FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 7 No. 1, February, 2023, pp 19 - 23
DOI: https://doi.org/10.33003/fjs-2023-0701-1226

CHARACTERIZATION OF BIS-SALICYLALDEHYDE O-PHENYLENEDIAMINE SCHIFF BASE AND ITS DY(III), GD(III), ND(III) AND SM(III) LANTHANOIDS COMPLEXES

***Mahmud S. D., Birnin-Yauri U. A., Liman M. G.**

Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto P.M.B 2346, Sokoto, Nigeria.

*Corresponding authors' email: searsweet01@gmail.com

ABSTRACT

Schiff bases have versatile chemical properties and numerous utilities in various industries consequent of their excellent coordination ability with numerous metal ions especially transition metals. To further exploit the chemical versatility of this promising compound, we thoroughly characterize the aged long synthesized Schiff base; Bis-salicylaldehyde o-phenylenediamine (Salphen) and its Lanthanoid (III) complexes of Neodymium, Samarium, Gadolinium and Dysprosium using solubility test, melting and decomposition analysis, FTIR, Uv-visible spectroscopy, conductivity measurement, elemental analysis, magnetic susceptibility and NMR. The Salphen ligand was soluble in chloroform and carbon tetra chloride among others while its complexes were not soluble in most common organic solvents tested. The melting point of Salphen was 165^0C while its Lanthanoid (III) complexes decompose in the range of 210-241^{0}C. The FTIR spectral patterns analysis of the ligand and its complexes conforms to fundamental vibration modes within the structure. Salphen and its Lanthanoid (III) complexes had low conductivity and were paramagnetic, non-hygroscopic and formed binuclear bridged structure with Metal: Ligand ratios of 2: 3. Series of characterization undertaken confirmed the formation of the bridged structured complex between Salphen and Lanthanoid (III) ions with high thermal stabilities, insolubility in most common organic solvents and poor electric conductance.

Keywords: Bis-salicylaldehyde O-phenylenediamine, Schiff base, Lanthanoid complexes, characterization

INTRODUCTION

Schiff base discovered by Hugo Schiff in 1864 is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group (da Silvaa *et al*., 2011; Sahu *et al*., 2012) and has general formula RHC=N-R'

Schiff bases continue to play important role in the expansion of coordination chemistry due to their ease of preparation, flexibility and structural inconsistency (Banthia and Samanta, 2006; Dib, 2013). These compounds have been extensively utilized in pigments and dyes, catalysis, organic synthesis, polymer stabilizations and metallo-enzymes (Nagajothi *et al*., 2012; Usharani *et al*., 2013; Leandro *et al*., 2017). There were several pieces of research conducted to study Bis-salicylaldehyde o-phenylenediamine (Salphen) properties, coordination chemistry and exploits its functions. However, the majority of these researches centered around its complexes with transition metals with little effort on its complexes with Lanthanoid ions (Khan *et. al.*, 1988; El-Shahawi and Smith, 1994; Drew *et. al*., 2010). Although, few researchers had previously worked on Lanthanoids complexes of Salphen base, all these works were unable to thoroughly characterize these complexes to come up with the physicochemical and structural details of the complexes (Lekha, 2014; Emaime and Pius, 2019). Hence, this work aimed to thoroughly characterize Bis-salicylaldehyde O-phenylenediamine Schiff base and its Lanthanoid (III) complexes of Neodymium, Samarium, Gadolinium and Dysprosium using solubility test, melting and decomposition analysis, FTIR, Uv-visible spectroscopy, conductivity measurement, elemental analysis, magnetic susceptibility and NMR with the hope of unveiling their physicochemical and structural properties.

MATERIAL AND METHODS

Chemicals and solvents were purchased from Sigma Aldrich, London, and used as purchased without further purification. The glass wares were washed with detergent, rinsed with distilled water and soaked in (1:4) HNO_3 then rinsed again with distilled water and dried in an oven at 110^{o}C. The preparation of Bis-salicylaldehyde O-phenylenediamine Schiff base and its complex formation with Lanthanoid (III) ions was undertaken according to procedure modified by Kendre et al., (2014).

