

## Study of Transition Metal Complexes of Hydrazones Derived from Different Acid Hydrazides: Synthesis and Characterization

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### ABSTRACT

The transition metal complexes of hydrazones were synthesized by taking two metals, i.e., Cu (II) and Ni (II). The hydrazones were prepared by the hydrazides of three acids, i.e., oxalic acid, malonic acid, and thiomalic acid reacting with the known amount of different aldehydes. Fourier-transform infrared (FTIR) bands in the region of 380–370, 460–450, and 320–300  $\text{cm}^{-1}$  confirm the formation of metal complexes with hydrazones. Synthesized hydrazones and their metal complexes were characterized through analytical techniques, i.e., FTIR, ultraviolet (UV)-visible, and elemental analysis, and the magnetic susceptibility was calculated by Gouy's method. The magnetic moment of copper complexes was 1.77–2.05 B.M. and for nickel complexes was 3.04–4.50 B.M. The metal complexes of hydrazones were gave encouraging results.

**Key words:** Hydrazones, Transition metal complexes, Hydrazine hydrate, Hydrazide, Aldehyde.

### 1. INTRODUCTION

Hydrazones are an important chemical compounds, which have applications in different fields and forms of remarkable type of chelating ligands [1,2]. These compounds attract the attention of researchers in the field of chemistry and pharmacology due to their remarkable antimicrobial, antiviral, and antimalarial properties [3,4]. In the current research scenario, these compounds showed the strong tendency to chelate transitional metals due to ligational properties [5,6]. Hydrazones exhibit several coordination sites, and they can easily coordinate with transitional metals to form transition metal complexes and show good biological properties. The biological activity of acid hydrazides  $\text{R-CO-NH-NH}_2$ , a class of Schiff base, their corresponding aroylhydrazones  $\text{R-CO-NH-N=CH-R}$ , and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [7]. In analytical chemistry, hydrazones find the application by acting as multidentate ligands with metals (usually from the transition group) [8]. Hydrazones derived from the condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than isonicotinic acid hydrazide [9,10]. When transitional metals coordinated with hydrazones, they play a significant role in many catalytic reactions such as oxidation, asymmetric cyclopropanation, and polymerization [11]. Babu, *et al.* prepared 2-acetylpyridine thiosemicarbazone (APT) by reacting 2-acetylpyridine with thiosemicarbazide and used as a reagent for non-extractive spectrophotometric determination of mercury (Hg) [12]. In another study, they used APT for determination of copper (II) in aqueous medium [13]. The current research study shows the simple synthetic route for the synthesis of new transitional metal hydrazone complexes from different five acids which may exhibit better molar conductance, magnetic properties, electronic properties as well as may be showed good biological activities.

Hence, in the present study, the attempt was made to synthesize hydrazone from the acid hydrazide of oxalic acid, malonic acid, and thiomalic acid with five different aldehydes. The synthesized hydrazones

were used to synthesize transition metal complexes of Cu (II) and Ni (II). The prepared hydrazones and transition metal complexes were characterized through elemental analysis, Fourier-transform infrared (FTIR), electronic spectroscopy, magnetic studies, etc.

### 2. EXPERIMENTAL

#### 2.1. Chemicals

Oxalic acid, malonic acid, benzaldehyde, salicylaldehyde, *o*-chloro benzaldehyde, *o*-bromo benzaldehyde, and *o*-iodo benzaldehyde were obtained from Merck India. Thiomalic acid was purchased from Sisco-Chem India. Dimethyl sulfide was purchased from SD Fine Chemicals, India. All chemical were in analytical grade and used as received.

#### 2.2. Characterizations

The percentage of carbon (C), hydrogen (H), and nitrogen (N) for determining molecular formula of the complexes were analyzed by elemental analyzer Euro-E 3000. The nature of chemical bonds and functional groups of prepared samples was analyzed through PerkinElmer FTIR Spectrometer Spectrum II in the range of 400–4000  $\text{cm}^{-1}$ . Transitions within a molecule at electronic levels are observed in the visible and ultraviolet region usually studied by selective absorption of radiation passing through them. Electronic spectra of ligand and complexes were recorded on a ELICO SL-159 UV-visible spectrophotometer in the range of 200–800 nm. Magnetic susceptibility was determined by Gouy's method at the room

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temperature ( $31 \pm 1^\circ\text{C}$ ). The specific magnetic susceptibility ( $\chi_s$ ) was calculated using the following expression:

$$\chi_s = \frac{\alpha + \beta(\Delta - \delta)}{m}$$

Where  $\alpha$  = constant,  $\beta$  = tube calibration constant,  $m$  = mass of the sample.

