

# Synthesis, Spectroscopic, and Biological Studies of Complexes of Unsymmetrical Thiosemicarbohydrazide ligand

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**Abstract** A new unsymmetrical p-fluorobenzaldehyde derivative of  $\alpha$ -benzilmonoximethiosemicarbohydrazide (HBMTSpFB) ligand is prepared via condensation of  $\alpha$ -benzilmonoximethiosemicarbohydrazide and p-fluorobenzaldehyde in the 1:1 ratio. Metal complexes of Fe(II), Co(II), Cu(II), Zn(II), Hg(II) and Ni(II) have been prepared. These prepared compounds were characterized by physicochemical study, PMR, FT(IR), electronic absorption, and magnetic moment, and the purity of the HBMTSpFB ligand was analyzed by thin layer chromatography study. All prepared compounds are color-solid, air-stable, and soluble in common organic solvents. On the basis of elemental analysis metal to ligand and stoichiometry is 1:2 ratio for all complexes. Comparison of the FT(IR) spectra of the HBMTSpFB ligand and its trivalent metal complexes confirm that the HBMTSpFB ligand is a monobasic, tridentate ligand towards the central trivalent metal ion with an ONS and sequence.

**Keywords** -  $\alpha$ -Benzilmonoxime, thiosemicarbohydrazide, metal complex, magnetic moments, and tridentate ligand.

## I. INTRODUCTION

Thiosemicarbohydrazide transition metal complexes are of interest particularly to inorganic chemists because their chemical, spectral, and structural properties are dependent strongly on the nature of the structure of ligands<sup>1-5</sup>. The substituted ketones coordination complexes have shown diverse structural and generating properties, a stereochemistry variety, and a wide range of interactions bonding<sup>6</sup>. The symmetrical coordination complex's construction interest in reacting trivalent transition metal ions with tridentate has been constantly growing over the years<sup>7-8</sup>. Within this increased knowledge and understanding lies molecular self-assembly, complexation of metal ligands, and metal binding sites disposition<sup>9</sup>. By mastering these areas, improved new systems related to the field of bio-engineering<sup>10</sup>, supramolecular chemistry<sup>11</sup>, and catalysis<sup>12</sup> can be achieved due to this coordination of complex applications. The preparation and characterization of some symmetrical tridentate

thiosemicarbohydrazide-based ligand complexes have been thoroughly studied but less study comparatively seems to have been done on complexes of unsymmetrical

thiosemicarbohydrazide derived from  $\alpha$ -benzilmonoxime<sup>13</sup>. A review of the literature revealed that no work has been done on trivalent transition metal complexes of the unsymmetrical thiosemicarbohydrazide bases ligand derived from p-fluorobenzaldehyde and  $\alpha$ -benzilmonoximethiosemicarbohydrazide. The complexes of Fe(II), Co(II), Cu(II), Zn(II), Hg(II), and Ni(II) with this HBMTSpFB ligand are also synthesized in the solid state and characterized by various physico-chemicals and spectral techniques.

### Experimental:

All required chemicals and solvents of AR grade and used as received. All metal chlorides were of S. D. fine Chemicals and used as received.

### Synthesis of HBMTSpFB ligand:

The  $\alpha$ -benzilmonoximethiosemicarbohydrazide was prepared by the reported method<sup>13</sup>. The HBMTSpFB

ligand was synthesized by the following method. A mixture of  $\alpha$ -benzilmonoximethiosemicarbohydrazide (29.3g, 0.10mol) and p-fluorobenzaldehyde (18.6g, 0.15mol) in ethanol was refluxed for about 15h. The reaction mixture was cooled to 301K and the yellow-colored solid was separated, filtered, and washed with hot distilled water and then dried over anhydrous calcium chloride under vacuum.