Experiments

Solubility test

Fifty (50) mg of each sample was mixed with 10 ml of respective organic solvent, stirred for a few seconds and allowed to stand for 15 min and observations were recorded in each case.

Melting point and decomposition temperature

Melting point and decomposition temperatures were determined using Gallenkamp (8B 2699C model) by placing the sample in a sealed capillary tube and thermometer into the appropriate hole, then switching the machine and recording the average of three (3) observed values as melting /decomposition temperature.

Electrical conductivity measurement

Electrical conductivity measurements were recorded using Jenway 4010 model where 0.1g of each of the samples was dissolved in 10ms/cm^3 of DMSO, electrode dip-in to record the electric conductance.

UV-visible spectroscopy

UV-visible spectroscopy was conducted on T60 UV-visible spectrophotometer and the determination of the number of ligands coordinated to the metal ion was carried out by Job's method of continuous variation (Angelici, 1971) in which 3mmol methanolic solution of Salphen and respective Lanthanoid (III) nitrates were mixed in the ratios [1:15, 3:13, 5:11, 7:9, 9:7, 11:5, 13:3, and 15:1] to maintained a total volume of 16ml and the solutions were scanned to determine

the wavelength of maximum absorption (λ_{max}) and plotted to obtain the number of coordinated ligand.

Magnetic susceptibility

The magnetic susceptibility was conducted on MBS MK1 Magnetic susceptibility balance. The balance was calibrated at 1 before introducing an empty capillary tube to record (R_0) in grams which is used to determine the actual weight after recording the weight of the capillary containing the sample in grammes.

Infrared spectral analyses

Infrared spectral analyses were carried out using Shimadzu FTIR-8400S spectrophotometer (500- 4000cm^{-1} region in KBr powder) at NARICT Zaria. The samples were placed on top of the crystal above the light source, where IR radiations passed through the samples and causes vibration of molecules within the sample leading to a specific absorption and / or transmission of energy.

Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H and ^{13}C NMR were determined using d_6-DMSO as a solvent in a Bruker 500MHz NMR spectrometer in which DEPT, HSQC DEPT, HMBC, COSY and NOISE NMR spectra were obtained in ppm and chemical shifts reported in ppm.

RESULT AND DISCUSSION

Salphen is soluble in acetone, benzaldehyde, sulphonic acid, formic acid, DMF and DMSO but insoluble in propanol, chloroform, ethanol, methanol and Distilled water while its complexes are soluble in benzaldehyde, sulphonic acid and formic acid but insoluble in DMF, DMSO, propanol, acetone, CCl_4, chloroform, ethanol, methanol and distilled water. This may be due to a bridge in the complexes; a finding earlier documented in the literature (El-ansary and Abdel-kader, 2012). The melting temperature of Salphen was recorded at 165^{0}C with a sharp melting point indicating the purity of the compound and the decomposition temperature of its lanthanoid (III) complexes were in the range of 210-241^{0}C indicating high thermal stabilities of the complexes. The electrical and molar conductivity of the complexes in 10ms/cm^3 in DMSO solvent reveals were in the range of 12.01 to 22.30 × 10^{-6} (ohm^{-1} cm^2) and 2.01 to 22.30 (ohm^{-1}cm^{2}mol^{-1}) respectively indicating their non-electrolytic nature and this may be attributed to the coordination of anion in the complex rather than the ionic association to the lanthanide (III) cations during complex formation (El-Ansary and Abdel-Kader, 2012; Maurya *et a*l., 2016). The results of melting point/decomposition temperature and electric conductance are depicted in Table 1

Table 1: Conductivity measurement, Melting Point/Decomposition Temperature of the ligand and its Lanthanoid (III) Complexes

