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Research article

**SPECTROSCOPIC AND BIOLOGICAL STUDIES ON NEWLY SYNTHESIZED COPPER (II) AND NICKEL (II) COMPLEXES WITH p-DIMETHYLAMINOBANZALDEHYDE SEMICARBAZONE AND p-DIMETHYLAMINOBANZALDEHYDE THIOSEMICARBAZONE**Sulekh Chandra<sup>1\*</sup>, Sanjay Goel<sup>2</sup>, Sudhanshu Dhar Dwivedi<sup>2</sup><sup>1</sup>Department of Chemistry, Zakir Husain Delhi College, University of Delhi, Delhi-110002<sup>2</sup>Department of Chemistry, Government Science & Commerce College (MP Bhoj (open) University), Benazeer, Bhopal

**ABSTRACT:** Cu (II) and Ni (II) complexes of general composition  $[ML_2]X_2$  (M = Cu(II), Ni(II); X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) were synthesized by the condensation of metal salts with semicarbazone / thiosemicarbazone derived from p-dimethylaminobenzaldehyde. The metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR and atomic absorption spectral studies. On the basis of electronic and infrared spectral studies, the metal complexes were found to have tetrahedral geometry. The Schiff bases and their metal complexes were tested for their antibacterial and antioxidant activities.

**Key words:** Semicarbazone, Thiosemicarbazone, p-dimethylaminobenzaldehyde, copper (II), nickel (II), antioxidant, antibacterial

**INTRODUCTION**

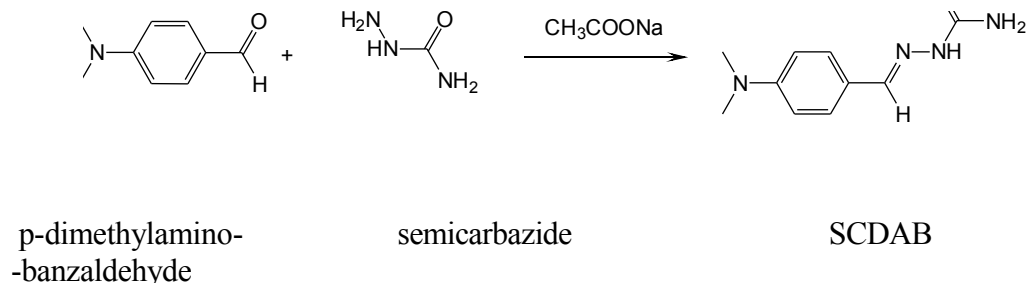
A large number of Schiff bases and their complexes have been studied for their interesting and important biological properties e.g. antimicrobial (Abd El-Wahab, et.al., 2004), antiviral (Kolocouris, et.al., 2002), antifungal (Rodríguez-Argüelles, 2009) antitumour (Ainscough, et. al., 1998) and other biological activities (Bharamagouclar, 1987; Zhu, et.al., 2003; Shalin et. al., 2009; Kothari and Sharma, 2011) particularly with first row of transition metal complexes. The formation of variety of metal complexes with Schiff base ligands as mentioned in our earlier studies (Chandra and Kumar, 2004; Chandra and Kumar, 2007; Chandra and Gupta, 2005) indicate the spectacular progress in coordination and bioinorganic chemistry. Schiff base complexes of transition metals containing ligand with N, O and S donors are known to exhibit interesting biological activities. Still, development of new Schiff bases long term administration for chelation of metal deposits. In the view of the facts that the metal complexes are better therapeutic agents (Chandra and Gupta, 2005; Chandra et.al., 2007; Chandra et.al. 2009; Kumar and Chandra, 2011) as compared to the Schiff bases, the aim of this study was to synthesize the new class of metal complexes with newly synthesized Schiff base ligands and different metal salts, to find their biological activity such as antioxidant and antibacterial activities and to observe impact of complexation on their therapeutic values.