#### Preparation of metal complexes:

To a hot alcoholic solution of 25ml of HBMTSpFB ligand (2 mol), an aqueous solution of 15ml of the desired metal (II) chloride (1 mol) was added by constant stirring. The final reaction mixture was refluxed for 3 h, and on cooling to 301K the color for separation, was filtered, washed with hot distilled water, and then dried over anhydrous calcium chloride.

#### Physical measurement:

Carbon, hydrogen, nitrogen, and sulfur elements analyses were obtained by using a Thermo-fining FLASH-1112 series analyzer. The FT(IR) spectra of the prepared compounds were recorded on a Perkin-Elmer-100 FT(IR) spectrometer using KBr pellets. PMR spectra were obtained using JEOL (Japan) ECZR-series 600MHz spectrometer deuterated

dimethyl sulfoxide solvent. The electronic absorption spectra were recorded on a JASCO V650 spectrophotometer (double beam). The room temperature magnetic moments were measured by Gouy's method using calibrants as  $Hg[Co(NCS)_4]$  and the diamagnetic corrections were made using the Pascal constant. The electrical conductivity measurements of prepared trivalent metal complexes at room temperature were measured by ELICO-CM 180 conductivity meter.

#### Results and Discussion:

The physical-chemical and analytical data of the HBMTSpFB ligand and its trivalent metal complexes are listed in Table 1. Prepared compounds are colored, non-hygroscopic, and soluble in common organic solvents. Thus, it can be concluded that the HBMTSpFB ligand behaves as a monobasic, tridentate ligand coordinating via the nitrogen atoms of the oximino and azomethine groups and the Sulphur atom of the thiosemicarbohydrazide group<sup>14-15</sup>. Molar conductivity studies of the prepared trivalent metal complexes at room temperature in nitrobenzene (10<sup>-3</sup> M) suggest that non-electrolytic in nature<sup>16-17</sup>.

Table 1: Physico-chemical and analytical data of HBMTSpFB ligand and its metal complexes

Comp	Color	MW	% Yield	MP/DP	Element Content							Cond	MM
					M	C	H	N	O	S	F		
HAMTS <sub>p</sub> FB	Yellow	404.46	73.57	189	-	65.33	4.24	13.85	3.96	7.93	4.70	-	-
Fe(AMTS <sub>p</sub> FB) <sub>2</sub>	Blue	862.76	81.26	208	6.47	61.20	3.71	12.98	3.71	7.42	2.20	1.29	5.49
Co(AMTS <sub>p</sub> FB) <sub>2</sub>	Brown	867.91	80.99	207	6.80	60.84	3.69	12.90	3.69	7.37	2.19	4.25	4.37
Ni(AMTS <sub>p</sub> FB) <sub>2</sub>	Brown	867.61	75.89	202	6.76	60.86	3.69	12.91	3.69	7.38	2.19	2.21	3.14
Cu(AMTS <sub>p</sub> FB) <sub>2</sub>	Green	872.47	81.98	207	7.28	60.52	3.67	12.84	3.67	7.34	2.18	1.49	1.95
Zn(AMTS <sub>p</sub> FB) <sub>2</sub>	Yellow	874.31	80.79	208	7.48	60.39	3.66	12.81	3.66	7.48	2.17	2.35	-
Hg(AMTS <sub>p</sub> FB) <sub>2</sub>	Yellow	1008.92	82.56	207	19.88	52.33	3.17	11.10	3.17	6.34	1.88	1.56	-

**FT(IR) spectra:** To study the HBMTSpFB ligand coordination complexes. The prepared trivalent metal complex's FT(IR) spectra were interpreted by

comparing the free HBMTSpFB ligand spectrum as shown in Table 2. The broadband revealed at 3140cm<sup>-1</sup> FT(IR) spectra of HBMTSpFB ligand due to oximino (-OH) group, disappeared this band in all prepared trivalent metal complexes, suggesting the coordination of HBMTSpFB ligand through oximino nitrogen via deprotonation<sup>18</sup>. The bands at 1516 and 1500cm<sup>-1</sup> due to azomethine (>C=NN-) and oximino (>C=NOH) groups respectively shifted

their position to lower frequencies on complexation<sup>19-20</sup>. The ν(NH) band of 3260cm<sup>-1</sup> does not change its position after complexation. In addition, all the divalent metal complexes displayed the new bands in the region 552-584 and 513-517cm<sup>-1</sup> were assigned to ν(M-N) and ν(M-S) vibrations respectively<sup>21-22</sup>.