The molar conductance of an electrolyte is defined as the conducting power of all the ions produced by 1 g mole of the electrolyte in a given solution. It may be expressed by the following relation:

$$\mu = 1000 \text{ k/c}$$

### 2.3. Synthesis of esters of oxalic acid, malonic acid, and thiomalic acid

The esters of oxalic acid, malonic acid, and thiomalic acid ester were prepared. For this, 0.02 M oxalic acid was dissolved in 25 ml of absolute alcohol. To this homogeneous solution, 1.46 mL of 0.02 M dimethyl sulfide was added and mixture was heated at  $80^\circ\text{C}$  for 6 h. The solution was then concentrated and cooled in freezing mixture for overnight to get white solid crystals. These crystals were filtered and washed with ethanol followed by ether and dried in vacuum over anhydrous  $\text{CaCl}_2$  in a desiccator and named as E1. To prepare, the esters of malonic acid and thiomalic acid were also prepared by following the above synthesis method and named as E2 and E3, respectively.

### 2.4. Synthesis of hydrazides of oxalic acid, malonic acid, and thiomalic acid esters

In this method, 0.01 M of oxalic acid ester was dissolved in absolute alcohol, and to this clear solution, 0.01 M of hydrazine hydrate was added dropwise with constant stirring. The resulting mixture was refluxed for 3 h. It was concentrated and cooled overnight to get bright white crystals. These crystals were filtered, washed with pure ethanol followed by ether, and dried in vacuum over anhydrous  $\text{CaCl}_2$  in a desiccator and named as H<sub>1</sub>. The process was repeated with malonic acid ester and thiomalic acid ester to synthesize malonic acid hydrazide and thiomalic acid hydrazide, named as H<sub>2</sub> and H<sub>3</sub>, respectively.

### 2.5. Synthesis of hydrazones from hydrazides

The hydrazones were synthesized by taking 5 different aldehydes, i.e., benzaldehyde, salicylaldehyde, *o*-chloro benzaldehyde, *o*-bromo benzaldehyde, and *o*-iodo benzaldehyde with prepared acid hydrazides.

#### 2.5.1. Benzaldehyde-based hydrazones

For this, 0.59 g of oxalic acid hydrazide was dissolved in 10 mL of 30% acetic acid and heated to get solution. 1.06 g benzaldehyde was added to cold solution, a cream-colored solid separated out which was washed with alcohol followed by ether. It was then dried under reduced pressure in a desiccator and named as BOH. Benzaldehyde hydrazones of malonic acid hydrazide and thiomalic acid hydrazide were also synthesized followed by the same synthetic procedure and named as BMH and BTMH, respectively.

#### 2.5.2. Salicylaldehyde based hydrazones

To prepare salicylaldehyde based hydrazones, 0.59 g of oxalic acid hydrazide was dissolved in 10 mL of 30% acetic acid and heated to get solution. 1.22 g salicylaldehyde was added to cold solution, a cream-colored solid separated out which was washed with alcohol followed by ether. It was then dried under reduced pressure in a desiccator and named as SOH. Salicylaldehyde hydrazones of malonic acid hydrazide and thiomalic acid hydrazide were also synthesized followed by the same synthetic procedure and named as SMH and STMH, respectively.

#### 2.5.3. *O*-chloro benzaldehyde based hydrazones

To prepare *o*-chloro benzaldehyde based hydrazones, 0.59 g of oxalic acid hydrazide was dissolved in 10 mL of 30% acetic acid and heated to get solution. 1.405 g *o*-chloro benzaldehyde was added to cold solution, a cream-colored solid separated out which was washed with alcohol followed by ether. It was then dried under reduced pressure in a desiccator and named as CBOH. *o*-chloro benzaldehyde hydrazones of malonic acid hydrazide and thiomalic acid hydrazide were also synthesized followed by the same synthetic procedure and named as CBMH and CBTMH, respectively.