**MATERIALS AND METHODS**

All the chemicals used in the present work were of high purity, Anala R grade and procured from Sigma-Aldrich. Metal salts were purchased from E. Merck and used as received. The solvent used were either spectroscopic pure from SRL/BDH or purified by the recommended methods (Vogel, 1962).

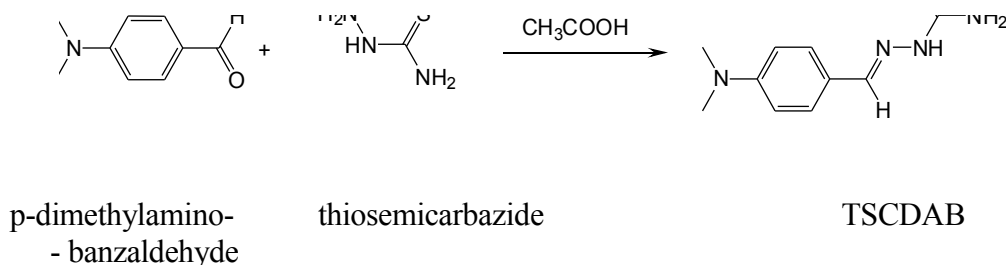
**Synthesis of p-Dimethylaminobenzaldehyde Semicarbazone (SCDAB)**

An aqueous solution of semicarbazide HCl (1.11 g, 0.01mol) was added to an ethanolic solution of p-dimethylaminobenzaldehyde (1.49 g, 0.01mol) in the presence of sodium acetate (0.82 g, 0.01mol). The reaction mixture was stirred vigorously for 2-3 h. The completion of the reaction was confirmed by the TLC. The light pink product formed was collected by filtration which was washed several times with hot water and dried in vacuum over P4O10. Yield 82%, Melting Point 232-233<sup>o</sup>C.



### Synthesis of p-Dimethylaminobenzaldehyde Thiosemicarbazone (TSCDAB)

Hot ethanolic solution of p-dimethylaminobenzaldehyde (1.49 g, 0.01mol) was mixed with hot ethanolic solution of thiosemicarbazide (0.91 g, 0.01mol) in the presence of 0.5 mL acetic acid. The contents were refluxed at 70–80°C for about 3–5 h. The completion of the reaction was confirmed by the TLC. The reaction mass was degassed on a rotatory evaporator, over a water bath. The degassed reaction mass on cooling gives light yellow coloured crystals. It was filtered, washed with cold ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. Yield 78%, Melting Point 220 °C.



### Synthesis of metal complexes

Hot ethanolic solution of metal salts (1mmol) e.g. nickel chloride hexahydrate (0.238 g), nickel nitrate hexahydrate (0.292 g), cupric chloride dihydrate (0.171 g) or cupric nitrate trihydrate (0.242 g) were mixed with hot ethanolic solution of the corresponding ligand (2 mmol) e.g. SCDAB (0.412 g) or TSCDAB (0.444 g). The mixture was refluxed for 4-5 hours at 70–80 °C. On cooling the contents, the complex was separated out in each case. It was filtered, washed with 50% ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. Purity of the complexes was checked by TLC, colour was noted, melting point was determined and yield of the complexes were calculated (Table 1).

**Table 1: Molar Conductance and Elemental Analysis data**

Ligand/Complex	Molar Conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Atomic Mass	Colour	M.P. ( $^{\circ}\text{C}$ )	Yield (%)	Elemental analysis data (%)			
						M	C	H	N
SCDAB	---	206	light pink	232	82	---	---	---	---
[Cu(SCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	182	547	yellow	230	83	11.56	43.65	5.27	20.74
[Cu(SCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	199	600	brown	240	79	10.35	40.12	4.79	23.52
[Ni(SCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	185	542	yellow	260	75	10.94	44.39	5.31	20.79
[Ni(SCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	192	595	Light brown	239	81	9.86	40.41	4.72	23.59
TSCDAB	---	222	light yellow	220	78	---	---	---	---
[Cu(TSCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	189	579	orange	200	80	10.79	41.21	5.34	19.56
[Cu(TSCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	203	634	yellow	226	76	10.09	37.73	4.88	22.03
[Ni(TSCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	194	574	yellow	235	83	10.23	41.73	5.29	19.34
[Ni(TSCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	205	629	brown	200	85	9.37	38.29	4.91	22.39