Table 2: FT(IR) spectral data of HBMTSpFB ligand and its metal complexes

Comp	-OH	-NH-	-CH=	>C=NN-	>C-NOH	C-F	C-S	N→M	S→M
HAMTS <sub>p</sub> FB	3140	3260	2971	1516	1500	1212	1252	-	-
Fe(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3266	2954	1510	1490	1230	1210	584	550
Co(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3265	2994	1514	1491	1233	1222	619	551
Ni(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3267	3060	1518	1492	1236	1217	553	513
Cu(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3266	3055	1485	1438	1238	1216	552	522
Zn(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3266	2979	1516	1493	1232	1226	552	-
Hg(AMTS <sub>p</sub> FB) <sub>2</sub>	-	3263	2979	1520	1493	1236	1221	517	-

### Electronic spectra and magnetic properties:

Table 3 shows that the HBMTSpFB ligand's electronic spectra feature two prominent broad bands at 265 and 283 nm. Two absorption bands are observed for Schiff bases because of their diastereomeric (keto and imine) structure<sup>23, 24</sup>. All the complexes exhibit a band of elevated energy absorption between 445 and 285 nm. This change is attributable to the charge transfer band<sup>25-26</sup>.

The effective magnetic moment of the Fe(II) complex is 5.49 BM, which is consistent with the presence of five unpaired electrons in the octahedral structure. The electronic spectra of the iron(II) complex revealed absorption bands at 585nm that correspond to the 5T<sub>2g</sub>→5E<sub>g</sub> electronic transition, indicating the presence of an octahedral iron(II) complex<sup>27-28</sup>.

The cobalt(II) complex exhibits the d-d transition bands at 900, 635, and 435 nm in its electronic spectrum. These transitions correspond to the

4T<sub>1g</sub>(F) → 4T<sub>2g</sub>(F) → 1, the 4T<sub>1g</sub>(F) → 4A<sub>2g</sub>(F) → 2, and the 4T<sub>1g</sub>(F) → 4T<sub>1g</sub>(P) → 3, respectively<sup>29-30</sup>. The transitions correspond to the complexes' octahedral geometry. The nickel (II) complex exhibits three d-d transition bands at 970, 620, and 529 nm in its absorption spectrum. The transitions correspond, respectively, to the 3A<sub>2g</sub>(F) → 3T<sub>2g</sub>(F) → 1, 3A<sub>2g</sub>(F) → 3T<sub>1g</sub>(F) → 2 and 3A<sub>2g</sub>(F) → 3T<sub>1g</sub>(P) → 3. These transitions demonstrate the nickel complex has an octahedral structure and D<sub>4h</sub> symmetry<sup>31-32</sup>.

For the Co(II) and Ni(II) complexes, the ligand field parameters Racah inter-electronic repulsion parameter B, ligand field splitting stabilization energy 10 Dq, covalency factor, and ligand field stabilization energy (LFSE) have been calculated. Using the 3/1 ratio, the values of B and Dq of Co(II) complexes were calculated from the transition energy ratio diagram. The value of Table 4 accounts for the covalent nature of the complexes under study containing the evaluated parameters. Cu(II) complex exhibited two absorptions at 686 and 490 nm, which correspond to 2B<sub>1g</sub>→2E<sub>g</sub> versus 2B<sub>1g</sub>→2B<sub>2g</sub>

transitions, corresponding to a deformed octahedral geometry surrounding copper(II)33-34.