#### 2.5.4. *O*-bromo benzaldehyde based hydrazones

To prepare *o*-bromo benzaldehyde based hydrazones, 0.59 g of oxalic acid hydrazide was dissolved in 10 mL of 30% acetic acid and heated to get solution. 1.85 g *o*-bromo benzaldehyde was added to cold solution, a cream-colored solid separated out which was washed with alcohol followed by ether. It was then dried under reduced pressure in a desiccator and named as BBOH. *o*-bromo benzaldehyde hydrazones of malonic acid hydrazide and thiomalic acid hydrazide were also synthesized followed by the same synthetic procedure and named as BBMH and BBTMH, respectively.

#### 2.5.5. *O*-iodo benzaldehyde based hydrazones

To prepare *o*-iodo benzaldehyde based hydrazones, 0.59 g of oxalic acid hydrazide was dissolved in 10 mL of 30% acetic acid and heated to get solution. 2.32 g *o*-iodo benzaldehyde was added to cold solution, a cream-colored solid separated out which was washed with alcohol followed by ether. It was then dried under reduced pressure in a desiccator and named as IBOH. *o*-iodo benzaldehyde hydrazones of malonic acid hydrazide and thiomalic acid hydrazide were also synthesized followed by the same synthetic procedure and named as IBMH and IBTMH, respectively.

### 2.6. Synthesis of Metal Complexes of Hydrazones

#### 2.6.1. Synthesis of copper complexes

To the synthesis of copper complex of synthesized hydrazones, the 0.005M acid hydrazide was dissolved in 25 mL of  $\text{CH}_3\text{OH}$  and heated till dissolved. To the above hot solution, 0.005M copper nitrate in  $\text{CH}_3\text{OH}$  and 0.01M aldehyde in  $\text{CH}_3\text{OH}$  were added with continuous stirring and then refluxed for 12 h. On cooling, the resulting precipitate was collected by filtration, washed with ethanol followed by ether, and dried in vacuum over anhydrous  $\text{CaCl}_2$ . The mixing concentration of different components to prepare a copper complex of hydrazones was reported in Table 1.

#### 2.6.2. Synthesis of nickel complexes

Nickel complexes of hydrazones were prepared using 0.005M nickel nitrate followed by the same synthetic method. The mixing of different constituents to prepare nickel complexes of hydrazones was reported in Table 2.

## 3. RESULTS AND DISCUSSION

### 3.1. Elemental Analysis and Molar Conductance

The elemental analysis data of the synthesized complexes are presented in Tables 3-5. All the complexes were soluble in common solvents such as methanol, acetone, and chloroform. Table 6 summarizes the molar conductance of these complexes.

### 3.2. FTIR spectroscopy

It had been observed that vibration bands associated with stretching of bond, involving coordinated atom, are usually shifted to a lower

**Table 1:** Data for synthesis of copper complexes of hydrazones.

Acid hydrazide 0.005M	Copper nitrate	Aldehyde 0.01M	Sample name
Oxalic acid hydrazide	0.005M	Benzaldehyde	CBOH
		Salicylaldehyde	CSOH
		<i>o</i> -Chloro benzaldehyde	CCBOH
		<i>o</i> -Bromo benzaldehyde	CBBOH
		<i>o</i> -Iodo benzaldehyde	CIBOH
Malonic acid hydrazide	0.005M	Benzaldehyde	CBMH
		Salicylaldehyde	CSMH
		<i>o</i> -Chloro benzaldehyde	CCBMH
		<i>o</i> -Bromo benzaldehyde	CBBMH
		<i>o</i> -Iodo benzaldehyde	CIBMH
Thio malic acid hydrazide	0.005M	Benzaldehyde	CBTMH
		Salicylaldehyde	CSTMH
		<i>o</i> -Chloro benzaldehyde	CCBTMH
		<i>o</i> -Bromo benzaldehyde	CBBTMH
		<i>o</i> -Iodo benzaldehyde	CIBTMH

