed at 1490 cm^{-1} and alcholic C–O is observed at 1115 cm^{-1} in the ligand. The stretching vibrational frequency of C-O (phenolic) is shifted to higher frequency indicating bond formation [14].

New bands are observed at ranges 1454–1420 cm^{-1} and 1304–1303 cm^{-1} are due to v_4 and v_1 modes of vibrations of coordinated nitrate group. The difference v_4–v_1 is taken as an approximate measure of the covalency of the metal–nitrate bonding [18]. When nitrate ion is coordinated, the symmetric vibrations of –NO$_2$ absorbs strongly near 1280 cm^{-1} which is not observed in the ligand. The stretching of the π bond of the –N=O linkage is observed at 822–840 cm^{-1}. Absorption at 688-740 cm^{-1} results from –NO$_2$ bending vibrations [19-20]. The separation between the two highest frequencies [21] (below 150 for all the complexes) reveals that the nitrate coordination is unidentate in nature. Upon coordination v_4 splits with a separation of about 22 cm^{-1} which also support that nitrate coordination is unidentate [22]. Lever *et al* have shown that the number and relative energies of nitrate combination frequencies (v_1+v_4) may be used as an aid to distinguish the various coordination modes of the nitrate group [23]. This combination frequency observed in the region of the IR spectrum 1800–1700 cm^{-1} corresponds to (v_1+v_4) for a monodentate coordination and are in good agreement with the suggested value of Lever *et al.* This concludes that nitrate ion is coordinated to the metal ion in a monodentate manner. The Ln–N and Ln–O stretching vibrations are observed at about 580–560 cm^{-1} and 468–500 cm^{-1} respectively [23]. Thus a coordination number of nine is assigned to the metal ion in these complexes.

Antibacterial Activities

In the present study, ligands and complexes have been tested for their effect on the growth of microbial cultures and were studied for their interaction with two species of bacteria *E.coli* and *B.subtilis.* These were streaked on nutrient agar plates. The samples were applied on the streaked nutrient agar plate as disc with 5mm diameter and leaving enough space between them. The plates were covered with another dish, then inverted and incubated at 37°C for 24 hrs. The inhibition zones were measured in millimeters and recorded. The inhibition diameter were recorded between 10–30 mm. Almost all complexes have significant antibacterial activity at 10^{-4} g/ml against the bacteria using agar diffusion and well methods. The growth was expressed as percentage of inhibition and are given in the Table 4. From the data, it is observed that the complexes show higher activity against the bacteria than the ligand.

The enhanced activity of the complexes over the Schiff base can be explained on the basis of chelation theory. Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of its positive charge with donor groups and possible

electron delocalization on the whole chelate ring. Chelation can reduce the polarity of the metal ion and increase the lipophilic character of the chelate and interaction between the metal ion and the cell wall is favoured [9]. This may lead to the breakdown of the permeability barrier of the cell resulting in interference with the normal cell processes. If the geometry and charge distributions around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot takes place and this will prevent the toxic reaction within the pores [25].

The interaction of metal ion with cellular compounds are due to the fact that all these structures contain a variety of functioning groups that can act as metal binding agents. The presence of polar substituents also enhances antibacterial activity.

Preparation of Discs

The discs of ligand and complex both were prepared as follows. 30 µg of the sample in DMSO were prepared from blotting paper (3mm diameter) with the help of a micro pipette. The discs were left in an incubator for 24 hrs at 37°C, and then applied on the bacteria grown on agar plates.

Preparation of Agar Plates

The agar plates prepared with minimum agar were used for the growth of the bacteria species. For Escherichia Coli, McConkey agar obtained from Merck Chemical Company was suspended in freshly distilled water. It was allowed to soak for 15 minutes and then boiled on a water bath until the agar was completely dissolved. The mixture was autoclaved for 15 min at 120°C and then poured into previously washed and sterilized petri dishes and stored at 40°C for inoculation. Inoculation was done with the help of platinum wire loop, which was heated to red hot in a flame, cooled and then used for the application on the bacterial stains.

