
Synthesis, Characterization, Thermal Degradation Studies of Transition Metal Complexes of 5-Methoxy-5,6-Bis(3-Nitrophenyl) - 4, 5-Dihydro-1, 2, 4- Triazine – 3 (2H) - Thione and Their Biological Activities

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Abstract: 5-methoxy-5,6-bis(3-nitrophenyl)-4,5-dihydro-1,2,4-triazine-3(2H)-thione (NBTS) and its Ni(II), Co(II) and Cu(II) metal complexes have been synthesized and their structure elucidated by elemental analysis, conductivity measurements, UV-Visible, FT-IR, ¹H-NMR, LC-Mass and thermal analysis. The complexes are soluble in almost all organic solvents and are non-electrolytes. Thermal analysis are investigated and showed either two or three thermal decomposition steps. Kinetic parameters such as E_a , ΔH , ΔS and ΔG of the thermal decomposition stages have been evaluated using Broido's method. The antibacterial and antioxidant activity of the uncoordinated ligand and its metal complexes have been studied. The results indicate that the complexes are more potent when compared to the ligand.

Keywords: Thiosemicarbazone, thermal analysis, conductivity measurements, antibacterial and antioxidant activity.

1. INTRODUCTION

Template reactions remain at the heart of macrocyclic chemistry and are the best aids for the preparation of macrocyclic complexes.^[1-2] Generally transition metal ions have been used as templates.^[3] The importance of macrocyclic complexes in coordination chemistry is because of its various applications in biological processes such as photosynthesis and dioxygen transport, catalytic properties, potential applications as metal extractants and radiotherapeutic agents.^[4] The importance of macrocyclic complexes is due to their resemblance with many natural systems like porphyrins and cobalamines.^[5] Some macrocyclic complexes have been reported to have anti-inflammatory approach.^[6]

Schiff's base macroligands derived from thiosemicarbazide and their complexes are of significant interest for their pharmacological properties as antibacterial and anticancer agents.^[7-8] One of the most promising areas in which thiosemicarbazone compounds are being developed is their use against cancer. The presence of metal ion increases the activity or contributes to mitigate the side effects of the organic parent compounds.^[9] Thiosemicarbazones are a unique and versatile type of ligand amongst the sulfur family not only because they possess a variety of flexible donor sets but also due to the fact that they exhibit diverse biological, structural and electrochemical properties.^[10] It is well established that their transition metal complexes are more potent antimalarial, antibacterial, antileprotic and antitumor agents than parent thiosemicarbazones.^[11] Literature survey reveals that many thiosemicarbazone derivatives are known to possess good biological activities like antimicrobial,^[12-13] anti-inflammatory, analgesic, diuretic and antiviral activities. Reactions of 5-methoxy-5, 6-bis (3-nitrophenyl)-4, 5-dihydro-1, 2, 4-triazine-3(2H)- thione with nickel (II), cobalt (II) and copper (II) chloride yield different complexes depending on the synthetic conditions.^[14]

In the present paper, we are reporting the template synthesis of thioamidemacrocyclic complexes of copper (II), cobalt (II) and nickel (II) ions. The new complexes are characterized with the help of various physicochemical techniques like IR, ¹H NMR, magnetic susceptibilities, elemental analysis, conductance measurements and the calculated activation kinetic parameters of the decomposition of

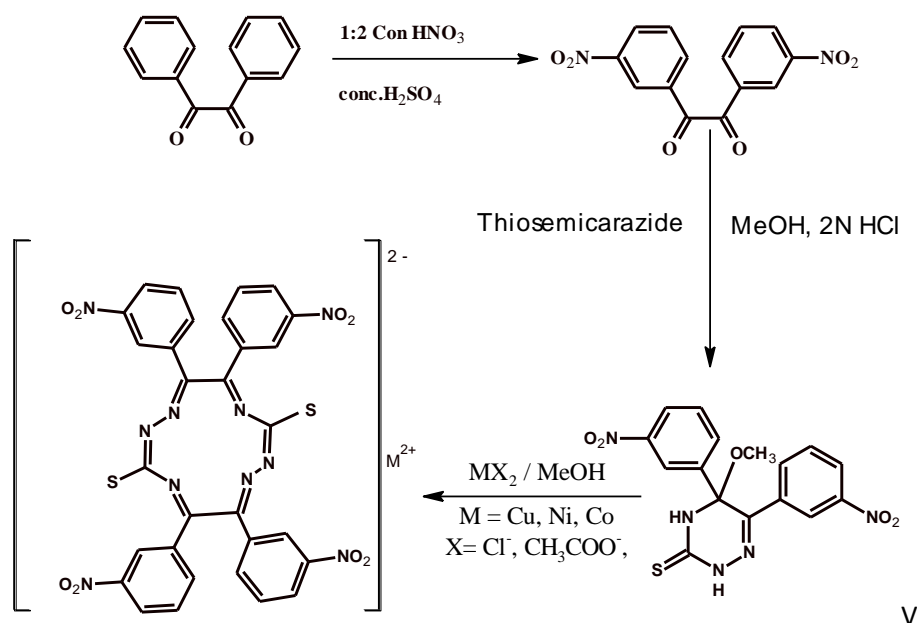
the prepared complexes, show that the thermal stability of metal complexes depends essentially on the nature of both the central metal ion and the ligand. The study includes the structural elucidation of the isolated complexes by conventional techniques, their thermal degradation kinetics by Broido's model.^[15] Also, the antioxidant activity of all complexes using ABTS or DPPH radical scavenging methods and antibacterial activities have been discussed.