**Table 2:** Data for synthesis of nickel complexes of hydrazones.

Acid hydrazide	Nickel nitrate	Aldehyde 0.01M	Sample name
Oxalic acid hydrazide	0.005M	Benzaldehyde	NBOH
		Salicylaldehyde	NSOH
		<i>o</i> -Chloro benzaldehyde	NCBOH
		<i>o</i> -Bromo benzaldehyde	NBBOH
		<i>o</i> -Iodo benzaldehyde	NIBOH
Malonic acid hydrazide	0.005M	Benzaldehyde	NBMH
		Salicylaldehyde	NSMH
		<i>o</i> -Chloro benzaldehyde	NCBMH
		<i>o</i> -Bromo benzaldehyde	NBBMH
		<i>o</i> -Iodo benzaldehyde	NIBMH
Thio malic acid hydrazide	0.005M	Benzaldehyde	NBTMH
		Salicylaldehyde	NSTMH
		<i>o</i> -Chloro benzaldehyde	NCBTMH
		<i>o</i> -Bromo benzaldehyde	NBBTMH
		<i>o</i> -Iodo benzaldehyde	NIBTMH

frequency on coordination. The effective symmetry of the ligand is normally reduced by coordination, which may cause the appearance of new bands and splitting of bands which may degenerate in the free ligand vibration involving coordinate bond. Stretching and banding modes generally appear in the low-frequency region. When a ligand coordinates with metal ions, the lowering by 10–30  $\text{cm}^{-1}$  in (C=N stretching) azomethine nitrogen band was observed [14].

In our study, around 1630–1600  $\text{cm}^{-1}$  along with lower intensity was observed which may be attributed to the stretching vibrations of azomethine group (>C=N-) suggested the coordination of ligand to the metal ion through imine N in coordination [15-18]. It was observed from FTIR spectra in Table 7, and certain bands were common in the spectra of metal complex and ligand which shows successfully synthesis of complex formation. IR spectra of metal complexes, the

peak due to  $\nu(\text{N-H})$ , did not show any shift ruling out its coordination with central metal ion. The band due to  $\nu(\text{C=O})$  experienced a negative shift by 40–50  $\text{cm}^{-1}$  appeared at 1660  $\text{cm}^{-1}$ , while N-N band shifted to higher wave number at 1080  $\text{cm}^{-1}$ . These observations led to the conclusion that the amide oxygen of C=O and nitrogen of N-N bond had involved in complexation. The phenolic stretching frequency at 1380  $\text{cm}^{-1}$  in salicylaldehyde ligand shifted to the higher region 1400–1390  $\text{cm}^{-1}$ , which was caused due to the coordination of O-H group.

Some new bands were also appeared in the FTIR of metal complexes in the region 380–370, 460–450, and 320–300  $\text{cm}^{-1}$  which may be attributed due to formation of M-N, M-O, and M-S bonds, respectively, which further give evidence in favor of coordination of metals through azomethine amide oxygen and C-S [19].

**Table 3:** Analytical data of metal complexes with oxaloyl hydrazine.

Sample	Molecular weight	Analytical data							
		C	H	N	M	O	Cl	Br	I
BOH	293.60	65.25	4.72	18.99	-	10.80	-	-	-
CBOH	514.30	37.00	3.46	16.30	12.00	30.99	-	-	-
NBOH	509.50	37.60	3.50	16.41	11.50	30.99	-	-	-
SOH	325.90	58.89	3.99	17.09	-	19.60	-	-	-
CSOH	387.00	49.00	2.85	14.40	16.30	16.50	-	-	-
NSOH	382.00	49.85	2.89	14.00	15.30	16.70	-	-	-
CBOH	362.00	52.01	3.00	15.00	-	8.60	19.01	-	-
CCBOH	586.00	32.11	2.31	14.01	10.60	27.00	12.00	-	-
NCBOH	581.00	32.90	2.40	14.05	9.90	26.89	12.01	-	-
BBOH	451.90	42.41	2.62	12.37	-	7.00	-	35.26	-
CBBOH	675.00	28.20	2.32	12.40	9.32	23.64	-	23.65	-
NBBOH	670.00	28.52	2.32	12.47	8.70	23.80	-	23.81	-
IBOH	545.00	35.00	2.11	10.26	-	5.80	-	-	46.49
CIBOH	769.00	24.91	2.06	10.90	8.20	20.70	-	-	32.09
NIBOH	764.00	25.00	2.07	10.91	7.60	20.91	-	-	33.18