Application of Discs

Sterilized forceps were used for the application of the paper discs on previously inoculated agar plates. The discs were incubated at 37°C for 24hrs. The zone of inhibition around the disc was then measured in millimeters.

Magnetic Moment Studies

The magnetic moment data at room temperature suggests that the complexes are paramagnetic [26-27] except for La. The values measured agree with Van Vleck values. These data suggest that the f-orbital is not participated in bonding. The magnetic moment data are given in Table 1.

Electronic Spectra

The electronic spectra of the ligand and complexes were recorded in solution state

at 10^{-3} M in DMSO. The spectra of the complexes exhibit alterations in intensity and shift in positions of the absorption bands relative to the ligand. The shift has been attributed to the effect on the crystal field of the metal ion, inter electronic repulsion between the 4f electrons and is related to the covalent character of the metal-ligand bond assessed by Sinha parameter δ, the nephelauxetic ratio β and the bonding parameter $b^{1/2}$ and are very similar. For the ligand, n→π*and π→π* transitions are obtained. In the complexes, n→π* bands are red shifted. The f-f transitions of the complexes are characteristic of the element concerned [28] and hardly influenced by the ligand. Metal ions with different number of f-electrons have different states and intensities. The f-orbitals are of u symmetry and the f-f transitions are forbidden [29]. Electric dipole and magnetic dipole give parity for the transition. The trivalent lanthanide ions possess unique spectral properties resulting from the electronic f-f transitions within the 4f shells which is shielded by the filled 5s and 5p orbitals. The shielding leads to minimal interactions with the field of surrounding molecules, so there are only weak perturbations of the electronic transitions between the energy levels of the f-orbitals. This results in nearly narrow line like absoption and emission spectra [30]. La^{3+}, Gd^{3+} and Lu^{3+} have no observable visible spectra and Ce^{3+} has no transition at this region. The f-f bands observed for other complexes and the ligand are given in Table 3.

Thermal Analysis

The different stages of decomposition pattern are tabulated in Table 5. Thermal analysis of these complexes suggests that they are highly stable up to 270°C and there is no mass loss up to this temperature indicating that there are no molecules of water or solvents. All compounds show similar decomposition pattern. In the first stage of decomposition at about 270°C, a mass loss of about 36% which corresponds to the loss of the one ligand molecule, and in the second stage, there is again a mass loss of about 36% which corresponds to the loss of the second ligand molecule. After the removal of the second ligand molecule we can observe the conversion of the corresponding metal nitrate to the metal oxide, finally the metal sublimes. The data suggests that the decomposition temperature of the complexes are higher than those of the ligand and that the complexes are highly stable.

<div align="center">

CONCLUSION

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The analytical data shows that one metal ion per two ligand molecules are involved in complex formation. Structure of the ligand and the complexes are given in Fig.1-2. The lanthanide complexes of the newly reported Schiff base were tested for antibacterial activity against bacteria *E.Coli* and *B.Subtilis* in which both ligand and metal complexes are active against the two microorganisms namely *E.Coli* and *B.Subtilis*. The results obtained by the diffusion method is reproduced by well method also. All metal complexes namely $[LaL_2(NO_3)_3]$, $[CeL_2(NO_3)_3]$, $[PrL_2(NO_3)_3]$, $[NdL_2(NO_3)_3]$, $[SmL_2(NO_3)_3]$, $[GdL_2(NO_3)_3]$, $[TbL_2(NO_3)_3]$, $[DyL_2(NO_3)_3]$ and $[ErL_2(NO_3)_3]$ are all highly active against the two bacteria. *E.coli* was found to show high activity towards complexes of praseodymium and erbium, moderately active towards lanthanum and samarium. *B.subtilis* was found to be highly active against cerium, praseodymium and erbium complexes and moderately active with lanthanum complex. The ligand was active towards both *E.coli* and *B.subtilis*.
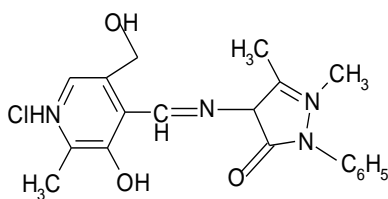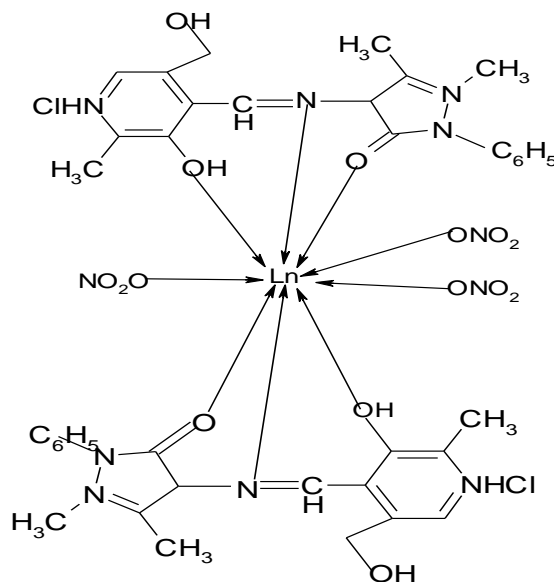
Fig. 1 Structure of the Ligand

