International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
www.chemijournal.com
IJCS 2023; 11(2): 05-11

Received: 05-12-2022
Accepted: 13-01-2023

Anant S Tekale
Department of Chemistry,
Shivaji Mahavidyalaya, Udgir,
Latur, Maharashtra, India

Thiazole ring containing lanthanide (III) nitrate metal complexes; synthesis, characterization and biological activity

Anant S Tekale

Abstract

The research on 16 novel Schiff base ligand lanthanide (III) nitrate complexes is discussed. By condensing 2-amino-4-(4-bromophenyl) thiazole with ortho hydroxy aldehyde and 3 distinct substituted ortho hydroxy aldehydes, Schiff bases were produced. To create novel complexes, lanthanide (III) nitrates such as lanthanum (III), cerium (III), neodymium (III), and samarium (III) nitrate were chosen. Physicochemical experiments, such as elemental analysis, spectral analysis in the IR and UV-Vis, and fluorescence studies, were used to characterise the complexes. The anti-bacterial and anti-fungal experiments also included the screening of the lanthanide (III) nitrate complexes.

Keywords: Lanthanide (III) nitrate complexes, schiff bases, spectral studies and anti-bacterial and anti-fungal studies

Introduction

Co-ordination chemistry is the most unique field of inorganic chemistry. It has expanded comprehension in hypothetical administration, auxiliary examinations, nature of holding of coordination mixes and test methodology. Coordination compounds have been an extraordinary test to the inorganic scientific expert from when they were distinguished in the nineteenth century. As more edifices were found, different hypotheses were proposed to legitimize for their development and furthermore their properties.

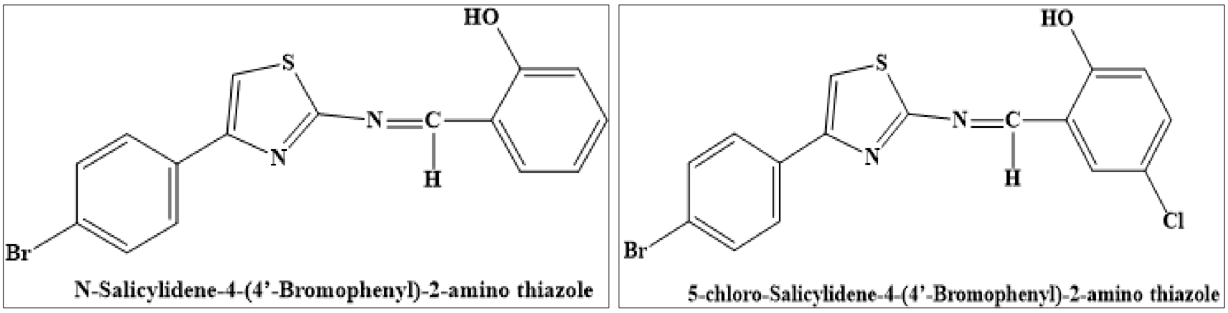
The diverse range of coordination abilities for metals is also considered to be important biologically, industrially, and medicinally. Presently, several coordination complexes possessing antimicrobial activities are reported.

Metal complexes of N and S chelating ligands have attracted considerable attention because of their interesting physicochemical properties and pronounced biological activities. The N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobimolecules. Schiff bases containing o-vanillin possesses antifungal, antibacterial properties [1] and it acts as a weak inhibitor of tyrosinase, display both antimutagenic and comutagenic properties in Escherichia coli ovanillin is a natural aldehyde found in Andropogen nardus. It is used to treat bellyaches and also used in spicery [2, 3]. Heterocycles containing thiazole ring is present in a number of pharmacologically and biologically active compounds. Compounds containing benzothiazole and sulphonamide derivatives were used as anti-inflammatory [6], antifungal [4, 5], antithyroid [11], anticancer [8], anticarbonic anhydrase [9], antimalarial and in therapeutic fields. In view of the pronounced biological activities of these compounds,

The periodic table's longest series is made up of lanthanides or lanthanons. It is a transition series of four. Because of their size and charge, lanthanide (III) ions are the best ions for forming stable complexes with high coordination numbers [12-17]. It has been reported that lanthanide coordination compounds with lanthanide ions exhibiting coordination numbers 6 to 10 exist.

Coordination chemistry has advanced significantly as a result of the contributions of Schiff base metal complexes [18–22]. In this paper, we report compounds of lanthanide (III) nitrate with some of the Schiff base ligands depicted in Figure 1.