2. MATERIALS AND METHODS

The chemicals thiosemicarbazide, benzil and methanol were purchased from the Sigma Aldrich, Laboratory chemicals, Bangalore, Karnataka, India. Nickel(II)acetate tetrahydrate, Cobalt(II)chloride tetrahydrate, Copper(II)acetate monohydrate were purchased from MERCK, Sudha Traders, Shimoga, Karnataka, India and were used as received. The solvents were distilled and dried before use by following the reported procedure.^[16]

2.1. Physical Measurements

The elemental analysis (C, H, N, S) was performed using Perkin-Elmer 2400 II CHNS/O Elemental analyzer. Melting point of the ligand and their metal complexes was measured by using melting point apparatus model code NAMPA/045 and are uncorrected. UV-Visible spectra were measured in DMF on an ocean optics USB 4000 USA spectrophotometer, using 1cm path length cuvette at room temperature. Infrared spectra were recorded using FT-IR 8400s Shimadzu spectrometer with KBr pellets in the range of 400-4000 cm^{-1} . The molar conductance data was measured using freshly prepared DMSO solutions (10^{-3}M) at 25°C with a EQUIP-TRONICS model-660A instrument. The ^1H NMR spectra have been recorded as 400 MHz Varian-AS NMR spectrometer in DMSO-d_6 using tetramethylsilane (TMS) as the internal standard. The thermal analysis (DTA and TGA) were carried out on a Shimadzu DT-30 and TG-50 thermal analyzers in the range $27-800^{\circ}\text{C}$ at the heating rate of $10^{\circ}\text{Cmin}^{-1}$ in nitrogen atmosphere 80.0mL/min. The magnetic susceptibility values measured at the room temperature using the Gouy method with mercuric tetrathiocyanatocobaltate (II) as standard. The diamagnetic corrections were made using Pascal's constants (El-Tabl1996). Mass spectra was recorded using the instrument Code; SC/AD/10-014.



Scheme 1. Synthesis of 5-methoxy-5,6-bis(3-nitrophenyl)-4,5-dihydro-1,2,4-triazine-3(2H)-thione and its complexes

2.2. Synthesis of 1,2-Bis(3-Nitrophenyl) Ethane-1,2-Dione

A solution of benzil (8.4g, 0.04mol) dissolved in 10mL of $\text{conc. H}_2\text{SO}_4$ and the solution containing conc. HNO_3 and $\text{conc. H}_2\text{SO}_4$ in (1:2) about 20mL was added dropwise and slowly with vigorous stirring under freezing mixture bath, after completing the addition of nitrating mixture, stirring was continued for about 12hrs at 60°C . After the reaction, solution was poured into crushed ice. The separated solid product was filtered and washed with cold water 5-6 times and dried at room temperature.