The complex's spectrum displays three bands due to three d-d spin-allowed transitions. These are the transitions between the three lower d orbitals and the vacant dx<sup>2</sup>-y<sup>2</sup> orbital. The ground state is 1A<sub>1g</sub>, and the excited states corresponding to the above

transitions are, in order of increasing energy, 1A<sub>2g</sub>, 1B<sub>1g</sub>, and 1E<sub>1g</sub>. Table 3 displays three d-d transition bands at 392, 319, and 283 nm. These bands are attributed to the transitions 1A<sub>1g</sub>→1A<sub>2g</sub>, 1A<sub>1g</sub>→1B<sub>1g</sub>, and 1A<sub>1g</sub>→1E<sub>1g</sub>, respectively. These complexes' electronic spectra indicate a square planar geometry.

Table 3: Electronic spectral data of HBMTSpFB ligand and its metal complexes

Compound	λnm	Transition
HAMTS <sub>p</sub> FB	265	π→π*
	283	π→π*
Fe(AMTS <sub>p</sub> FB) <sub>2</sub>	585	<sup>5</sup> T <sub>2g</sub> → <sup>5</sup> E <sub>g</sub>
	442, 368, 273	L → M charge transfer
Co(AMTS <sub>p</sub> FB) <sub>2</sub>	~900	<sup>4</sup> T <sub>1g(F)}</sub> → <sup>4</sup> T <sub>2g(F)}</sub> (v <sub>1</sub> )
	635	<sup>4</sup> T <sub>1g(F)}</sub> → <sup>4</sup> T <sub>2g(P)}</sub> (v <sub>2</sub> )
Ni(AMTS <sub>p</sub> FB) <sub>2</sub>	970	<sup>3</sup> A <sub>2g(F)}</sub> → <sup>3</sup> T <sub>2g(F)}</sub> (v <sub>1</sub> )
	620	<sup>3</sup> A <sub>2g(F)}</sub> → <sup>3</sup> T <sub>1g(F)}</sub> (v <sub>2</sub> )
Cu(AMTS <sub>p</sub> FB) <sub>2</sub>	686	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> (v <sub>1</sub> )
Zn(AMTS <sub>p</sub> FB) <sub>2</sub>	392, 307, 384	L → M charge transfer
Hg(AMTS <sub>p</sub> FB) <sub>2</sub>	373, 330, 285	L → M charge transfer

### NMR Spectra:

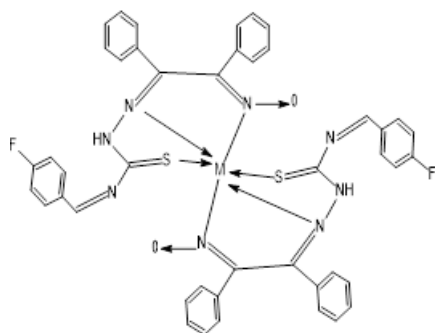
The ligand HBMTSpFB and its metal complexes in DMSO-d<sub>6</sub> are shown in Table 4, along with their respective <sup>1</sup>H NMR spectra (ppm). D<sub>2</sub>O neutralizes the acidic oximino -OH protons (•12.494 ppm) in the HBMTSpFB ligand, suggesting that the hydroxyl group participates in metal ion interaction. ligand HBMTSpFB <sup>1</sup>H-NMR spectrum shows a singlet at •10.56 ppm (s, 1H, Ar-NH), and one singlet at •8.09 ppm (s, 1H, -CH=), caused by a methyl group

attached to the azomethine group, as well as multiplets at •7.472-7.919ppm. Due to the absence of the oximino -OH proton in the Hg(II) complex, the spectrum of the HBMTSpFB ligand displays a broad signal. The absence of this signal indicates that this proton was lost during complexation, and oxygen coordination has occurred<sup>35-36</sup>. The multiplets in the region •7.472-7.919ppm ppm due to aromatic protons, the singlet in the region •10.56 ppm due to the Ar-NH group, and the singlet in the region •8.09