### Physical measurements

The C, H, and N were analyzed on Carlo-Erba 1106 elemental analyzer. Metal contents were determined by Atomic Absorption spectral studies recorded on Shimadzu Atomic Absorption Spectrophotometer model AA-6300. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as callibrant. IR spectra (KBr) were recorded on FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. The  $^1\text{H}$  NMR spectra of the ligands were recorded on Jeol FT-NMR Spectrometer using DMSO as a solvent. Thermogravimetry (TG) and Differential thermogravimetric (DTA) analysis for the metal complexes were carried out on Perkin Elmer (Diamond) TG-DTA spectrometer for the determination of complex entrapped water.

## RESULTS AND DISCUSSION

### Infrared Spectra of SCDAB

The IR spectrum of ligand SCDAB (Fig.1) shows bands at 3465 and 3290  $\text{cm}^{-1}$  which may be assigned to  $[\nu(\text{NH}_2)]$  and  $[\nu(\text{NH})]$  vibrations, respectively. The bands due to  $[\nu(\text{C}=\text{O})]$  appeared at 1689  $\text{cm}^{-1}$  and the bands at 1642 or 1608  $\text{cm}^{-1}$  may be assigned to symmetric or asymmetric  $[\nu(\text{C}=\text{N})]$  group.

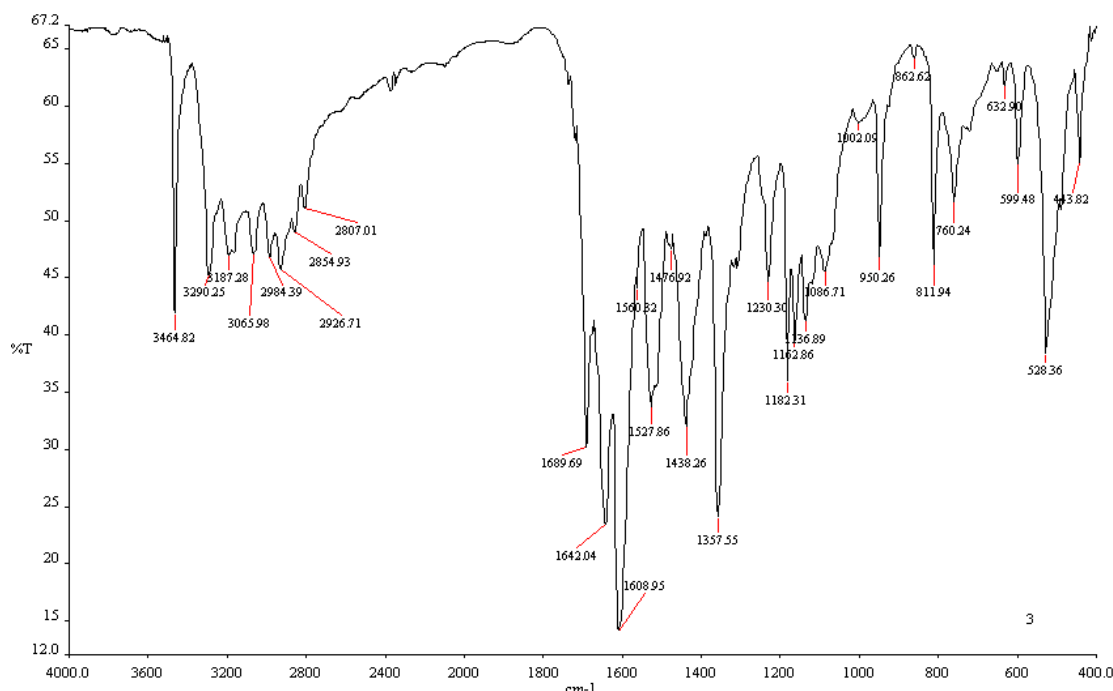


Fig. 1: IR Spectra of SCDAB

### The $^1\text{H}$ NMR spectra of SCDAB

The  $^1\text{H}$  NMR spectrum of the ligand SCDAB (Fig. 2) in DMSO was recorded, it shows signals at:  $\delta$  2.892 ppm (6H, s, two  $\text{CH}_3$ ),  $\delta$  6.295 ppm (2H, s,  $\text{NH}_2\text{-CO}$ ),  $\delta$  9.898 ppm (1H, s,  $\text{N-NH-CO}$ ),  $\delta$  7.678 ppm (1H, s,  $\text{Ph-CH-C}$ ),  $\delta$  7.470 (2H, Ph, d),  $\delta$  6.659 ppm (2H, Ph, d).

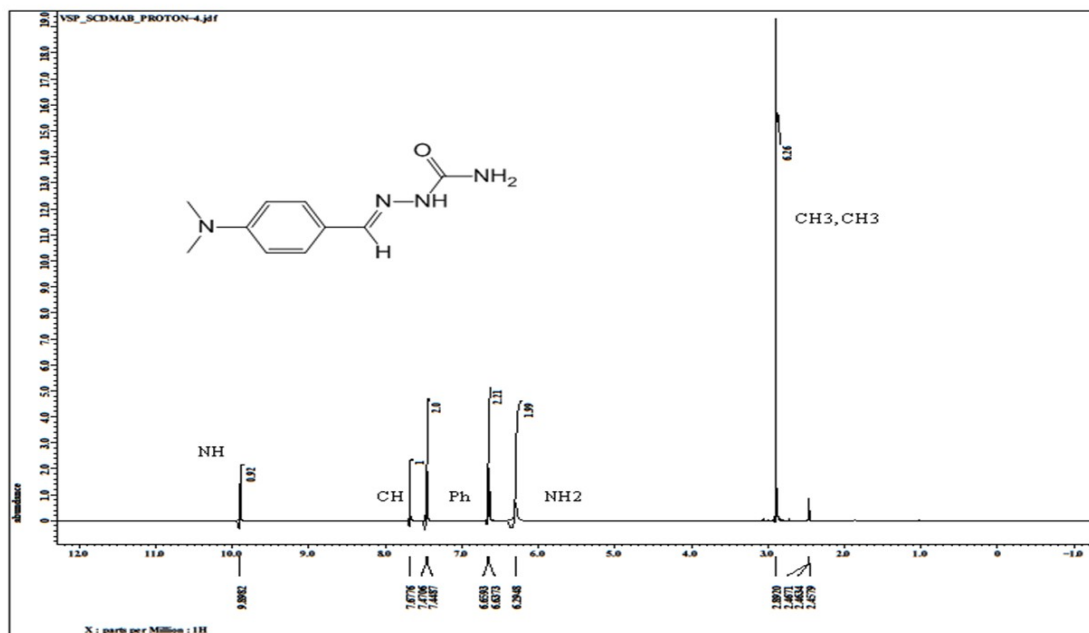


Fig. 2: NMR spectra of SCDAB

### Infrared Spectra of TSCDAB

The IR spectrum of the ligand TSCDAB (Fig. 3) shows bands at 3374 and 3333  $\text{cm}^{-1}$  which may be assigned to  $[\nu(\text{NH}_2)]$  and  $[\nu(\text{NH})]$  groups, respectively. The bands due to  $[\nu(\text{C}=\text{S})]$  appeared at 821  $\text{cm}^{-1}$  and the bands at 1601 or 1507  $\text{cm}^{-1}$  may be assigned to symmetric or asymmetric  $[\nu(\text{C}=\text{N})]$  group.