Corresponding Author:
Anant S Tekale
Department of Chemistry,
Shivaji Mahavidyalaya, Udgir,
Latur, Maharashtra, India


N-Salicylidene-4-(4'-Bromophenyl)-2-amino thiazole
5-chloro-Salicylidene-4-(4'-Bromophenyl)-2-amino thiazole

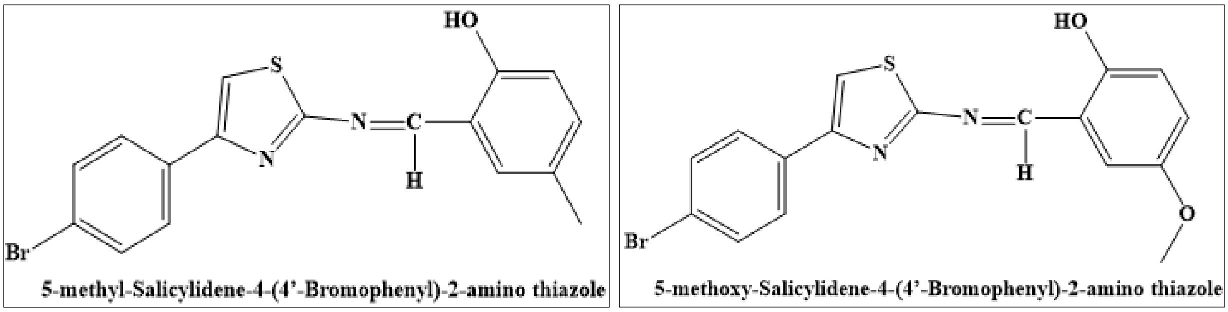

5-methyl-Salicylidene-4-(4'-Bromophenyl)-2-amino thiazole
5-methoxy-Salicylidene-4-(4'-Bromophenyl)-2-amino thiazole

Fig 1: Structure of Schiff base ligands L1 to L4

Experimental

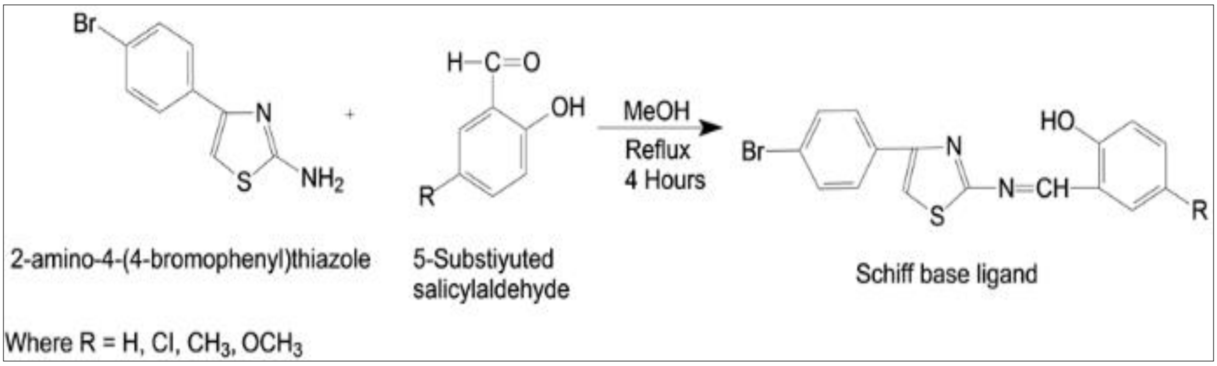
Materials and instrumentation

All solvents, organic chemicals and inorganic salts those used in this work, were all highly purified and directly used without any further purification, chemicals supplied from Sigma-Aldrich, Merck, BDH, Fluka, Scharlau, Companies, Fourier Transform Infrared (FT-IR) spectra were recorded on a Shimadzu model 8400s FT-IR spectrometer scanning at range between (4000-400 cm-1) via a KBr pellets. UV-Visible spectra were measured on a Shimadzu model UV-1650 UV-Visible spectrophotometer Double beam scanning at range of (200-1100 nm) using absolute ethanol as solvent for measurement. The Melting points were taken in open capillary tube by using OMEGA Digital Melting Point Apparatus model MPS10-120.

Synthesis of ligand (L)

The Schiff base ligands [L1, L2, L3, L4] was synthesised by using following procedure, (Scheme 1) reported by Furniss BS, Hannaford AJ, Smith PWG and Tatchell AR, Vogel's practical organic chem. 5th Ed. (Longman Scientific Technical, John Wiley and Sons), 1989. [23] In a 100 ml round bottom flask a solution of 5-Substituted Orth hydroxy aldehydes(1mmol) in a 25 ml of methanol was dissolved and added to a solution of 2-amino-4-(4-bromophenyl) thiazole (1mmol) in a 25 ml of methanol and the reaction mixture was refluxed on a water bath for about 4 hours. after completion of reaction time the reaction mixture kept for cooling for few minutes at RT and after cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with methanol, and recrystallised from DMF and DMSO and dried under reduced pressure at ambient temperature.

The purity of ligand was checked by TLC, elemental analysis and melting point. It was also characterized by Mass, IR, ^{1}H, ^{13}C, UV, Fluorescence spectral studies. And the Yield was 72.01%. The pathway for the synthesis of ligand (L) is presented in Scheme 1.



Scheme 1: Synthesis of thiazole ring containing Schiff base ligands.