Fig. 2 Structure of the Complex [LnL$_2$(NO$_3$)$_3$]

Table 1: Analytical Data of the Ligand and the Complexes

Complexes	M%	C%	H%	N%	μ_{eff}	Mp °C	Yield %	Molar conductance*
[LaL$_2$(NO$_3$)$_3$]	12.6 (12.1)	50.50 (50.44)	4.2 (4.3)	15.4 (15.4)	--	278	93	6.0
[CeL$_2$(NO$_3$)$_3$]	12.2 (12.0)	50.40 (50.38)	4.1 (4.3)	14.3 (15.4)	2.4792	>300	90	5.2
[PrL$_2$(NO$_3$)$_3$]	12.7 (13.0)	52.40 (50.33)	4.4 (4.3)	15.7 (15.4)	2.7044	300	87	7.1
[NdL$_2$(NO$_3$)$_3$]	12.8 (13.2)	53.30 (50.16)	4.5 (4.3)	16.0 (15.4)	4.4199	300	83	6.3
[SmL$_2$(NO$_3$)$_3$]	12.4 (13.4)	48.0 (49.8)	4.4 (4.2)	14.1 (15.3)	0.2677	300	85	8.4
[GdL$_2$(NO$_3$)$_3$]	14.1 (13.2)	50.5 (49.4)	4.6 (4.2)	15.5 (15.1)	3.8914	300	78	7.0
[TbL$_2$(NO$_3$)$_3$]	13.9 (14.1)	50.8 (49.1)	4.6 (4.2)	15.6 (15.0)	8.1672	300	81	6.5
[DyL$_2$(NO$_3$)$_3$]	14.1 (14.4)	52.0 (51.6)	4.6 (4.2)	15.9 (15.0)	3.7135	300	82	5.8
[ErL$_2$(NO$_3$)$_3$]	13.9 (14.7)	50.6 (50.1)	4.4 (4.2)	15.8 (15.1)	8.4329	300	83	6.3