### The $^1\text{H}$ NMR spectra of TSCDAB

The  $^1\text{H}$  NMR spectrum of the ligand TSCDAB (Fig. 4) in DMSO was recorded, it shows signals at:  $\delta$  2.915 ppm (6H, s, two  $\text{CH}_3$ ),  $\delta$  7.947 ppm (2H, s,  $\text{NH}_2\text{-CO}$ ),  $\delta$  11.129 ppm (1H, s,  $\text{N-NH-CO}$ ),  $\delta$  7.885 ppm (1H, s,  $\text{Ph-CH-C}$ ),  $\delta$  7.548 (2H, Ph, d),  $\delta$  6.668 ppm (2H, Ph, d).

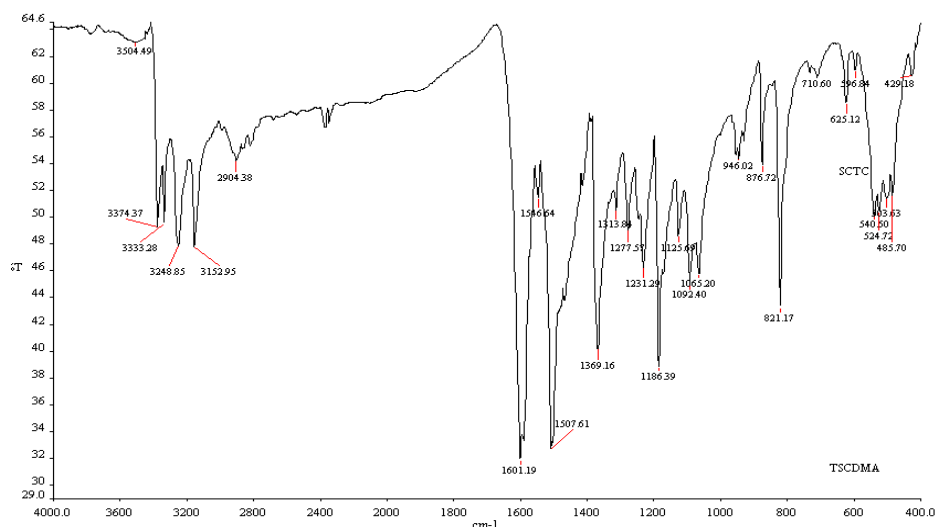


Fig. 3: IR Spectra of TSCDAB

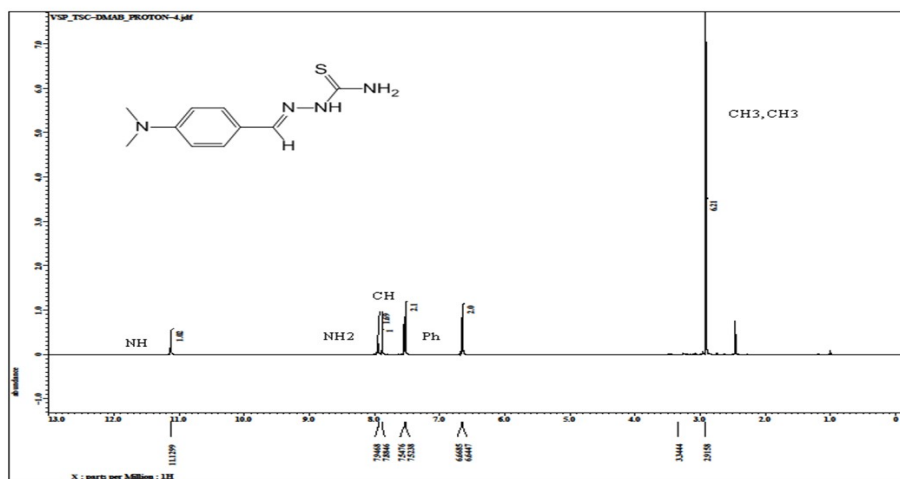


Fig. 4: NMR spectra of TSCDAB

### Infrared Spectra of metal complexes

The assignment of the significant IR spectral bands of the metal complexes are shown in fig. 5-6 clearly shows the shifting of the bands corresponding to  $\nu(-C=N)$  and  $\nu(-C=S)$  in thiosemicarbazone or  $\nu(-C=O)$  in semicarbazone towards lower side (around ca. 20–50  $\text{cm}^{-1}$ ) on complexation. This suggests that both the ligands act as bidentate chelating agents coordinating with the metal ion through nitrogen of  $C=N$  group and sulphur of  $C=S$  group or oxygen of  $C=O$ .