**Table 4:** Analytical data of metal complexes with malonoyl hydrazones.

Sample	Molecular weight	Analytical data							
		C	H	N	M	O	Cl	Br	I
BMH	307.00	66.00	5.00	18.00	-	10.00	-	-	-
CBMH	528.00	38.00	3.00	15.30	12.00	30.99	-	-	-
NBMH	523.00	38.05	3.02	16.00	11.00	30.00	-	-	-
SMH	339.50	59.50	4.61	16.40	-	18.00	-	-	-
CSMH	401.00	50.60	3.40	13.80	15.60	15.90	-	-	-
NSMH	396.00	51.00	3.32	13.90	14.95	15.90	-	-	-
CBMH	369.50	54.00	3.00	14.00	-	8.00	18.00	-	-
CCBMH	600.00	33.04	2.90	13.00	10.00	26.00	11.00	-	-
NCBMH	595.00	34.00	3.00	14.00	9.00	26.05	11.05	-	-
BBMH	469.50	43.74	2.98	12.00	-	6.83	-	34.29	-
CBBMH	689.00	29.53	2.59	12.13	9.18	23.12	-	23.14	-
NBBMH	684.00	29.72	2.60	12.22	8.53	23.34	-	23.32	-
IBMH	560.00	36.40	2.46	9.98	-	5.70	-	-	45.32
CIBMH	783.00	26.00	2.28	10.60	8.00	20.40	-	-	32.38
NIBMH	778.00	26.16	2.28	10.71	7.50	20.51	-	-	32.55

### 3.3. Magnetic Studies of Hydrazone Complexes of Cu (II) and Ni (II)

For copper complexes, many of researchers reported the value of magnetic moment lies between 1.75 and 2.20 B.M. [20] which is reported in Table 8. The value of magnetic moment in our study lies between 1.77 and 2.05 B.M. which may be attributed to the orbital contribution and to the distortion of octahedral structure leading to a square planer geometry of the molecule [21]. Due to the polymeric species formation, a decrease in the normal magnetic moment value has been reported in most of the Cu(II) complexes. This subnormal value of magnetic moment of the Cu(II) complexes at room temperature indicated a partial spin. The magnetic moment observed for the nickel (II) complexes was in the range of 3.04–4.50 B.M. which was slightly

higher than the spin-only value of 2.83 B.M. for high-spin octahedral complexes and reported in Table 9.

### 3.4. Electronic Spectral Studies

#### 3.4.1. Cu (II) complexes

The planner complexes of Cu(II) are theoretically expected to show three or even four bands, of these two bands are observed. The main bands were concentrated in the range of 15000–18500  $\text{cm}^{-1}$ , in all complexes. The position of this main d-d transition depends on the nature of ligands in the coordination sphere and the degree of distortion from cubic symmetry. It was found that the distortion from cubic symmetry was not large when the band was concentrated around

**Table 5:** Analytical data of metal complexes of thio maloyl hydrazones.

Sample	molecular weight	analytical data								
		C	H	N	M	O	S	Cl	Br	I
BTMH	353.90	61.00	5.00	15.00	-	8.90	9.00	-	-	-
CBTMH	577.00	37.02	3.05	14.00	10.00	27.00	5.00	-	-	-
NBTMH	572.70	37.00	3.07	14.05	9.80	27.02	5.03	-	-	-
STMH	385.90	55.00	4.00	14.00	-	16.00	8.00	-	-	-
CSTMH	447.00	48.02	3.00	12.00	14.00	14.00	7.00	-	-	-
NSTMH	442.00	48.10	3.05	12.05	13.02	14.02	7.02	-	-	-
CBTMH	422.90	51.00	3.00	13.00	-	7.00	7.05	16.05	-	-
CCBTMH	646.00	33.00	2.90	12.00	9.00	24.00	4.00	10.10	-	-
NCBTMH	641.00	33.05	2.99	12.90	8.90	24.05	4.01	11.00	-	-
BBTMH	511.90	42.00	3.00	10.70	-	6.00	7.05	-	31.18	-
CBBTMH	735.00	29.00	2.55	11.01	8.00	21.60	4.30	-	21.68	-
NBBTMH	730.00	29.34	2.56	11.04	7.89	21.75	4.01	-	21.88	-
IBTMH	599.00	35.00	2.00	9.00	-	5.00	5.00	-	-	41.00
CIBTMH	829.00	26.00	1.90	10.00	7.00	19.00	3.00	-	-	30.01
NIBTMH	824.10	26.02	1.92	10.01	7.90	19.02	3.02	-	-	30.05