Compounds	Melting Point (^{0}C)	Decomposition Temperature (^{0}C)	Electrical Conductance (ohm^{-1} cm^2)	Molar Conductance (ohm^{-1}cm^{2}mol^{-1})
Salphen	165	_		
[Dy_2(salphen)$_3$]	_	229	12.01× 10^{-6}	12.01
[Gd_2(salphen)$_3$]	_	210	22.60× 10^{-6}	22.60
[Nd_2(salphen)$_3$]	_	235	17.58× 10^{-6}	17.58
[Sm_2(salphen)$_3$]	_	241	22.30× 10^{-6}	22.30

Salphen = Bis-salicylaldehyde O-phenylenediamine

All the complexes show paramagnetic behavior as shown in Table 2 and this is due to the presence of unpaired 4f electrons and the contribution of spin and orbital magnetic moments of the lanthanides as against d-block elements whose magnetic moment corresponds to spin values only. The presence of magnetic interactions between the two metal centers and /or strong influence of the ligand field on the magnetic moment is a result of the non-involvement of the 4f electrons in the coordination. The observed μ_{eff} values are near to the values for the free lanthanoid ions reported by van Vleck and Frank (Gueye *et al*., 2017).

Table 2: Magnetic Susceptibility of Lanthanoid (III) Complexes

Ln^{3+}	Electronic configuration	No. of unpaired electrons	L	S	Ground state	g_J	Calculated μ_{eff}(B.M)	Observed μ_{eff} (B.M)
Nd^{3+}	[Xe] 4F^3	3	6	3/2	$^4I_{9/2}$	8/11	3.62	3.5- 3.6
Sm^{3+}	[Xe] 4F^5	5	5	5/2	$^6H_{5/2}$	2/7	1.42	1.4- 1.7
Gd^{3+}	[Xe] 4F^7	7	0	7/2	$^8S_{7/2}$	2	7.93	7.9- 8.0
Dy^{3+}	[Xe] 4F^9	5	5	5/2	$^6H_{15/2}$	4/3	10.62	10.4-10.6

The structurally important IR bands and their assignment in the ligands and their lanthanoid (III) complexes are summarized in Table 3. The diagnostic and relevant vibrational frequencies obtained from the spectra of the compounds are assigned to fundamental vibrational modes based on literature reports on similar compounds (Sani and Mahmud, *2016*).

Table 3: Important IR Spectral Bands of Salphen Ligand and its Lanthanide (III) Complexes

Compound	ν(C=N)cm^{-1}	ν(-OH)cm^{-1}	ν(C-O)	ν(M-N)
Salphen	1627	3441	1373	—
[Dy_2(salphen)$_3$]	1620	—	1388	532
[Gd_2(salphen)$_3$]	1604	3456	1388	540

$[Nd_2(salen)_3]$	1604	3441	1388	532
$[Sm_2(salen)_3]$	1635	3448	1388	524

Estimation of Ligand to lanthanoid ratio according to the plot of absorbance against mole fraction suggested a 2:3 Lanthanoid: Ligand ratio in all the complexes. The principal peaks of the ^1H and ^{13}C NMR in d_6 –DMSO and CHN elemental analysis of Salphen and its complexes are given in Table 4. The ^1H NMR, ^{13}C NMR, DEPT, HSQC, HMBC COSY supported the structure of the complexes assigned based on infrared vibrations (Ajlouni *et al*., 2016), the presence of the aromatic H group confirmed the formation of the rings in the complexes. And COSY (homonuclear correlation spectroscopy) show which protons are coupled to each other in the binuclear structure. CHN elemental analysis also confirmed their binuclear chemical structures which correspond with the tentative formula of the complexes. Following the results of the characterization conducted the proposed structure of the metal complexes is given in figure 2 wherein Ln stands for the respective Lanthanoid metal.