Physical properties of Schiff base ligands

Analytical data as well as physical parameters of the Ligands are presented in below table No. 1. ligands formed by different Orth hydroxy aldehydes possess yellow and brown colours. All the ligands are insoluble in water and soluble in organic solvents such as $CHCI_3$, DMSO and DMF. The yield of the all ligands is nearly corresponding up to 72% and which is shown in the table. No.1 and which is good. The decomposition points of the all ligands are relatively 160^0C-187 °C, Indicating good thermal stability at normal conditions. And on the basis of elemental analysis ligands are assigned with empirical formula. The melting point was recorded on digital melting point apparatus.

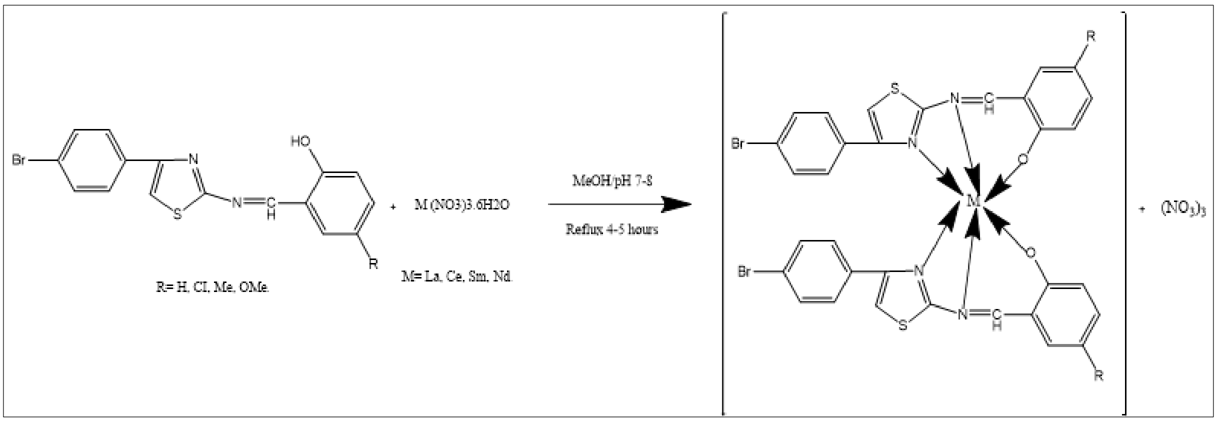
Table 1: Physical parameters of Synthesized Schiff base ligands L1 To L4.

Sr. No. /ligand	Molecular formula of Compound	M.P. in °C	% Yield in GM	Colour And Solubility	Rf	Molecular Weight.	Elemental analysis in %						
							C	H	N	S	O	CI	Br
1/L1	C16H11N2OSBrL1	168-170	72.01	Yellow DMF, DMSO, $CHCI_3$	0.66	359.24	53.49	3.08	7.79	8.92	4.45	-	22.24
2/L2	C16H10N2OSCIBrL2	170-174	67.68	Pale brown DMF, DMSO $CHCI_3$	0.65	393.69	48.81	2.55	7.11	8.14	4.06	9.00	20.29
3/L3	C17H13N2OSBrL3	170	66.66	Whitish, Yellow DMF, DMSO $CHCI_3$	0.64	373.27	54.70	3.50	7.50	8.58	4.28	-	21.40
4/L4	C17H13N2O2SBrL4	162-165	67.60	Yellow $CHCI_3$	0.62	389.27	52.45	3.36	7.19	8.23	8.21	-	20.52

Preparation of metal complexes

The metal complexes are formulated by, the adding 0.02 mol hot methanolic solution of ligand to the 0.01 mol methanolic solution of cerium (III) nitrate with constant stirring at 7-8 pH for about 4 or less than 4 hours. Their action mixture was cooled to room temperature and poured in to distilled water. The coloured solids separated were collected by filtration, washed with distilled water, then with hot ethanol and finally dried in a vacuum over anhydrous calcium chloride in a desiccator [24]

The pathway for the synthesis of Metal Complexes is presented in Scheme 2.



Scheme 2: Synthesis of Metal Complexes.

Results and Discussion

Interaction of lanthanide (III) nitrates *viz*. lanthanum (III) nitrate, cerium (III) nitrate, samarium (III) nitrate and neodymium nitrate (III) with Schiff base ligands results in the formation of complexes. [Where M = La, Ce, Sm and Nd].

The physical parameters of the metal complexes are presented in below table No. 2 and the elemental analysis of these complexes is given in Table 3. New complexes are fairly stable and can be stored for a long period. All are sufficiently soluble in common organic solvents and are non-hygroscopic in nature. These complexes show almost negligible electrical conductivity in PhNO2 medium which shows their non-electrolytic nature

The molecular weight data of the complexes also supports this fact. Magnetic moment data show that lanthanum (III) nitrate complexes are essentially diamagnetic in nature while all other complexes are paramagnetic due to presence of 4*f*-electrons which are effectively shielded by 5*s*2*p*2 electrons [25]. This shows that 4*f*-electrons do not participate in the bond formation [26].

Physical parameters of the metal complexes

The metal complexes i.e. (La,^{III} Ce, ^{III} Nd ^{III} and Sm ^{III}) are crystalline having sharp melting point and soluble in organic solvent, the complexes are exhibits whitish and creamish colour. They are paramagnetic in nature.