**Table 6:** Molar conductance of metal complexes of hydrazones.

Sample	Molar conductance ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Sample	Molar conductance ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
CBOH	222	NBOH	223
CSOH	-	NSOH	-
CCBOH	220	NCBOH	220
CBBOH	224	NBBOH	224
CIBOH	226	NIBOH	224
CBMH	220	NBMH	220
CSMH	-	NSMH	-
CCBMH	222	NCBMH	222
CBBMH	224	NBBMH	223
CIBMH	220	NIBMH	220
CBTMH	220	NBTMH	220
CSTMH	-	NSTMH	-
CCBTMH	224	NCBTMH	222
CBBTMH	222	NBBTMH	222
CIBTMH	-	NIBTMH	-

$15000 \text{ cm}^{-1}$ , while in case of strong distortion, it was observed at  $1800 \text{ cm}^{-1}$  or even at higher wave number. In several copper-amine complexes, the band range was  $15500\text{--}18500 \text{ cm}^{-1}$ , while in copper-aquo complex ion, the main band was seen at about  $12500 \text{ cm}^{-1}$  suggesting amines as strong field ligands [22].

Copper (II)  $d^9$  has one paired electron, and in the environment of ligand field,  $t_{2g}^6 e_g^3$  configuration is attained due to the relatively low symmetry (i.e., less than cubic) of the environments in which the copper (II) ion is found. The  $d^9$  configuration makes Cu (II) subject to Jahn-Teller distortion I octahedral or tetrahedral ligand field [23]. The Cu (II) ion gives  $^2D$  ground state. In six coordinated octahedral field, a single absorption band representing the transition  $2E_g \rightarrow 2T_{2g}$ , i.e.,  $10 Dq$  expected was reported in Table 10.

#### 3.4.2. Ni (II) complexes

In general, the ligand field spectra of octahedrally coordinated nickel (II) ions consist of three bands: The first band ( $\nu_1$ ) assigned to the transition  $^3A_{2g} \rightarrow ^3T_{2g}$  is usually found in the region  $7000\text{--}12000 \text{ cm}^{-1}$ , and the second band ( $\nu_2$ ) is assigned to the transition  $^3A_{2g} \rightarrow ^3T_{1g}(P)$  and is usually found in the region  $21000\text{--}30000 \text{ cm}^{-1}$ . Furthermore, two spin-forbidden transitions are sometimes found: ( $\nu_4$ ) in the region  $11500\text{--}15500 \text{ cm}^{-1}$  and ( $\nu_5$ ) in the region  $17000\text{--}24000 \text{ cm}^{-1}$  [24]. From the electronic spectra of prepared metal complexes, the bands were observed in the range of  $10500\text{--}12850 \text{ cm}^{-1}$  for  $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$ ,  $16300\text{--}20300 \text{ cm}^{-1}$  for  $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$ , and  $25350\text{--}28700 \text{ cm}^{-1}$  for  $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$  transitions as reported in Table 11.