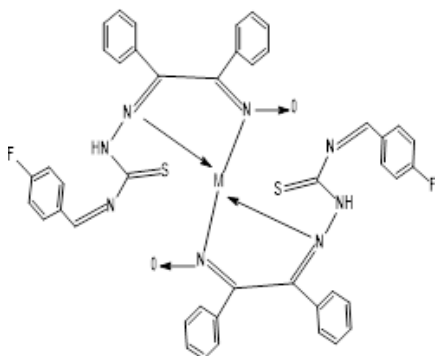
ppm due to  $-\text{CH}=\text{}$  protons of the ring do not change in the metal complexes, indicating that these groups are not involved in coordination ( $\cdot$ ).

## II. CONCLUSION

Analytical, IR, electronic, magnetic, and magnetic moments all pointed to the HBMTSpFB ligand's binding to metal. The present study revealed that HBMTSpFB, a Schiff base, was monobasic tridentate concerning transition metal ions. The tetrahedral geometry was attributed to the Zn(II), and Hg(II) complexes, while the octahedral geometry was allocated to the Co(II), Cu(II), Ni(II), and Fe(II) complexes were determined by analytical and physicochemical research. Based on spectral studies, the structures of complexes are assigned as follows;



Where M = Fe(II), Co(II), Ni(II) and Cu(II)



Where M = Zn(II) and Hg(II)

## REFERENCES

1. Khan, S., Ullah, H., Hussain, R., Khan, Y., Khan, M. U., Khan, M., ... & Khan, M. S. (2023). Synthesis, in vitro bio-evaluation, and molecular docking study of thiosemicarbazone-based isatin/bis-
2. Schiff base hybrid analogs as effective cholinesterase inhibitors. *Journal of Molecular Structure*, 1284, 135351.
3. Yakan, H. (2020). Novel Schiff bases derived from isothiocyanates: synthesis, characterization, and antioxidant activity. *Research on Chemical Intermediates*, 46(8), 3979-3995.
4. Geyer, G. (1971). New histochemical techniques for the demonstration of carboxyl groups in mucosubstances. *The Histochemical Journal*, 3, 241-250.
5. Foroughifar, N., Mobinikhaledi, A., & Rafiee, A. (2014). Efficient synthesis of some novel symmetrical and unsymmetrical pyridine bis-1, 2, 4-triazoles and bis-1, 3, 4-thiadiazoles. *Journal of Chemical Research*, 38(2), 111-114.
6. Hopwood, D., Wood, R. A. B., & Milne, G. (1988). The fine structure and histochemistry of human bile duct in obstruction and choledocholithiasis. *The Journal of pathology*, 155(1), 49-59.
7. Liu, X., Manzur, C., Novoa, N., Celedón, S., Carrillo, D., & Hamon, J. R. (2018). Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. *Coordination Chemistry Reviews*, 357, 144-172.
8. Al-Khodir, F. A., & Refat, M. S. (2015). Synthesis, structural characterization and biological studies of some nalidixic acid-metal complexes: Metalloantibiotic complexes of some divalent and trivalent metal ions. *Journal of Molecular Structure*, 1094, 22-35.
9. Karmakar, M., & Chattopadhyay, S. (2019). A comprehensive overview of the orientation of tetradentate N<sub>2</sub>O<sub>2</sub> donor Schiff base ligands in octahedral complexes of trivalent 3d metals. *Journal of Molecular Structure*, 1186, 155-186.
10. Takroni, K. M., El-Ghamry, H. A., & Fawzy, A. (2019). Evaluation of the catalytic activities of some synthesized divalent and trivalent metal complexes and their inhibition efficiencies for the corrosion of mild steel in sulfuric acid medium. *Journal of Inorganic and Organometallic Polymers and Materials*, 29, 1927-1940.
11. Dhanker, R., Hussain, T., Tyagi, P., Singh, K. J., & Kamble, S. S. (2021). The emerging trend of bio-