Table 2: Physical parameters of the metal complexes

Sr. No.	Comp	M.P. in °C	% Yield in gm	Colour	solubility	Rf Value	Molecular weight
1	C_1	290 ºC	88.88	Creamish	DMF, DMSO	0.59	857.39
2	C2	> 300 ºC	76.41	Creamish	DMF, DMSO	0.57	926.28
3	C3	>295 ºC	88.23	Whitish	DMF, DMSO	0.60	885.45
4	C4	> 300 ºC	67.14	Creamish	DMF, DMSO	0.52	917.45
5	D1	> 300 ºC	85.71	Creamish	DMF, DMSO	0.55	858.60
6	D2	>295 ºC	88.67	Whitish	DMF, DMSO	0.58	927.49
7	D3	> 300 ºC	72.50	Creamish	DMF, DMSO	0.59	886.66
8	D4	> 300 ºC	65.07	Creamish	DMF, DMSO	0.53	918.66
9	E1	> 300 ºC	61.53	Creamish	DMF, DMSO	0.56	862.73
10	E2	>295 ºC	55.35	Whitish	DMF, DMSO	0.58	931.62
11	E3	>299 ºC	58.00	Creamish	DMF, DMSO	0.58	890.78
12	E4	>300 ºC	70.25	Creamish	DMF, DMSO	0.54	922.78
13	F1	> 300 ºC	65.18	Creamish	DMF, DMSO	0.53	868.85
14	F2	> 300 ºC	67.23	Creamish	DMF, DMSO	0.59	937.74
15	F3	> 300 ºC	80.74	Creamish	DMF, DMSO	0.55	896.90
16	F4	> 300 ºC	85.57	Creamish	DMF, DMSO	0.56	928.90

Table 3: Elemental analysis of the metal complexes

Sr. No.	Comp	La	C	H	N	S	O	CI	Br
1	C_1	16.20	44.82	2.58	6.53	7.47	3.73	_	18.63
2	C2	14.99	41.49	2.17	6.04	6.92	3.45	7.65	17.25
3	C3	15.68	46.12	2.95	6.32	7.24	3.61	_	18.04
4	C4	25.13	44.51	2.85	6.10	6.99	6.97	_	17.41
Sr.no	Comp	Ce	C	H	N	S	O	CI	Br
1	D1	16.31	44.78	2.58	6.52	7.46	3.72	_	18.61
2	D2	15.10	41.43	2.17	6.03	6.91	3.44	7.64	17.22
3	D3	15.80	46.05	2.95	6.31	7.23	3.60	_	18.02
4	D4	15.25	44.45	2.85	6.09	6.98	6.96	_	17.39
Sr.no	Comp	Nd	C	H	N	S	O	CI	Br
1	E1	16.71	44.55	2.56	6.49	7.43	3.70	_	18.52
2	E2	15.48	41.26	2.16	6.01	6.88	3.43	7.61	17.15
3	E3	16.19	45.84	2.94	6.28	7.19	3.59	_	17.93
4	E4	15.63	44.25	2.83	6.07	6.94	6.93	_	17.31
Sr.no	Comp	Sm	C	H	N	S	O	CI	Br
1	F1	17.30	44.23	2.55	6.44	7.38	3.68	_	18.39
2	F2	16.03	40.98	2.40	5.97	6.83	3.41	7.56	17.04
3	F3	16.76	45.53	2.92	6.24	7.15	3.56	_	17.81
4	F4	16.18	43.96	2.82	6.03	6.19	6.88	_	17.20

Elemental analysis of the metal complexes

The below table shows the elemental analysis for all newly synthesized metal complexes.

IR Spectra of the Ligands and Their Complexes

The infrared spectra of the prepared complexes are compared with those of the free ligands in order to determine the site of coordination that may be involved in chelation (Table No. 4). There are some guide peaks in the spectra of the ligands which are of good help for achieving this goal. These peaks are expected to be involved in chelation. The presence of the broad band at 3430–3281 cm^{-1} of the stretching vibrations of phenolic OH groups in the IR spectra of the ligands indicate that the OH groups of these Schiff bases are involved in intramolecular hydrogen bonds [27-28]. On the other hand, the broadbands around 3425–3417 cm^{-1} in the IR spectra of the complexes are due to *v* (OH) of water molecules in the prepared complexes; this finding is also confirmed by elemental and thermal analysis. Coordination, through the phenolic oxygen after deprotonation, causes the shift of this band to higher frequency in all the complexes compared to that of the free ligands, suggesting that hydroxyl groups of the Schiff bases coordinate with Ln in C–O–Ln bond. The IR spectra of the Schiff bases L1, L2, L3 and L4 show strong O-H stretching band at and 3427, 2723, 2725 cm^{-1}, respectively [29], and the IR spectra of the three Schiff bases show the stretching vibration of azomethine group at 1628, 1630, and 1630 cm^{-1} [30], respectively.