**Table 7:** FTIR observations for hydrazones and metal complexes of hydrazones.

Sample	FTIR bands ( $\text{cm}^{-1}$ )								
	-NH	-C=O	-N-N	-C=N	-OH	-M-O	-M-N	-CH <sub>2</sub>	-C-S
BOH	3150	1710	1050	1630	-	-	-	-	-
CBOH	3165	1660	1080	1590	860	450	370	-	-
NBOH	3155	1670	1075	1580	850	460	375	-	-
SOH	3158	1710	1050	1630	1380	-	-	-	-
CSOH	3152	1665	1080	1590	1390	460	375	-	-
NSOH	3161	1660	1075	1580	1400	450	380	-	-
CBOH	3160	1710	1050	1630	-	-	-	-	-
CCBOH	3150	1665	1075	1585	860	450	370	-	-
NCBOH	3166	1670	1075	1580	850	460	375	-	-
BBOH	3169	1710	1050	1630	-	-	-	-	-
CBBOH	3158	1670	1060	1585	865	455	365	-	-
NBBOH	3159	1670	1075	1580	850	460	375	-	-
IBOH	3154	1710	1050	1630	-	-	-	-	-
CIBOH	3158	1670	1065	1580	860	450	360	-	-
NIBOH	3162	1670	1075	1580	850	460	375	-	-
BMH	3169	1710	1050	1630	-	-	-	2910	-
CBMH	3162	1665	1085	1590	865	450	370	2915	-
NBMH	3150	1670	1070	1585	850	460	375	2912	-
SMH	3156	1710	1050	1630	1380	-	-	2905	-
CSMH	3167	1665	1080	1590	1390	460	375	2911	-
NSMH	3159	1665	1070	1585	1400	450	380	2908	-
CBMH	3163	1710	1050	1630	-	-	-	2903	-
CCBMH	3155	1660	1070	1580	865	455	375	2922	-
NCBMH	3156	1670	1075	1580	850	460	375	2920	-
BBMH	3151	1710	1050	1630	-	-	-	2914	-
CBBMH	3165	1660	1070	1580	865	455	375	2906	-
NBBMH	3160	1670	1070	1585	855	465	370	2900	-
IBMH	3161	1710	1050	1630	-	-	-	2907	-
CIBMH	3159	1660	1070	1580	865	455	375	2919	-
NIBMH	3154	1670	1075	1580	850	460	370	2921	-
BTMH	3158	1710	1050	1630	-	-	-	2902	1190
CBTMH	3151	1660	1070	1580	865	455	375	2910	1195
NBTMH	3160	1670	1075	1580	850	460	370	2905	1200
STMH	3156	1710	1050	1630	1380	-	-	2903	1190
CSTMH	3156	1665	1080	1590	1390	460	375	2910	1195
NSTMH	3153	1660	1075	1580	1140	450	380	2922	1200
CBTMH	3169	1710	1050	1630	-	-	-	2931	1190
CCBTMH	3150	1660	1070	1580	865	455	375	2905	1195
NCBTMH	3156	1670	1070	1585	855	465	375	2914	1200
BBTMH	3151	1710	1050	1630	-	-	-	2918	1190
CBBTMH	3168	1660	1070	1580	865	455	375	2909	1195
NBBTMH	3163	1670	1070	1585	855	465	375	2900	1200
IBTMH	3156	1710	1050	1630	-	-	-	2900	1190
CIBTMH	3169	1660	1070	1580	865	455	375	2906	1130
NIBTMH	3150	1670	1070	1585	855	465	375	2903	1120

**Table 8:** Magnetic data for copper complexes.

Sample	Molar susceptibility ( $\chi_M \times 10^6$ )	Corrected molar susceptibility ( $\chi_{M\text{Corr}} \times 10^6$ )	Effective magnetic moment ( $\mu_{\text{eff}}$ ) B.M.
CBOH	1209.05	1229.02	1.77
CSOH	1325.43	1365.12	1.88
CCBOH	1419.23	1485.22	1.96
CBBOH	1350.65	1380.88	1.95
CIBOH	1283.47	1299.12	1.83
CBMH	1558.04	1590.11	2.03
CSMH	1487.89	1520.01	2.05
CCBMH	1255.18	1300.10	1.98
CBBMH	1579.81	1610.18	1.85
CIBMH	1385.14	1415.13	2.01
CBTMH	1494.09	1550.22	1.94
CSTMH	1198.58	1225.20	1.97
CCBTMH	1494.09	1550.22	1.94
CBBTMH	1385.14	1415.13	2.01
CIBTMH	1579.81	1610.18	1.85