Table 4: Some Diagnostic Peaks of ^1H and ^{13}C NMR and CHN elemental analysis of the Salphen and its complexes

Chemical shift, δ(ppm)							
^1H NMR				^{13}C NMR			
Compounds	**N=CH**	**Aromatic H**	**CH_2-CH_2**	**O-H**	**N=CH**	**Aromatic C**	**CH_2-CH_2**
Salphen	8.55(s)	6.94-7.65(m)	—	13.07(s)	159.8(s)	115.7-131.3(m)	—
$[Nd_2(salphen)_3]$	8.90(s)	6.84-7.40(m)	—	—	159.8(s)	116-131(m)	—
$[Sm_2(salphen)_3]$	8.61(s)	7.00-7.66(m)	—	—	165.2(s)	117.3-134.7(m)	—

CHN elemental analysis of Salphen and its complexes			
	Experimental (Theoretical)		
	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Salphen	75.93 (74.96)	5.10 (5.21)	8.86 (7.98)
$[Dy_2(salphen)_3].H_20$	48.54 (47.74)	5.66 (6.58)	3.66 (3.41)
$[Gd_2(salphen)_3].6\ H_20$	50.00 (49.37)	3.28 (3.33)	5.87 (6.02)
$[Nd_2(salphen)_3].6\ H_20$	51.00 (51.86)	3.48 (3.41)	6.03 (5.92)
$[Sm_2(salphen)_3].6\ H_20$	51.36 (52.12)	3.09 (2.98)	5.99 (5.92)

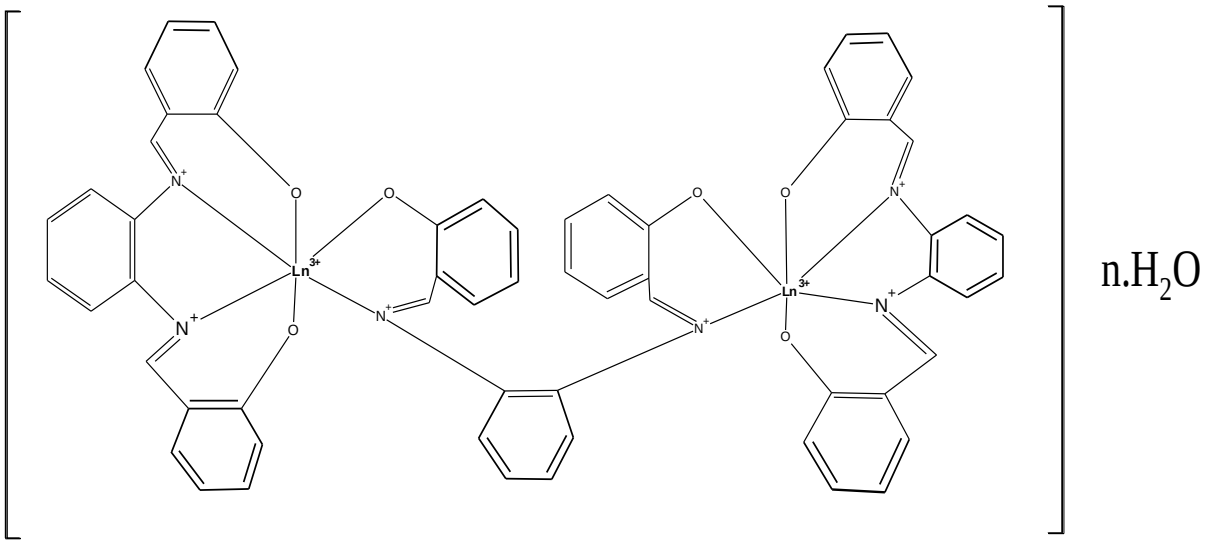


Figure 1: Proposed Salphen-Lanthanoid (III) Complexes [where Ln= Nd, Sm, Gd and Dy.]

CONCLUSION

In this study bis-salicylaldehyde o-phenylene diamine ligand (Salphen) and its lanthanoid (III) complexes of Dysprosium, Gadolinium, Neodymium and Samarium were successfully characterized based on solubility test, conductivity measurement, magnetic susceptibility, Infrared analysis, Uv-visible spectroscopy, elemental analysis, melting point/decomposition temperature and NMR spectroscopy. The results obtained reveal that the lanthanoid (III) complexes are non-electrolytic and non-hygroscopic in nature with have high thermal stability and non-solubility in most common organic solvents which may be accounted for by the bridge in the complexes. The ^1H NMR, ^{13}C NMR, DEPT, HSQC, HMBC COSY supported the structure of the complexes assigned based on infrared vibrations. This successful characterization and proposed structure of these complexes

will serve as a bridge in the existing gap of knowledge in the field and pave the ways for future research on their utility in various fields of human endeavour.