2.3. Synthesis of 5-Methoxy-5, 6-Bis (3-nitrophenyl) - 4, 5-Dihydro- 1, 2, 4 – Triazine –3(2H)-Thione (NBTS)

A solution of thiosemicarbazide (2.00g, 0.022mol) in 50mL of methanol and 20 mL of 4N HCl to the solution of 1, 2-bis(3-nitrophenyl)ethane-1,2-dione (6.08g, 0.02mol) in 75mL hot methanol was added slowly drop wise with vigorous stirring. After the addition of the reactants, the reaction mixture was stirred upto 12hrs at about 45^o C. The reaction was monitored by TLC by using silica gel-G coated plates and using methanol and chloroform in the ratio (0.1:0.9) as an eluent. The reaction mixture on standing overnight an ivory coloured solid separated out, which was filtered off. The precipitate was washed with cold solution of water and methanol in the ratio (9:1). The solid so obtained, then recrystallised from the ethanol and dried in vacuo. Yield: 88%; IR (KBr, cm⁻¹): 3069 (N-H), 1556 (C=N), 1071 (N-N), 1218, 808 (C=S), 1527 (thioamide I), 851 (thioamide II), 2955 (Ar C-H), 1442 (Ar C=C), 1349 (C-C), 1260 (C-O), 1349 (NO₂). ¹H NMR (DMSO-d₆, 400MHz): 10.36 (1H, s, NH), 12.56 (1H, s, NH), 7.59-7.22 (2H, m, Ar-H), 7.92-7.61 (2H, d, Ar-H), 8.15-8.08 (2H, d, Ar-H), 8.36- 8.30 (2H, d, Ar-H) and 3.32 (3H, s, OCH₃). Mass Spectra (M⁺) at m/z 388, 356 (M⁺ OCH₃)

2.4. Synthesis of Metal Complexes

A solution of nickel(II) chloride hexahydrate (0.474g, 0.002mol), cobalt(II) chloride hexahydrate (0.474g, 0.002mol) and copper(II) chloride dihydrate (0.340g, 0.002mol) in 10 mL methanol was added to a solution of 5-methoxy-5,6-bis(3-nitrophenyl)-4,5-dihydro-1,2,4-triazine-3(2H)-thione (1.548g, 0.004mol) in 20 mL methanol to obtain corresponding metal complexes. The resulting reaction mixture was reflux with stirred for 6hrs. The coloured solid formed was filtered and washed with the solution of cold water and methanol in the ratio (1:1). The solid obtained was dried in vacuo. [17]

[Ni (NBTS)₂]Cl₂ complex; Yield: 78%.; IR (KBr, cm⁻¹): 3047 (Ar-H), 1344 (C-N), 121 (C-S), 1555 (Ar C-C), 1517 (NO₂), 1045 (N-N), 468 (Ni-S)

[Co (NBTS)₂]Cl₂ complex; Yield: 68%. IR (KBr, cm⁻¹): 3056 (Ar-H), 1344.88 (C-N), 1215 (C-S), 1557 (Ar C-C), 1519 (NO₂), 1047 (N-N), 417 (Co-S)

[Cu (NBTS)₂]Cl₂ complex; Yield: 81%; IR (KBr, cm⁻¹): 3076 (Ar-H), 1349 (C-N), 1184 (C-S), 1524 (Ar C-C), 1499 (NO₂), 1095 (N-N), 417 (Cu-S)

3. RESULTS AND DISCUSSION

The colours, elemental analysis, stoichiometries of ligand and its complexes are presented in Table 1. Elemental analysis data are consistent with 1:2 ratio of ligand and metal ion. The metal chelates derived from 1,2-bis(3-nitrophenyl)ethane-1,2-dione and thiosemicarbazide may be represented formula: [M(C₃₀H₁₆N₁₀O₈S₂)]X₂ where M = Cu(II), Co(II), Ni(II) and X = Cl⁻¹, CH₃COO⁻¹. The measurements of molar conductance show that these chelates are 1:2 electrolytes. The ¹H NMR signals at 10.36, 12.56 and 3.32 ppm are assigned to –NH and –OCH₃ protons respectively. The aromatic protons show doublet and multiplet at 7.92-7.61, 8.15-8.08, 8.36-8.30 and 7.59-7.22 ppm range. The NMR spectra of ligand was shown in Fig.1. Mass spectra data confirm the structure of ligand and complexes as indicated by molecular ion peak (M⁺) corresponding to their molecular weight. The Mass spectrum of uncoordinated ligand with its metal complexes were presented in Fig.2 and Fig.3.

Table 1. Physical and analytical data of the ligand (NBTS) and its metal complexes

Empirical Formula	% chemical analysis: Found (Calculated)					ΩM in DMSO (ohm ⁻¹ cm ² mol ⁻¹)	M.P in (°C) Colour	μ _{eff} (B. M.)	Mol. Wt. Found (Calcd)
	C	H	N	S	Metal				
C ₁₆ H ₁₃ N ₅ O ₅ S	49.61 (49.22)	3.34 (3.38)	18.29 (18.08)	8.28 (8.18)	---	---	186-188 Ivory	---	388 (387.37)
[Cu(C ₃₀ H ₁₆ N ₁₀ O ₈ S ₂)]Cl ₂	43.24 (42.74)	1.99 (1.91)	16.61 (16.87)	7.71 (7.61)	---	62.4 (7.54)	220-223 maroon	2.56	845.70 (843.18)