The IR data found in the literature revealed that the >C=N double bond most commonly encountered in Schiffs bases (azomethines) absorb in the 1690-1640 cm^{-1}region. In most cases it is a strong and fairly sharp band located at somewhat lower frequencies than the bands of carbonyl groups and close to >C=C< stretching frequencies. In the absence of strain, steric hindrance or other complicated factors and to dilute solutions, prepared from neutral solvent, the stretching frequency of >C=N- is found to be 1670 cm^{-1}.

Meanwhile, the IR spectra of complexes show a shift in the *v*C=N (azomethine group) band towards higher or lower wave number, indicating that the chelation occurs in these complexes through the azomethine group [31] and deprotonated hydroxyl group in position seven of the benzene moiety (C3-OH). This is confirmed by appearance of new weak bands in the range of 620-690 cm^{-1} in the IR spectra of all complexes is tentatively assigned to *v*Ln-N. [32] The appearance of the new bands in the spectra of the isolated solid complexes in the range 588-499 cm^{-1} with different intensities is characteristic for the stretching vibration of Ln-O. These bands are not present in the IR spectra of the ligands.

A nitrate ligand can coordinate to the metal ion in three types, as Tridentate, Hexadentate ligand, or uncoordinated ion. presence of nitrate as counter ion was indicated from the IR spectra of L1 and 2: 1 (M: L) complexes of L2. These complexes show a band at 1384-1387 cm^{-1} [33, 34].

Table 4: IR Data for complex compounds in Cm^{-1}

Sr. no	Compound code	HC=N	C=C	C-S-C	Ln-N	Ln-O
1	C1	1650	1444	1077	540	675
2	C2	1624	1467	1038	571	651
3	C3	1584	1460	1080	560	647
4	C4	1640	1455	1079	529	669
5	D1	1624	1457	1080	551	692
6	D2	1625	1468	1037	570	651
7	D3	1632	1470	1066	567	629
8	D4	1631	1480	1086	-	650
9	E1	1632	1463	1069	557	657
10	E2	1635	1480	1071	511	647
11	E3	1633	1532	1069	499	667
12	E4	1642	1480	1071	510	670
13	F1	1639	1440	1089	530	658
14	F2	1633	1483	1072	520	648
15	F3	1587	1434	1069	512	673
16	F4	1587	1437	1080	519	670

Ultra-Violet and Fluorescence Spectroscopy

The UV electronic spectra of lanthanide (III) edifices shows the progress is moved towards sequential frequencies which affirm the coordination of the ligand to the metal ion [35-37].

The electronic otherworldly information of the both compounds should a wide, this broadness of band is likely because of n-π* progress of azomethine nitrogen of thiazole buildings. Ordinary unearthly information for the arrangement of some agent lanthanide (III) i.e., 4f metal buildings explored in lanthanide edifices are recorded. Every single other parameter shows positive qualities recommend some covalent character in metal ligand band, especially the estimation of B ½ proposes the similar association of 4f orbital metal ligand band. The covalence declines from Pr (III) to Sm (III) edifices which is because of lanthanide contraction [38] move band position towards the lower wave number when contrasted with those of the metal. Lanthanum (III) has no critical retention in the unmistakable locale. The band saw on account of Ce (III), Nd (III) and Sm (III) buildings could be allocated to the progress from ground state to the energized J-level of the separate 4f configuration [39].