- engineering approaches for microbial nanomaterial synthesis and its applications. *Frontiers in Microbiology*, 12, 638003.
- Wei, C., He, Y., Shi, X., & Song, Z. (2019). Terpyridine-metal complexes: Applications in catalysis and supramolecular chemistry. *Coordination chemistry reviews*, 385, 1-19.
  - Liu, X., Manzur, C., Novoa, N., Celedón, S., Carrillo, D., & Hamon, J. R. (2018). Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. *Coordination Chemistry Reviews*, 357, 144-172.
  - Sawant, D. C., Pingale, S. G., & Deshmukh, R. G. (2008). Stability studies of some transition metal chelates of alpha-benzilmonoximethiosemicarbazone. *Asian Journal of Chemistry*, 20(3), 2464.
  - Abu-Dief, A. M., & Mohamed, I. M. (2015). A review on versatile applications of transition metal complexes incorporating Schiff bases. *Beni-suef university journal of basic and applied sciences*, 4(2), 119-133.
  - Ali, A., Pervaiz, M., Saeed, Z., Younas, U., Bashir, R., Ullah, S., ... & Adnan, A. (2022). Synthesis and biological evaluation of 4-dimethylaminobenzaldehyde derivatives of Schiff bases metal complexes: A review. *Inorganic Chemistry Communications*, 145, 109903.
  - Mahmood, R. S., Awad, M. A., & Muslim, R. F. (2020). Preparation of some metallic complexes from selected organic ligands and characterization it spectrophotometry as a model of a ligand scavenger to metals in health applications. *Annals of Tropical Medicine & Public Health*, 23.
  - Jayaseelan, P., Prasad, S., Vedanayaki, S., & Rajavel, R. (2016). Synthesis, characterization, anti-microbial, DNA binding and cleavage studies of Schiff base metal complexes. *Arabian Journal of Chemistry*, 9, S668-S677.
  - Bhagwat, R., Badekar, R., Jain, K. P., & Lokhande, R. (2021). Synthesis and characterization of schiff base 3-[2-(hydroperoxyimino)-1, 2-diphenylethylidene] hydrazinylidene} methyl] phenol metal (II) complexes. *Journal of Advanced Scientific Research*, 12(02 Suppl 1), 230-234.
  - Bhagwat, R., Badekar, R., Jain, K. P., & Lokhande, R. (2021). Synthesis and spectroscopic analyses of Co (II), Ni (II), and Fe (II) complexes with salicylaldehyde derivatives of benzilmonoximehydrazide. *Journal of Advanced Scientific Research*, 12(02 Suppl 1), 225-229.
  - Chaugule, S., Badekar, R., & Lokhande, R. (2019). Antibacterial investigation of  $\alpha$ -Benzilmonoximehydrazone-N, N-dimethylaminobenzaldehyde and its Fe (II), Ni (II) and Pd (II) complexes.
  - Singh, D., Badekar, R., & Lokhande, R. (2018). Structural and Analytical studies of o-, m-and p-substituted bromobenzaldehyde derivatives of benzilmonoximethiocarbohydrazide. *Advance and Innovative Research*, 11.
  - Badekar, R. R., Lokhande, R. S., Kulkarni, S. W., & Patil, R. M. *Journal Homepage:-www. journalijar. com.*
  - Yadav, P., Badekar, R., & Lokhande, R. (2019). SYNTHESIS AND CHARACTERIZATION OF NEWLY SYNTHESIZED COMPOUND OF (2E)-2-[(2E)-(2-BROMOBENZYLIDENE) HYDRAZINYLIDENE]-1, 2-DIPHENYLETHANIMINE. *Advance and Innovative Research*, 6(2), 100.
  - Kamble, P. S., Badekar, R. R., & Singh, V. H. SYNTHESIS AND CHARACTERISATION OF NOVEL COORDINATION COMPOUNDS OF Cr (III), Fe (III), WITH  $\alpha$ -BENZILMONOXIMETHIOCARBOHYDRAZIDE.
  - Yadav, P., Badekar, R., Nag, P., & Lokhande, R. (2021). Synthesis, complexation and spectral study of novel 2-bromobenzaldehyde derived benzilmonoximehydrazone. *Journal of Advanced Scientific Research*, 12(01), 231-234.
  - Chaugule, S., Badekar, R., Shimpi, P., & Lokhande, R. Synthesis and Characterization of Novel Compound derived from  $\alpha$ Benzilmonoximehydrazone with 4, 4-dimethylaminobenzaldehyde and its Fe (II). Ni (II) and Pd (II) Complexes, 1233-1237.
  - Basheer, S. M., Rasin, P., Kumar, S. L. A., Kumar, M. S., & Sreekanth, A. (2022). Investigation on DNA/Protein interaction of thiosemicarbazone based octahedral nickel (II) and iron (III)