### Magnetic Moment and electronic spectral data of metal complexes

At room temperature Ni (II) complexes show magnetic moment in the range 3.00–3.80 B.M. (Table 2) corresponding to two unpaired electrons and Cu(II) complexes show magnetic moment in the range 1.70–2.00 B.M. (Table 2) corresponding to one unpaired electron. These values correspond to high spin configurations of the metal complexes.

Table 2: Magnetic moment and Electronic spectral data of complexes

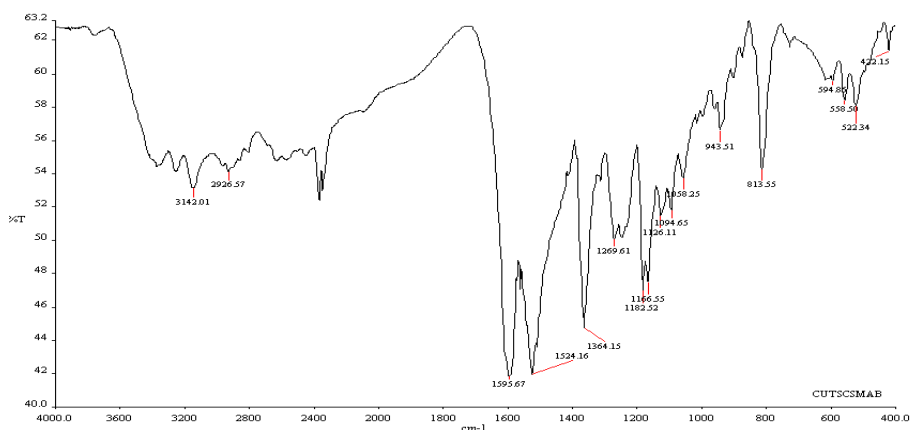
Complex	$\mu_{\text{eff}}$ (B.M.)	Electronic spectral data		
		$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )	$\nu_3$ ( $\text{cm}^{-1}$ )
$[\text{Cu}(\text{SCDAB})_2](\text{Cl})_2$	1.86	5720	13880	20220
$[\text{Cu}(\text{SCDAB})_2](\text{NO}_3)_2$	1.95	5800	14210	21450
$[\text{Ni}(\text{SCDAB})_2](\text{Cl})_2$	3.09	5450	14570	20340
$[\text{Ni}(\text{SCDAB})_2](\text{NO}_3)_2$	3.35	5910	13790	20880
$[\text{Cu}(\text{TSCDAB})_2](\text{Cl})_2$	1.76	5250	13550	21010
$[\text{Cu}(\text{TSCDAB})_2](\text{NO}_3)_2$	1.81	5390	13900	20460
$[\text{Ni}(\text{TSCDAB})_2](\text{Cl})_2$	3.06	5780	14410	21710
$[\text{Ni}(\text{TSCDAB})_2](\text{NO}_3)_2$	3.72	5620	14780	21230

The electronic spectrum of chlorido and nitrate complexes show three electronic spectral bands in the range 5000  $\text{cm}^{-1}$ , 8000  $\text{cm}^{-1}$  and 20000  $\text{cm}^{-1}$  (Table 2) corresponding to the following transitions  $\nu_1: {}^4A_2 \rightarrow {}^4T_2$  (F),  $\nu_2: {}^4A_2 \rightarrow {}^4T_1$  (F) and  ${}^4A_2 \rightarrow {}^4T_1$  (P) which indicates the tetrahedral geometry of the complexes.