[Co(C ₃₀ H ₁₆ N ₁₀ O ₈ S ₂)]Cl ₂	42.99 (42.97)	1.97 (1.92)	16.95 (16.70)	7.75 (7.65)	---	81.3	192-193 Gray	3.53	838.91 (838.33)
[Ni(C ₃₀ H ₁₆ N ₁₀ O ₈ S ₂)]Cl ₂	43.03 (42.99)	1.98 (1.92)	16.85 (16.71)	7.95 (7.65)	---	71.4	206-208 Olive	Diamagnetic	838.91 (838.13)

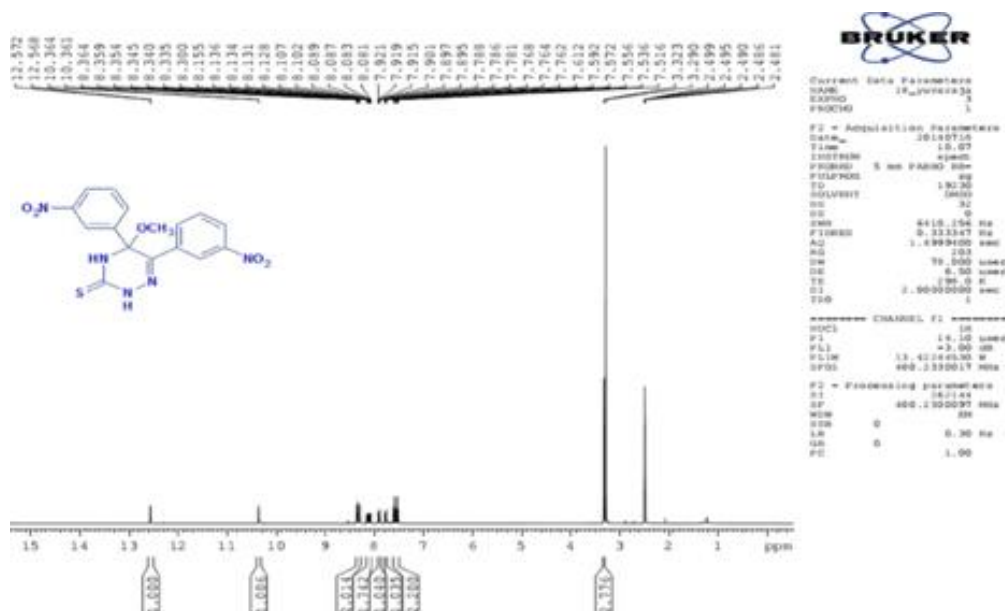


Fig1. ¹H NMR Spectra of NBTS

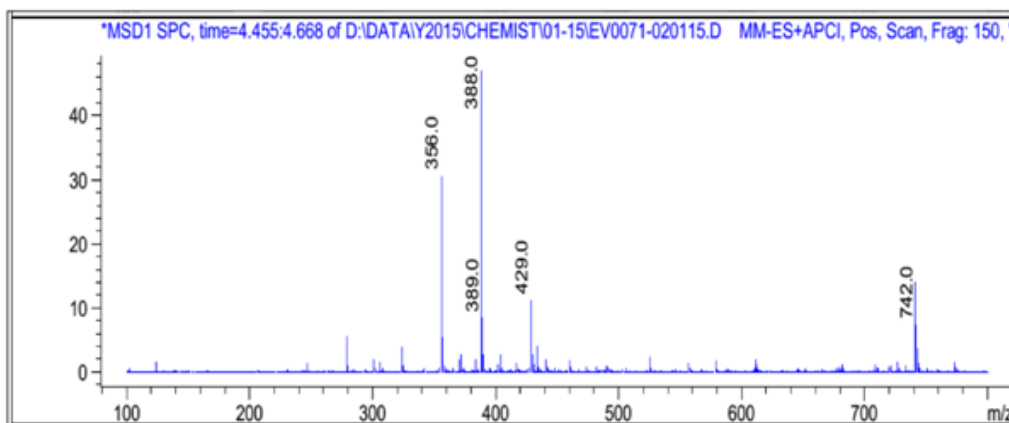


Fig2. LC - Mass Spectra of NBTS

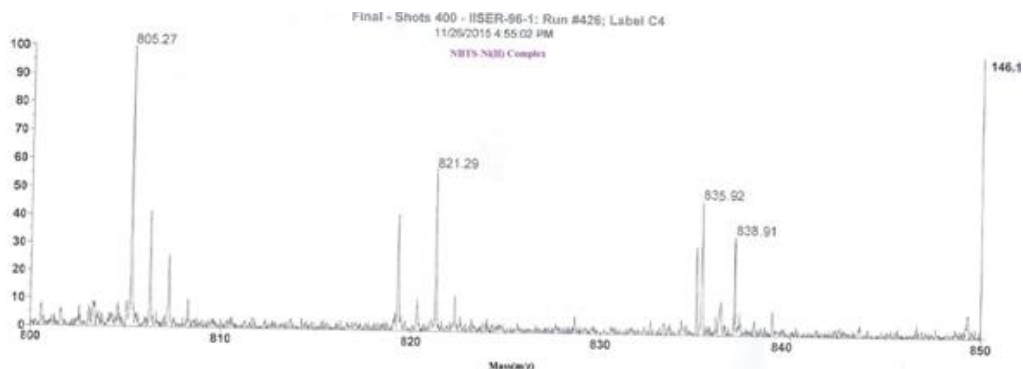


Fig3. Maldi Mass Spectra of [Ni(NBTS)₂]Cl₂

3.1. FT-IR Spectral Studies

The IR spectrum of the ligand showed a strong absorption band at 1671cm⁻¹ which was assigned to the azomethene group (C=N),^[18-19] the strong band observed at 1527cm⁻¹ and 732cm⁻¹ in the spectrum

was due to the (C=S).^[20-22] The bands observed at 3069cm^{-1} and 3047cm^{-1} were assigned to (N-H) and (Ar-H) vibrations respectively. This indicates that the ligand present in thione form. The comparison of IR spectrum of uncoordinated ligand with its metal complexes were presented in Fig.4. The spectrum indicate that the presence due to the azomethene moiety C=N was shifted to lower frequency as compared to the uncoordinated ligand,^[23] indicating that coordination of ligand with metal ion. In addition C=S stretching frequency observed at 1256cm^{-1} in ligand was shifted in the spectra of the complexes, showed the sulphur in the coordination with metal ion. The appearance of new band at 440cm^{-1} in the spectrum of the complexes also support it,^[24-25] which were assignable to (M-S) vibration, respectively in nickel, copper and cobalt complexes.^[26]

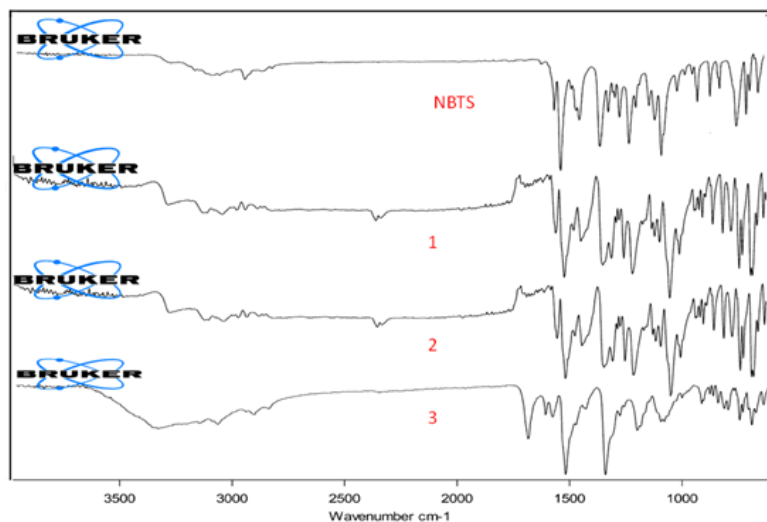


Fig4. IR Spectra of NBTS and metal complexes

3.2. Molar Conductance