REFERENCES

Ajlouni, A. M., Abu-Salem, Q., Taha, Z. A., Hijazi, A. K. and, and Al Momani, W., (2016). Synthesis, characterization, biological activities and luminescent properties of lanthanide complexes with [2-thiophenecarboxylic acid, 2-(2-pyridinylmethylene)hydrazide] Schiff bases ligand. *Journal of Rare Earths*, *34*(10), 986–993. https://doi.org/10.1016/S1002-0721(16)60125-4

Angelici, R. J., (1971). Synthesis and techniques in inorganic chemistry. *W. B. Saunders Campany*, *2nd editio*, pp 115-125. Banthia, S., and Samanta, A., (2006). A New Strategy for Ratiometric Fluorescence Detection of Transition Metal Ions. *Journal of Physical Chemistry B*, *110*(13), 6437–6440.

da Silvaa, C. M., da Silvaa, D. L., Modolob, L. V., Alvesa, R. B., Martins, C. V. B., and Fátima, Â. de., (2011). Schiff bases: A short review of their antimicrobial activities. *Journal of Advanced Research*, *2*(1), 1–8.

Dib, A., (2013). Synthesis And Characterization Of Schiff Bases Derived From Acetylacetone And Their Theoretical Study. *International Journal of Chem Tech Research*, *5*(1), 204–211.

El-ansary, A. L., & Abdel-kader, N. S. (2012). Synthesis , Characterization of La (III), Nd (III), and Er (III) Complexes with Schiff Bases Derived from Benzopyran-4-one and Thier Fluorescence Study. *International Journal of Inorganic Chemistry*, *2012*(1), 13. https://doi.org/10.1155/2012/901415

El-ansary, A. L., and Abdel-kader, N. S., (2012). Synthesis , Characterization of La (III), Nd (III), and Er (III) Complexes with Schiff Bases Derived from Benzopyran-4-one and Thier Fluorescence Study. *International Journal of Inorganic Chemistry*, *2012*(1), 13. https://doi.org/10.1155/2012/901415

El-Shahawi, M. S., and Smith, W. E. (1994). Spectroelectrochemistry of nickel(II) complexes of N,N-Bis(salicylaldehyde) -o-phenylenediamine and N,N-Bis(2-hydroxy- 1-naphthaldehyde)-o-phenylenediamine using an optically transparent thin-layer electrode. *The Analyst*, *119*(2), 327–331. https://doi.org/10.1039/AN9941900327

Emaime, J., and Pius, O., (2019). Synthesis and Characterization of Neodymium (III) and Praseodymium (III) Complexes Containing Bis (Salicylaldehyde) Orthophenylenediamine as Ligand, *IV*(VII), 67–69.

Gueye, M. N., Dieng, M., Thiam, I. E., Lo, D., Hamady, A., Gaye, M., and Retailleau, P., (2017). Lanthanide (III) Complexes with Tridentate Schiff Base Ligand , Antioxidant Activity and X-Ray Crystal Structures of the Nd (III) and Sm (III) Complexes, 8–15.

Leandro de Araújo, E., Goncalves Barbosa, H. F., Dockal, E. . R., and Tadeu, É. G. C. (2017). Synthesis , characterization and biological activity of Cu (II), Ni (II) and Zn (II) complexes of biopolymeric Schiff bases of salicylaldehydes and chitosan. *International Journal of Biological Macromolecules*, *95*, 168–176. https://doi.org/10.1016/j.ijbiomac.2016.10.109

Lekha, L. (2014). *S*tudies on the synthesis , characterisation and antimicrobial applications of rare earth metal. (D. D. Easwaramoorthy, Ed.) (First).