*ohm^{-1}mol^{-1}cm^{-2}

Table 2: IR Spectral Data of the Ligand and Complexes

Compound	v(C=O)	v(C=N)	v(CO)	ν C-O) phenol	v(NO_3)	v(NO_3)	v(NO_3)	v(NO_3)	Ln–O	Ln–N
Ligand	1649*s*	1603*s*	1115*m*	1498*s*	--	--	--	--	502*w*	560*w*
LaL$_2$(NO$_3$)$_3$	1621*s*	1594*s*	1099*m*	1500*s*	1454*m*	1363*m*	1303*m*	1282*m*	503*w*	580*w*
CeL$_2$(NO$_3$)$_3$	1622*s*	1570*s*	1098*m*	1500*s*	1465*m*	1361*m*	1304*m*	1281*m*	503*w*	598*w*
PrL$_2$(NO$_3$)$_3$	1621*s*	1594*s*	1098*m*	1500*s*	1454*m*	1360*m*	1303*m*	1281*L*	465*w*	560*w*
NdL$_2$(NO$_3$)$_3$	1624*s*	1594*s*	1099*m*	1501*s*	1423*m*	1361*m*	1304*m*	1282*m*	436*w*	536*w*
SmL$_2$(NO$_3$)$_3$	1621*s*	1593*s*	1090*m*	1500*s*	1456*m*	1363*m*	1304*m*	1282*m*	503*w*	580*w*
GdL$_2$(NO$_3$)$_3$	1621*s*	1595*s*	1098*m*	1501*s*	1460*m*	1368*m*	1303*m*	1280*m*	460*w*	540*w*
TbL$_2$(NO$_3$)$_3$	1621*s*	1594*s*	1098*m*	1500*s*	1465*m*	1365*m*	1303*m*	1281*m*	501*w*	570*w*
DyL$_2$(NO$_3$)$_3$	1621*s*	1594*s*	1099*m*	1501*s*	1465*m*	1360*m*	1303*m*	1280*m*	502*w*	575*w*
ErL$_2$(NO$_3$)$_3$	1621*s*	1594*s*	1099*m*	1501*s*	1465*m*	1360*m*	1303*m*	1280*m*	502*w*	575*w*

Table 3: UV–Visible Absorptions

Complexes	Wavelength (cm^{-1})	Assigned transition
[PrL$_2$(NO$_3$)$_3$]	16949 22321	$^3H_4 \rightarrow {}^1D_2$ $^3H_4 \rightarrow {}^3P_2$
[NdL$_2$(NO$_3$)$_3$]	11389 13334	$^4I_{9/2} \rightarrow {}^4F_{7/2}$ $^4I_{9/2} \rightarrow {}^4F_{3/2}$
[DyL$_2$(NO$_3$)$_3$]	12280 11494	$^6H_{15/2} \rightarrow {}^4F_{5/2}$ $^6H_{15/2} \rightarrow {}^6F_{7/2}$
[ErL$_2$(NO$_3$)$_3$]	15384 19417	$^4I_{15/2} \rightarrow {}^4F_{9/2}$ $^4I_{15/2} \rightarrow {}^2H_{11/2}$

Table 4 : Antibacterial Activity Results

Compound	E.coli		B.subtilis	
	Activity (mm)	Percentage of inhibition (%)	Activity (mm)	Percentage of inhibition (%)
Ligand	16	+++	14	+++
$[LaL_2(NO_3)_3]$	14	+++	16	+++
$[CeL_2(NO_3)_3]$	5	+	20	++++
$[PrL_2(NO_3)_3]$	30	++++	30	++++
$[NdL_2(NO_3)_3]$	5	+	8	+
$[SmL_2(NO_3)_3]$	16	+++	8	+
$[GdL_2(NO_3)_3]$	10	++	14	++
$[TbL_2(NO_3)_3]$	14	++	10	+
$[DyL_2(NO_3)_3]$	6	+	8	+
$[Er L_2(NO_3)_3]$	28	++++	36	++++

Percentage of Inhibition: Below 5mm = (-)

5mm-10mm   = (+)

10mm-15mm = (++)

15mm-20mm = (+++)

>20mm   = (++++)

Table 5: Thermogravimetric Analysis Data

Complex	Stage of decomposition	T.G. Temp. Range ^{0}C	Mass loss %
$[LaL_2(NO_3)_3]$	I	275-380	36.0
	II	380-450	36.0
$[CeL_2(NO_3)_3]$	I	280-385	35.7
	II	385-450	36.0
$[PrL_2(NO_3)_3]$	I	262-379	35.5
	II	379-450	36.0
$[NdL_2(NO_3)_3]$	I	278-380	36.0
	II	380-458	35.9
$[SmL_2(NO_3)_3]$	I	379-382	35.0
	II	382-450	35.8
$[GdL_2(NO_3)_3]$	I	280-383	35.1
	II	383-450	35.8
$[TbL_2(NO_3)_3]$	I	277-380	37.0
	II	380-449	36.0
$[DyL_2(NO_3)_3]$	I	280-381	36.0
	II	381-451	37.0
$[ErL_2(NO_3)_3]$	I	273-380	35.9
	II	380-448	36.2

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