**Table 9:** Magnetic data for nickel complexes.

Sample	Molar susceptibility ( $\chi_M \times 10^6$ )	Corrected molar susceptibility ( $\chi_{M\text{Opp}} \times 10^6$ )	Effective magnetic moment ( $\mu_{\text{eff}}$ ) B.M.
NBOH	3558.23	4659.40	3.04
NSOH	4370.85	3574.50	3.12
NCBOH	3778.91	3888.50	3.43
NBBOH	3996.62	4056.45	4.21
NIBOH	3866.15	3955.23	4.16
NBMH	3654.29	3754.45	4.09
NSMH	3434.34	3536.54	3.33
NCBMH	3465.50	3569.15	3.65
NBBMH	3678.56	3788.45	3.85
NIBMH	3758.45	3852.56	3.78
NBTMH	3788.59	3856.57	3.89
NSTMH	3859.54	3955.68	4.50
NCBTMH	3660.23	4658.20	3.04
NBBTMH	3472.85	3572.50	3.12
NIBTMH	3778.91	3886.50	3.43

**Table 10:** Electronic spectral data for copper hydrazone complexes.

Sample	Bands ( $\text{cm}^{-1}$ )	Transition	Sample	Bands ( $\text{cm}^{-1}$ )	Transition
CBOH	13350	${}^2E_g \rightarrow {}^2T_g^2$	CCBMH	13800	${}^2E_g \rightarrow {}^2T_g^2$
CSOH	1350	${}^2E_g \rightarrow {}^2T_g^2$	CBBMH	14600	${}^2E_g \rightarrow {}^2T_g^2$
CCBOH	13700	${}^2E_g \rightarrow {}^2T_g^2$	CIBMH	14200	${}^2E_g \rightarrow {}^2T_g^2$
CBBOH	14520	${}^2E_g \rightarrow {}^2T_g^2$	CBTMH	13350	${}^2E_g \rightarrow {}^2T_g^2$
CIBOH	14820	${}^2E_g \rightarrow {}^2T_g^2$	CSTMH	14880	${}^2E_g \rightarrow {}^2T_g^2$
CBMH	15000	${}^2E_g \rightarrow {}^2T_g^2$	CCBTMH	13350	${}^2E_g \rightarrow {}^2T_g^2$
CSMH	16000	${}^2E_g \rightarrow {}^2T_g^2$	CBBTMH	13560	${}^2E_g \rightarrow {}^2T_g^2$
CIBTMH	13765	${}^2E_g \rightarrow {}^2T_g^2$			

**Table 11:** Electronic spectral data of nickel hydrazone complexes.

Sample	Bands (cm <sup>-1</sup> )	Transition	Sample	Bands (cm <sup>-1</sup> )	Transition
NBOH	11400	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NBBMH	12500	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	19800	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		17800	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	26300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		28700	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NSOH	10500	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NIBMH	11300	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	18400	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		16950	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	27600	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		25350	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NCBOH	11200	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NBTMH	12850	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	19300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		16300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	26800	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		26100	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NBBOH	12200	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NSTMH	11450	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	20300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		18900	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	28300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		27500	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NIBOH	10700	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NCBTMH	12400	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	17200	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		17100	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	25700	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		28250	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NBMH	12300	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NBBTMH	11200	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	19500	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		19300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
				26800	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NSMH	10700	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$	NIBTMH	12200	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	17200	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$		20300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
	25700	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$		28300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
NCBMH	11600	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$			
	18300	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$			
	27400	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$			

#### 4. CONCLUSION

Hydrazones of acid hydrazides were synthesized by reacting hydrazides with aldehydes. The esters of oxalic acid, malonic acid, and thiomalic acid were reacted with hydrazine hydrate to form hydrazides, then the hydrazides were reacted with benzaldehyde, salicylaldehyde, *o*-chloro benzaldehyde, *o*-bromo benzaldehyde, and *o*-iodo benzaldehyde to synthesize hydrazones. Copper nitrate and nickel nitrate were reacted with as prepared hydrazones to synthesize metal complexes. The hydrazones and metal complexes were characterized through FTIR, UV-visible, elemental analysis and the molar conductance, and magnetic susceptibility was also calculated. The FTIR bands observed around 1630–1600 cm<sup>-1</sup> due to (>C=N-) group, while bands at 380–370, 460–450, and 320–300 cm<sup>-1</sup> were observed due to the formation of M-N, M-O, and M-S bonds, which confirms the formation of metal complexes. UV-visible spectroscopy confirms that copper complexes showed  $^2E_g \rightarrow ^2T_{2g}$  transitions, while nickel complexes showed

$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ ,  $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ , and  $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$  transitions. The synthesized products showed encouraging results and may be used in different inorganic applications.

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