Maity, D., Drew, M. G. B., Godsell, J. F., Roy, S., and Mukhopadhyay, G. (2010). Synthesis and characterization of Cu(II) complexes of tetradentate and tridentate symmetrical Schiff base ligands involving o-phenelenediamine, salicylaldehyde and diacetylmonoxime. *Transition Metal Chemistry*, *35*(2), 197–204. https://doi.org/10.1007/s11243-009-9314-9

Maurya, R. C., Chourasia, J., Rajak, D., Malik, B. A., Mir, J. M., Jain, N., and Batalia, S., (2016). Oxovanadium (IV) complexes of bioinorganic and medicinal relevance : Synthesis , characterization and 3D molecular modeling of some oxovanadium (IV) complexes involving O , N-donor environment of salicylaldehyde-based sulfa drug Schiff bases. *Arabian Journal of Chemistry*, *9*, S1084–S1100. https://doi.org/10.1016/j.arabjc.2011.12.012

Nagajothi, A., Kiruthika, A., Chitra, S., and Parameswari, K., (2012). Synthesis and Characterization of Tetradentate Co (II) Schiff Base Complexes : Antimicrobial and DNA Cleavage Studies. *International Journal of Research in Pharmaceutical and Biomedical Sciences*, *3*(II), 1768–1778.

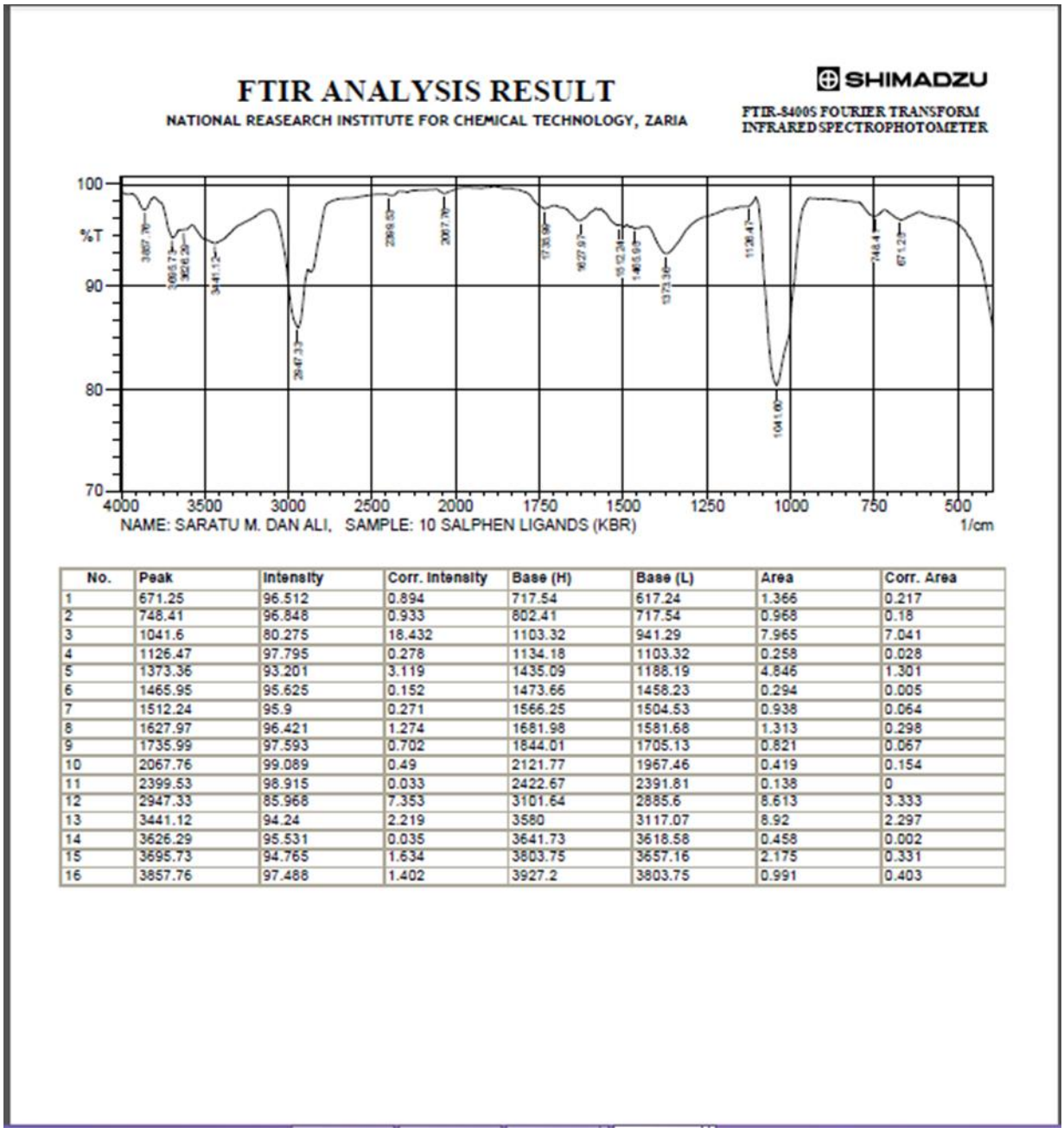
Sahu, R., Thakur, D. S., and Kashyap, P., (2012). Schiff Base: An Overview of its Medicinal Chemistry Potential for New Drug Molecules. *International Journal of Pharmaceutical Sciences and Nanotechnology*, *5*(3), 1757–1764.