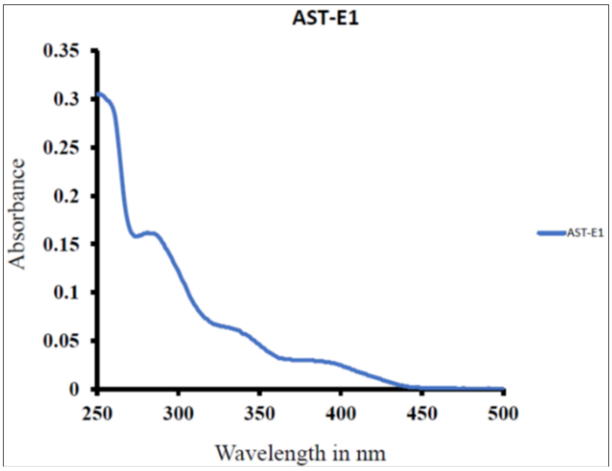


Fig 2: UV spectra of compound-E1

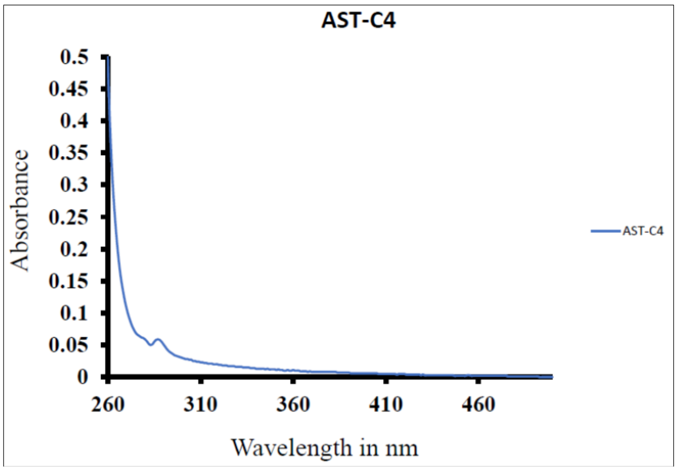


Fig 3: UV spectra of compound-C4

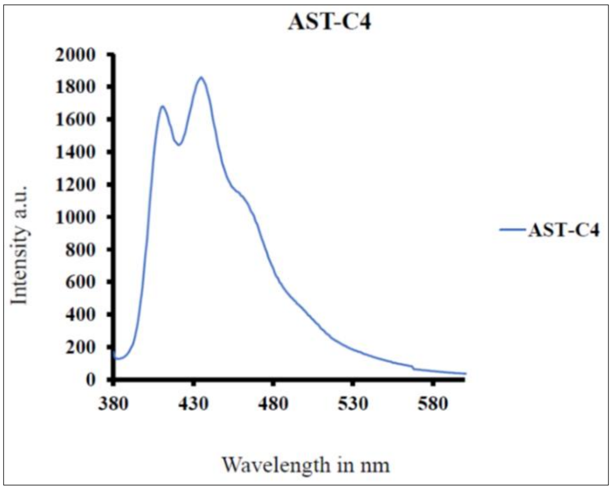


Fig 4: Fluorescence spectra of compound-C4

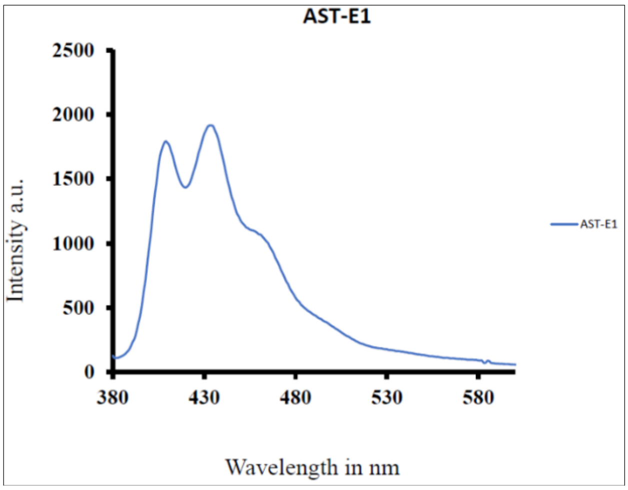


Fig 5: Fluorescence spectra of compound-E1

Biological Activity

The ligand and its metal complexes were tried for antibacterial and antifungal action against certain pathogens. All the metal complexes were seen as dynamic against the microscopic organisms *E. coli*, *B. Subtilis* and growth *A. niger*, *C. Albicans*. All the integrated edifices demonstrated noteworthy action especially the combined metal complexes indicated upgraded antimicrobial action than those of ligands from which they are incorporated.

Medium: Muller Hinton **Method:** Agar well method
Dose of Compound: 1mg/ml **Cup Size:** 10 mm

Table 5: Antibacterial activity of lanthanide complexes

Sr. No.	Compound	*E. Coli*	*B. Subtilis*
1	A-B1-Ligand	1.6	1.5
2	A-B2-Ligand	1	1
3	A-B3-Ligand	1.8	1.5
4	A-B4-Ligand	1.6	1.8
5	C1-Complex	1.7	1.8
6	C2-Complex	1.8	2.1
7	C3-Complex	1.3	1.1
8	C4-Complex	2.1	1.2
9	D1-Complex	0.9	-
10	D2-Complex	0.9	0.9
11	D3-Complex	1.3	1.3
12	D4-Complex	-	0.8
13	E1-Complex	1.9	2.1
14	E2-Complex	1.4	1.8
15	E3-Complex	2.1	2.0
16	E4-Complex	1.6	1.9

17	F1-Complex	1.8	1.2
18	F2-Complex	1.7	1.4
19	F3-Complex	2.0	1.4
20	F4-Complex	1.9	1.9
21	Amphicillin	0.9	1.5

Medium – Muller Hinton Cup Size - 10 mm
Dose of compound - 1mg/ml Zone of Inhibition - mm
Method - Agar well method

Medium: Potato Dextrose Agar **Method:** Agar well method
Dose of Compound: 1 mg/ml **Cup Size:** 10 mm

Table 6: Antifungal activity of Lanthanide complexes

Sr. No.	Compound	*Aspergillus niger*	*C. Albicans*
1	A-B1-Ligand	1.2	1.3
2	A-B2-Ligand	0.9	1.9
3	A-B3-Ligand	1.4	0.8
4	A-B4-Ligand	1.5	1.1
5	C1-Complex	1.4	1.7
6	C2-Complex	1.5	1.6
7	C3-Complex	1.2	1.1
8	C4-Complex	1.2	1.3
9	D1-Complex	1.4	0.9
10	D2-Complex	1.2	1.3
11	D3-Complex	1.5	1.6
12	D4-Complex	1.8	1.2
13	E1-Complex	1.9	1.2
14	E2-Complex	0.5	1.5
15	E3-Complex	1.6	1.4
16	E4-Complex	1.4	1.1
17	F1-Complex	1.1	1.5
18	F2-Complex	1.4	1.7
19	F3-Complex	1.2	1.3
20	F4-Complex	1.7	1.5
21	Fluconyzol	0.7	-