It is observed that the molar conductance values of the complexes are in the range of $62\text{-}81\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. The values indicate that these complexes behave as uni-bivalent electrolytes. The tests for anions are positive before decomposing and decomposing the chelates showing their presence outside of coordination sphere.^[27]

3.3. Electronic Absorption Spectra

The observed electronic transitions found to agree with the expected transitions for octahedral geometry conclusions arrived from magnetic susceptibility measurements.^[28-29] The solid state $[\text{Co}(\text{NBTS})_2]\text{Cl}_2$ complex showed the band at $14,705\text{cm}^{-1}$ which can be ascribed into ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})[\nu_1]$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})[\nu_2]$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})[\nu_3]$. The electronic spectrum of Co(II) are two bands at $14,705\text{cm}^{-1}$ and $22,321\text{cm}^{-1}$ due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions corresponding to octahedral geometry. The Gray colour of cobalt (II) complex is also suggestive of octahedral geometry.^[30-31] The $[\text{Ni}(\text{NBTS})_2]\text{Cl}_2$ complex exhibit two transitions in the electronic spectra at about $24,390\text{cm}^{-1}$ and $17,857\text{cm}^{-1}$ due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})[\nu_1]$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})[\nu_2]$ transitions respectively are due to octahedral geometry of the complex.^[32] The well separated bands indicate that the cobalt(II) have an octahedral geometry. The broad band at $15,355\text{cm}^{-1}$ and a shoulder at $23,809\text{cm}^{-1}$ indicative of distorted octahedral geometry for $[\text{Cu}(\text{NBTS})_2]\text{Cl}_2$ complex. The comparison of solid UV- spectrum of ligand with its metal complexes were presented in Fig.5.