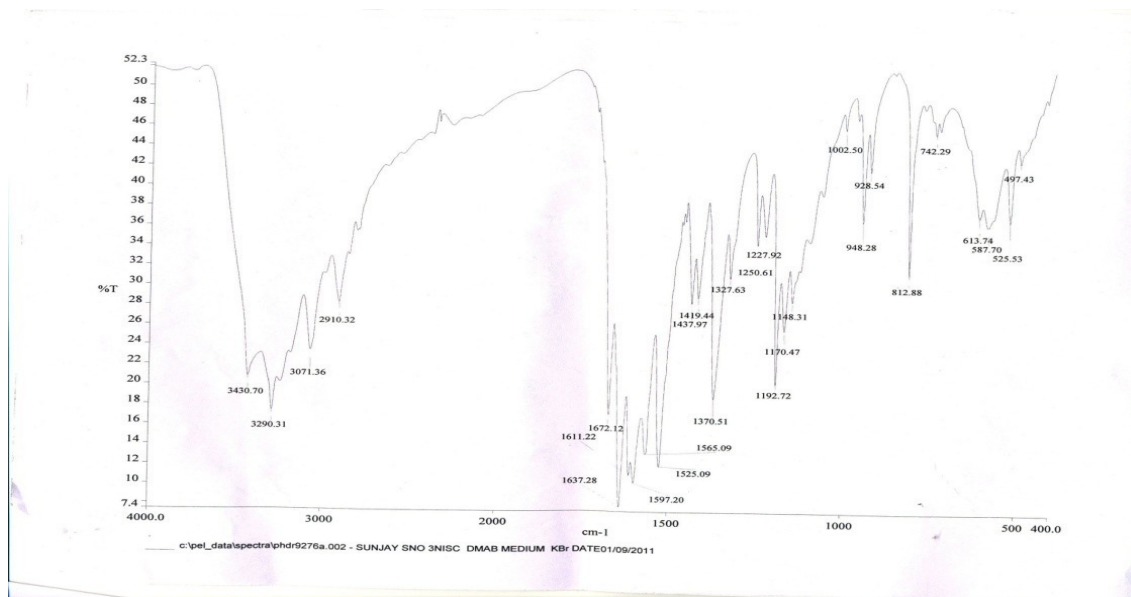
**Elemental Analysis data and Molar Conductance of Metal Complexes**

The metal contents were determined by the Atomic Absorption studies as shown in fig. 7-8. The C, H and N contents in the metal complexes were analyzed by Elemental Analyzer and are tabulated in Table 1.

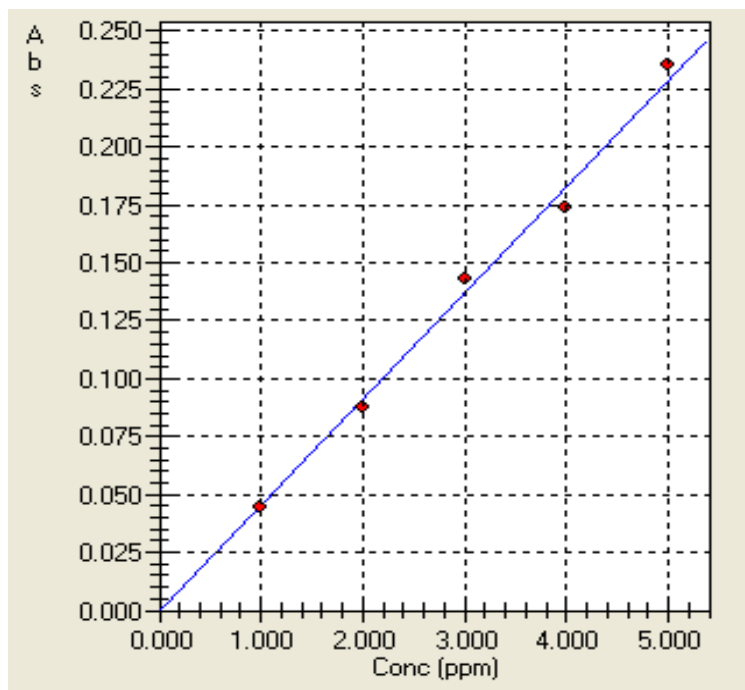
The molar conductance values of the complexes (Table 1) measured in DMSO are in the range 180-210  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . The high values correspond to 1:2 electrolytic nature (Shakir et. al., 1993; Chandra and Kumar, 2004) of the metal complexes. Thus the metal complexes may be formulated as  $[\text{ML}_2] \text{X}_2$  (where M = Cu(II), Ni (II); X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>).