Medium – Pottato Dextrose Agar Dose of compound - 1mg/ml
Method - Agar well method Cup Size - 10 mm
Zone of Inhibition – mm

Sr. No	Name of the Metal Complexes	Abbreviations of Metal Complexes
1	N-Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Lanthanum (III) Nitrate Complex	C1
2	5-chloro -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Lanthanum (III) Nitrate Complex	C2
3	5-methyl -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Lanthanum (III) Nitrate Complex	C3
4	5-methoxy -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Lanthanum (III) Nitrate Complex	C4
5	N-Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Cerium (III) Nitrate Complex	D1
6	5-chloro -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Cerium (III) Nitrate Complex	D2
7	5-methyl -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Cerium (III) Nitrate Complex	D3
8	5-methoxy -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Cerium (III) Nitrate Complex	D4
9	N-Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Neodymium (III) Nitrate Complex	E1
10	5-chloro -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Neodymium (III) Nitrate Complex	E2
11	5-methyl -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Neodymium (III) Nitrate Complex	E3
12	5-methoxy -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Neodymium (III) Nitrate Complex	E4
13	N-Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Samarium (III) Nitrate Complex	F1
14	5-chloro -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Samarium (III) Nitrate Complex	F2
15	5-methyl -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Samarium (III) Nitrate Complex	F3
16	5-methoxy -Salicylidene-4-(4-bromophenyl)-2-Amino thiazole Samarium (III) Nitrate Complex	F4

Conclusion

The synthesis of Schiff bases using 2-amino-4-(4-bromophenyl) thiazole, Ortho hydroxy aldehyde, and 3 distinct substituted Ortho hydroxy aldehydes was characterised as being environmentally beneficial. The conventional condensation reaction approach was used to prepare the complex. A series of metal complexes were prepared from reactions of lanthanide nitrate salts [Nd^{+3}, La^{+3}, Ce^{+3} and Sm^{+3}] with a Schiff base ligand. The structures of the complexes were confirmed by analytical studies, spectral measurements, and thermal studies, and the prepared ligand was characterized using UV-Visible, infrared. The results showed that these complexes have a consistency of 10 in which the elements are bonded with the ligand through the two nitrogen atoms at C=N and that the bonding ratio between the metal: ligand is in 1:2 ratio. By using agar disc-spreading, we tested several *in vitro* compounds for their antibacterial and antifungal activity against four pathogenic bacteria, including. *E. Coli*, *B. Subtilis*, *Aspergillus Niger* and *C. Albicans*

Acknowledgment

The authors are grateful to the Director of IICT Hyderabad for providing spectral characterization and also to the director of school of life science, S.R.T.M.U Nanded for help in screening the compounds for biological activity. We also wish to thank to the Principal of Shivaji college, Udgir for providing laboratory facilities.

References

1. Werner A, Anorg Z. Allg. Chem. 1893;3(1):267-330.
2. Rossotti FJC, Rossotti H. The Determination of Stability Constants, McGraw Hill Book Co., N. Y; c1961.
3. Shaaban S, Davies C, Waldmann H. Applications of chiral cyclopentadienyl (Cpx) metal complexes in asymmetric catalysis. Eur. J Org. Chem; c2020. p. 6512-6524. Tian B, Xiao D, Hei T, Ping R, Hua S, Liu J. The