3.4. Thermal Analysis Studies of Metal Complexes

The synthesised complexes were subjected to thermal analysis. The mass loss consideration during the decomposition used to evaluate the kinetic parameters such as E_a^* , ΔH^* , ΔG^* and ΔS^* . The nature of decomposition curve indicate that the complexes have been converted to corresponding metal oxides. The weight loss curves and the corresponding differential thermo gravimetric curves for the complex are shown in fig.5. The thermal behavior of cobalt(II), nickel(II) and copper(II) complexes has been studied as a function of temperature.^[33] The thermal decomposition of $[\text{Cu}(\text{NBTS})_2]\text{Cl}_2$ complex has occurred in three steps as indicated by DTG curves around 196, 260 and

385⁰C corresponding to the loss of two coordinated chloride ions, loss of four nitro group and macro cyclic ligand respectively.^[34] In the case of [Ni(NBTS)₂]Cl₂ and [Co(NBTS)₂]Cl₂ complexes, decomposition corresponding to the loss of two coordinated chloride ions in the first step 196-200⁰C, loss of four nitro group around 260–390⁰C in the second step and greater loss in weight of macro cyclic ligand and in the range 385–440⁰C in the third step.^[35] Finally, the mass decomposes gradually with the formation of metal oxide above 720⁰C. The nature of proposed chemical change with the temperature range and the percentage of metal oxide obtained are given in Table 2. The TGA curves of metal complex were showed in Fig.6.

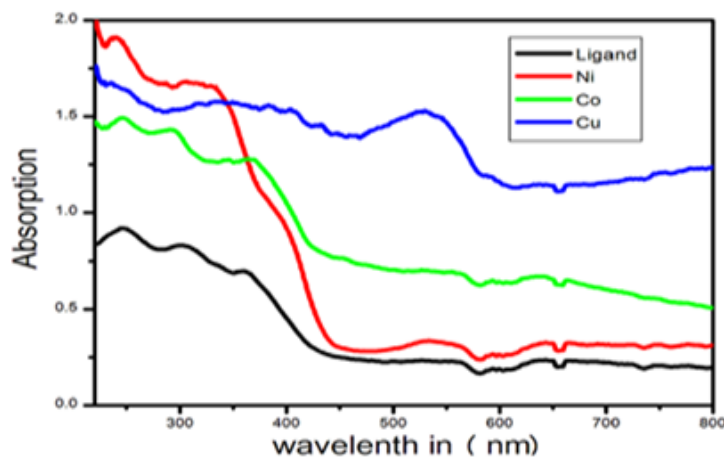


Fig5. Electronic spectra of metal complexes

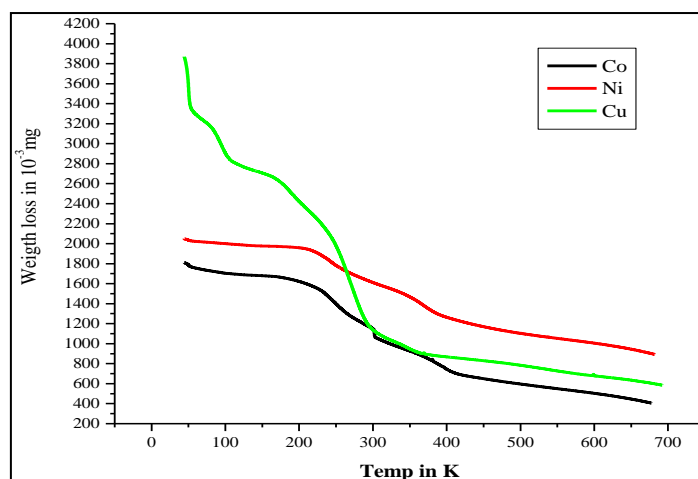


Fig6. TGA Thermogram of metal complexes

Table2. TGA analysis data of the NBTS Complexes with copper (II), cobalt (II) and nickel (II)