Taqui Khan, M. M., Sreelatha, C., Mirza, S. A., Ramachandraiah, G., and Abdi, S. H. R. (1988). Synthesis and characterization of some ruthenium(V) oxo complexes of the Schiff base, bis(salicylaldehyde)-o-phenylenediamine, with appended Cl-, imidazole and 2-methylimidazole: the first examples of stable oxo complexes via direct oxygenation. *Inorganica Chimica Acta*, *154*(1), 103–108. https://doi.org/10.1016/S0020-1693(00)85173-7

Usharani, M., Akila, E., Ashokan, R., and Rajavel, R., (2013). Pharmacological properties of Schiff base Metal complexes derived from substituted pyridine and aromatic amine. *International Journal of Pharmaceutical Sciences and Health Care*, *5*(3), 1–11.

Yusuf, S., Salga, M. S., and Sani, M., (2018). Synthesis, Characterization and Antibacterial Studies of Macrocyclic Schiff Base Derived From Malonic Acid and O-Phenylenediamine and Its Cd (II), Co (II), Cu (II), Ni (II), and Zn (II) Comlplexes. *Science World Journal*, *13*(4), 65–68.

Appendix I: Infrared spectra: IR Spectrum of Salphen Ligand



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	671.25	96.512	0.894	717.54	617.24	1.366	0.217
2	748.41	96.848	0.933	802.41	717.54	0.968	0.18
3	1041.6	80.275	18.432	1103.32	941.29	7.965	7.041
4	1126.47	97.795	0.278	1134.18	1103.32	0.258	0.028
5	1373.36	93.201	3.119	1435.09	1188.19	4.846	1.301
6	1465.95	95.625	0.152	1473.66	1458.23	0.294	0.005
7	1512.24	95.9	0.271	1566.25	1504.53	0.938	0.064
8	1627.97	96.421	1.274	1681.98	1581.68	1.313	0.298
9	1735.99	97.593	0.702	1844.01	1705.13	0.821	0.057
10	2067.76	99.089	0.49	2121.77	1967.46	0.419	0.154
11	2399.53	98.915	0.033	2422.67	2391.81	0.138	0
12	2947.33	85.968	7.353	3101.64	2885.6	8.613	3.333
13	3441.12	94.24	2.219	3580	3117.07	8.92	2.297
14	3626.29	95.531	0.035	3641.73	3618.58	0.458	0.002
15	3695.73	94.765	1.634	3803.75	3657.16	2.175	0.331
16	3857.76	97.488	1.402	3927.2	3803.75	0.991	0.403