- complexes. *Journal of Molecular Structure*, 1260, 132913.
28. Wicholas, M., Mustacich, R., Johnson, B., Smedley, T., & May, J. (1975). Proton nuclear magnetic resonance contact shifts of octahedral iron (II), cobalt (II), and nickel (II) imidazole complexes. *Journal of the American Chemical Society*, 97(8), 2113-2117.
  29. Kumar, V., Singh, R. K., Kumari, V., Kumar, B., & Sharma, S. (2018). Studies of Distorted Octahedral Complexes of Cobalt, Nickel and Copper and Their Antibacterial Properties. *Oriental Journal of Chemistry*, 34(4).
  30. Angelusiu, M. V., Barbuceanu, S. F., Draghici, C., & Almajan, G. L. (2010). New Cu (II), Co (II), Ni (II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation. *European journal of medicinal chemistry*, 45(5), 2055-2062.
  31. Chandra, S., & Gupta, L. K. (2004). EPR and electronic spectral studies on Co (II), Ni (II) and Cu (II) complexes with a new tetradentate [N4] macrocyclic ligand and their biological activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 60(7), 1563-1571.
  32. Afrasiabi, Z., Sinn, E., Padhye, S., Dutta, S., Padhye, S., Newton, C., & Powell, A. K. (2003). Transition metal complexes of phenanthrenequinone thiosemicarbazone as potential anticancer agents: synthesis, structure, spectroscopy, electrochemistry and in vitro anticancer activity against human breast cancer cell-line, T47D. *Journal of Inorganic Biochemistry*, 95(4), 306-314.
  33. Chandra, S., & Gupta, L. K. (2004). EPR and electronic spectral studies on Co (II), Ni (II) and Cu (II) complexes with a new tetradentate [N4] macrocyclic ligand and their biological activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 60(7), 1563-1571.
  34. Angelusiu, M. V., Barbuceanu, S. F., Draghici, C., & Almajan, G. L. (2010). New Cu (II), Co (II), Ni (II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation. *European journal of medicinal chemistry*, 45(5), 2055-2062.
  35. Sawant, D. C., & Deshmukh, R. G. (2011). Structural studies of Co (II), Ni (II), Cu (II) and Zn (II) complexes of N''-[(1Z, 2E)-2-(hydroxyimino)-1-phenylpropylidene]-N'''-[(1E) phenylmethylene] thiocarbonohydrazide. *J. Chem. Pharm. Res*, 3(6), 464-477.
  36. Deshmukh, R. G., Sawant, D. C., & Pingale, S. G. (2008). Synthesis and Characterization of Zn (II), Cd (II), Hg (II) and Pd (II) Complexes of N''-[(1E, 2Z)-2-(hydroxyimino)-1-phenylpropylidene] thiocarbonohydrazide. *Asian Journal of Chemistry*, 20(3), 1723.