Complex	First step Loss of two chloride ion	Mass loss % Found (Cal)	Second step loss of four nitro group	Mass loss % Found (Cal)	Third step Loss of one Macro cyclic Compound	Mass loss % Found (Cal)	Residue	Temp. in 0C	% found (Cal)
[Cu(NBTS) ₂]Cl ₂	196 ⁰ C	8.42 (9.21)	260 ⁰ C	26.56 (26.12)	385 ⁰ C	55.5 (54.82)	CuO	700	9.43 (9.12)
[Co(NBTS) ₂]Cl ₂	199 ⁰ C	8.46 (8.33)	340 ⁰ C	26.72 (27.67)	600 ⁰ C	55.75 (56.48)	CoO	720	8.94 (9.40)
[Ni(NBTS) ₂]Cl ₂	200 ⁰ C	8.47 (8.82)	390 ⁰ C	26.72 (26.56)	440 ⁰ C	55.55 (56.12)	NiO	710	8.90 (8.33)

The kinetic and thermodynamic activation parameters of decomposition processes of dehydrated complexes, namely activation energy (E_a^*), enthalpy (ΔH^*), entropy (ΔS^*), and Gibbs free energy change of the decomposition (ΔG^*), were evaluated graphically by employing the Broido's relation: $-\ln[\ln(1/y)] = E_a^*/RT_d - \ln A - \ln(8.314/T_d)$ (1)

Where T_d is the decomposition temperature, R is the gas constant and E_a^* is the activation energy in $\text{kJ}\cdot\text{mol}^{-1}$. A plot of the left-hand side of equation (1) against $1/T$ gave a slope from which E_a^* was calculated and A (Arrhenius factor) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following Eyring equations:

$$\Delta S^* = 2.303[\log(Ah/kT)] R \quad (2)$$

$$\Delta H^* = E_a^* - RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

The data are summarized in Table 3. The activation energies of decomposition were in the range $1.79 - 5.23 \text{ kJ mol}^{-1}$. The high values of the activation energies reflect the thermal stability of the complexes.^[36] The positive sign of ΔG^* for the investigated complexes indicates that the free energy of the final residue is higher than that of the initial compound and all the decomposition steps are non-spontaneous processes. Also, the negative values of ΔS^* and ΔH^* are owing to the increase of the order as a result of solvation process and the chelation process is exothermic and it is favorable at lower temperatures.^[37-38] The entropy of activation had negative values in all the complexes, which indicates that the decomposition reactions proceed with a lower rate than the normal ones.

Table 3. Kinetic and Thermodynamic parameters of NBTS complexes

Metal Complex	Decomposition Temperature ($^{\circ}\text{C}$)	DTA _{max} ($^{\circ}\text{C}$)	Activation Energy E_a^* (KJ/mole)	Frequency Factor $\ln A \text{ Min}^{-1}$	ΔH^* (KJ/mole)	ΔS^* (J/mole)	ΔG^* (KJ/mole)
[Cu(NBTS) ₂]Cl ₂	180-500	340	5.2329	17.6140	2.4061	-152.37	51.8882
[Co(NBTS) ₂]Cl ₂	220-580	400	1.7927	3.5670	-1.5328	-150.67	60.2584
[Ni(NBTS) ₂]Cl ₂	240-500	370	3.6609	3.4723	5.8475	-151.77	56.1607

4. IN VITRO - ANTIOXIDANTS STUDIES

4.1. DPPH Free Radical Scavenging Activity

1,1-Diphenyl-2-picrylhydrazyl (DPPH) is a stable free radical which has maximum optical absorbance at 517 nm .^[39] The radical scavenging ability of synthesized compounds and the ascorbic acid (standard) was tested on the basis of the radical scavenging effect on DPPH free radical.^[40-41] Different concentration of compounds and standard namely 25, 50, 100, 200, and 250 $\mu\text{g/mL}$ were prepared in methanol. In clean and labeled test tubes, 2 mL of DPPH solution (0.002% in methanol) was mixed with 2 mL of different concentration of compounds and standard separately. The tubes were incubated at room temperature in dark for 30 min. and the optical density was measured at 517 nm using UV-Visible Spectrophotometer.^[42-43] The absorbance of the DPPH control was also noted. The scavenging activity was calculated using the formula:

$$\text{Scavenging activity (\%)} = [(A_{\text{DPPH}} - A_{\text{TEST}})/A_{\text{DPPH}}] \times 100$$

Where A_{DPPH} is the absorbance of DPPH without test sample (control) and A_{TEST} is the absorbance of DPPH in the presence of test sample.

Antioxidant activity of different concentration of complexes in methanol and ascorbic acid in terms of free radical scavenging ability was evaluated using DPPH free radical assay. The compounds exhibited marked antioxidant activity by scavenging DPPH* (free radical) and converting into DPPH and the activity was found to be dose dependent. The complex [Cu(NBTS)₂]Cl₂ was shown more potent followed by other complexes. The result was tabulated in Table 4.