application and prospects of cyclodextrin inclusion complexes and polymers in the food industry: A Review. Polym. Int. 2020;69:597-603.
4. Karges J. Combining Inorganic Chemistry and Biology: The underestimated potential of metal complexes in medicine. Chem Bio Chem. 2020;21:3044-3046.
5. Zhu RH, Xue QC. Handbook of synthesis practical spicery. Beijing: Light Industry press; c1986. p. 167. 1a. Temel H, Sekerci M. Novel complexes of Manganese(II), Cobalt(II), Copper(II) and Zinc(II) with Schiff base derived from 1,2-bis-(p-aminophenoxy) ethane and salicylaldehyde. Synth React Inorg Met Org Chem. 2001;31:849-57.
6. Watanabe K, Ohta T, Shirasu Y. Enhancement and inhibition of mutation by o-vanillin in Escherichia coli. Mutat Res. 1989;218:105-9.
7. Chavan AA, Pai NR. Synthesis and biological activity of N-substituted-3- chloro-2-azetidinones. Molecules 2007;12:2467-77.
8. Chohan ZH, Ul-Hassan M, Khan KM, Supuran CT. *In vitro* antibacterial, antifungal and cytotoxic properties of sulfonamide - derived Schiff's bases and their metal complexes. J EnzInhib Med Chem. 2005;20:183-8.
9. Sushilkumar SB, Devanand BS. Synthesis and Anti-inflammatory Activity of [2-(Benzothiazol-2-ylimino)-4-oxo-3-phenylthiazolidin-5-yl]-acetic acid derivatives. J Korean Chem Soc. 2003;47:237-40.
10. Caleta I, Grdisa M, Sermek DM, Cetina M, Kulenovic VT, Pavelic K, *et al*. Synthesis, crystal structure and antiproliferative evaluation of some new substituted benzothiazoles and styrylbenzothiazoles. Farmaco. 2004;59:297-305.
11. Supuran CT, Scozzafava A. Carbonic anhydrase and their therapeutic potentials. Exp Opin Ther Pat. 2000;10:575-600.
12. Supuran CT, Scozzafava A, Mastrolorenzo A. Bacterial proteases: Current therapeutic use and future prospects for the development of new antibiotics. Exp Opin Ther Pat. 2000;111:221-59.
13. Huneey JE, Keiter EA, Keiter RL. Inorganic Chemistry Principles of Structure and Reactivity, Pearson Education, Singapore; c2002.
14. Kleber EV. Rare Earth Research, Macmillan, New York; c1961.
15. Moeller T. The Chemistry of Lanthanides, Reinhold, New York; c1963.
16. Cotton FA, Wilkinson G. Advanced inorganic Chemistry, 3rd Edn., Interscience New York; c1972.
17. Koppikar DK, Sivapulliah PV, Ramakrishna L, Soundararajan S. Structure and Bonding. 1978;34:135.
18. Bradley JG, Gothra JS, Hart FA. J Chem Soc Dalton; c1973, 1021.
19. Harrison E. Acta Chem Scand. 1975;27:2827.
20. Kuma H, Yamada S. Inorg Chim Acta. 1975;16:213.
21. Mittal SP, Singh RV, Jadon JP. Curr Sc., (India). 1980;49:130.
22. Agarwal SK, Tandon JP. J Inorg Nucl Chem. 1975;37:1994.
23. Agarwal SK, Tandon JP. Montash Chem. 1979;110:401.
24. Ballchausen CJ, Gray HB. Inorg. Chem. 1962;1:11.
25. Sadigova SE, Magerramov AM, Allakhverdiev MA, Alieva RA, Chyragov FM, Vekilova TM. Russian Journal of General Chemistry. 2003;73:12, 1932-1935, Translated from Zhurnal Obshchei Khimii. 2003;73:12:2043-2046.
26. Agarwal RK, Himanshu Agarwal. Synth React Inorg Met Org Chem., 2001;31:263.
27. Indersenan P, Raj NK Kala. J Indian Chem Soc. 2000;77:259.
28. Nakamoto K. Infrareed and Raman Spectral of Inorganic coordination Comnpounds, 3rd edn.(John Wiley, New York); c1978.
29. Ashmawy FM, Issa RM, Amer SA, Auliffe CA, Parish RV. J Chem. Soc., Dalton Trans; c1987, 2009.
30. Zhang Bin, Lin Yan, Tang Xiaoning, Xu Yinhua, XieGang. Mechanism of antibacterial activity of silver and praseodymiumloaded white carbon black, J Rare earths. 2010;28:442-448.
31. Maheswaran S, Ramesh R. Synthesis, Spectra, Dioxygenaffinity and antifungal activity of Ru (III) Schiff base complexes, J Inorg. Bio Chem. 2003;96:457-462.
32. Braunstein P. Functional ligands and complexes for new structures, homogeneous catalysts and nanomaterials, J Organomet. Chem. 2004;689:3953-3967.
33. Omar MM, Mohamed GG, Ibrahim AA. Spectroscopic characterization of metal complexes of novel Schiff base. Synthesis,thermal and biological activity studies, Spect. Chimi. Acta Part A. 2009;73:358-369.
34. Zhang Li, Yufei Ji, Xuebin Xu, Zhiliang Liuan, Jinkui Tang. Synthesis, structure and luminescence properties of a series of dinuclear LnIIIcomplexes (Ln=Gd, Tb, Dy, Ho, Er), J Lumi. 2012;132:1906-1909.
35. Kulkarni A, Patil SA, Badami PS. Synthesis, characterisation, DNA cleavage and *in vitro* antimicrobial studies of La(III), Th(IV) andVO(IV) complexes with Schiff bases of coumarin derivatives, Europ J Med. Chem. 2009;44:2904-2912.
36. Kavita L Kendre, Girish Pande, Pingalkars R. Der Pharmacia letter, 2014;6 (4):38-43.
37. Inorganic Spectroscopy by ABP Lever.
38. Seetharama Rao T, Laxma Reddy K, Lingaih. Ind. Acad. Sci. (Chem. Science). 1988;100(5):333-373.
39. Agarwal RK, Khan AA, Singh P, Kumar V. Journal of Applied chemical Research. 2009;11:62-70.
40. Mohammed Shafi AP, Prakash GA, Shreedhar DD. Main Group Chem. 2008;7(4):271-283.