Table 4. DPPH Free Radical Scavenging Activity of NBTS and its metal complexes

Compound	Scavenging activity of different concentrations ($\mu\text{g/mL}$) in %				
	25	50	100	200	250
NBTS	77.10	70.74	67.51	62.5	56.25
[Cu(NBTS) ₂]Cl ₂	95.42	81.52	74.69	72.48	59.19
[Co(NBTS) ₂]Cl ₂	55.41	35.61	30.58	26.55	24.91
[Ni(NBTS) ₂]Cl ₂	55.48	47.11	39.41	31.81	25.88
Standard	81.16	86.36	91.56	93.18	96.36

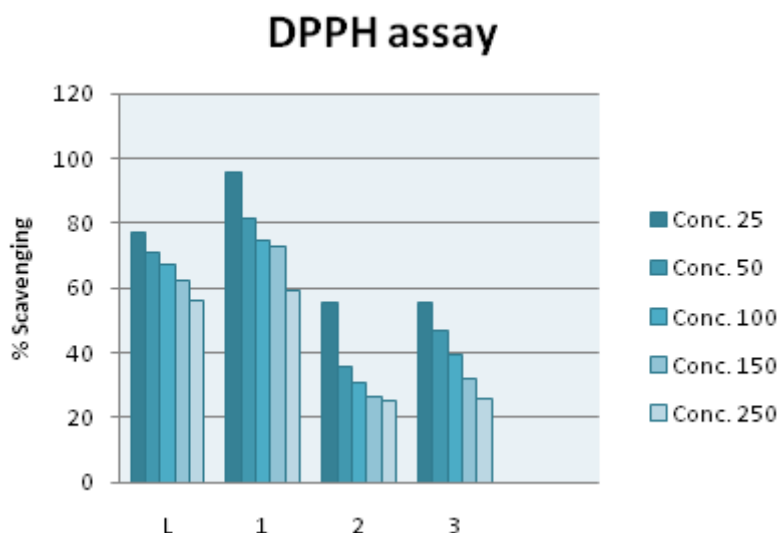


Fig7. DPPH method of radical scavenging activity

4.2. Antibacterial Activity

The antibacterial efficacy of the compounds was tested against two Gram positive bacteria namely *Staphylococcus aureus* and *Bacillus cereus* and Gram negative bacteria namely *Pseudomonas aeruginosa* and *Escherichia coli* by agar well diffusion method. [44] Twenty four old Muller-Hinton broth cultures of test bacteria were swabbed on sterile Muller-Hinton agar plates using sterile cotton swab followed by punching wells of 6mm with the help of sterile cork borer. The standard drug (Chloramphenicol, 1mg/ml of sterile distilled water), compounds (2-4) (20mg/ml in 10% DMSO) and control (10% DMSO) were added to respectively labeled wells. The plates are allowed to stand for 30 min. and were incubated at 37°C for 24 hrs in upright position and the zone of inhibition was recorded. [45]

The result of antibacterial activity of the complexesis shown in Table5. In the antibacterial study, the compounds have shown inhibition of test bacteria. Among the compounds, marked inhibition of test bacteria was observed in compound $[\text{Cu}(\text{NBTS})_2]\text{Cl}_2$ as compared with standard drugs.

Table5. Antibacterial activity of NBTS and its metal complexes

Compound	Zone of inhibition in (cm)				
	B. cereus	S. aureus	P. aeruginosa	K. pneumonia	E. coli
NBTS	1.0	1.5	1.3	1.4	1.6
$[\text{Cu}(\text{NBTS})_2]\text{Cl}_2$	2.5	1.9	1.8	2.2	2.4
$[\text{Co}(\text{NBTS})_2]\text{Cl}_2$	1.1	1.3	1.5	1.4	1.2
$[\text{Ni}(\text{NBTS})_2]\text{Cl}_2$	1.5	1.2	1.7	1.6	1.4
Control	0	0	0	0	0
Standard	2.8	2.7	3.1	2.8	2.9

5. CONCLUSIONS

In the present work, we successfully designed and developed a 5-methoxy-5,6-bis(3-nitrophenyl)-4,5-dihydro-1,2,4-triazine-3(2H)-thione (NBTS) and its metal complexes. The ligand and their complexes have been characterized by various physicochemical techniques. The spectral data show that the complexes having octahedral geometry. The TGA/DTA data indicate stepwise degradation and from this, the kinetic parameters are evaluated. The obtained results are in good agreement with the proposed structure. The IR spectra indicate that the ligand coordinated through two donor sulphur atoms. The antibacterial and antioxidant activity results reveal that the $[\text{Cu}(\text{NBTS})_2]\text{Cl}_2$ complex exhibited good activity compared to the uncoordinated ligand and the other two complexes in Fig.7.

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