**Fig. 5: IR Spectra of [Cu (TSCDAB)<sub>2</sub>](Cl)<sub>2</sub>**



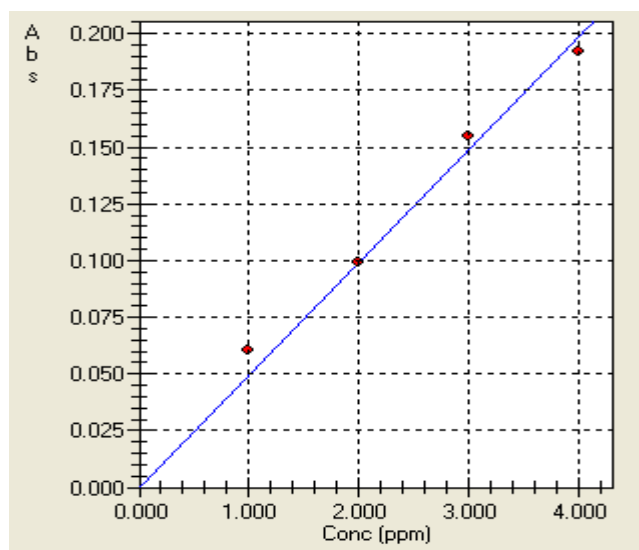
**Fig. 6: IR Spectra of [Ni(SCDAB)<sub>2</sub>](Cl)<sub>2</sub>**



**Fig. 7: Standard plot for Cu metal complexes (Atomic Absorption studies). The solution of copper complexes (10 ppm) i.e.  $[\text{Cu}(\text{SCDAB})_2](\text{Cl})_2$ ;  $[\text{Cu}(\text{SCDAB})_2](\text{NO}_3)_2$ ;  $[\text{Cu}(\text{TSCDAB})_2](\text{Cl})_2$ ;  $[\text{Cu}(\text{TSCDAB})_2](\text{NO}_3)_2$  shows the absorbance as 0.0520 (11.56% Cu); 0.0465 (10.35% Cu); 0.0485 (10.79% Cu); 0.0454 (10.09% Cu) respectively**

#### TG-DTA data of metal complexes

All the metal complexes show major weight loss above 175 °C (Fig. 9-10) which indicates that metal complexes are free of any entrapped water. The peaks due to melting of complexes in TG-DTA curve agree well with the melting point of the complexes as determined by the MP apparatus (Make: BUCHI, Model: M-560).



**Fig. 8: Standard plot for Ni metal complexes (Atomic Absorption studies). The solution of copper complexes (10 ppm) i.e.  $[\text{Ni}(\text{SCDAB})_2](\text{Cl})_2$ ;  $[\text{Ni}(\text{SCDAB})_2](\text{NO}_3)_2$ ;  $[\text{Ni}(\text{TSCDAB})_2](\text{Cl})_2$ ;  $[\text{Ni}(\text{TSCDAB})_2](\text{NO}_3)_2$  shows the absorbance as 0.0547 (10.94% Ni); 0.0493 (9.86% Ni); 0.0511 (10.23% Ni); 0.0468 (9.37% Ni) respectively.**

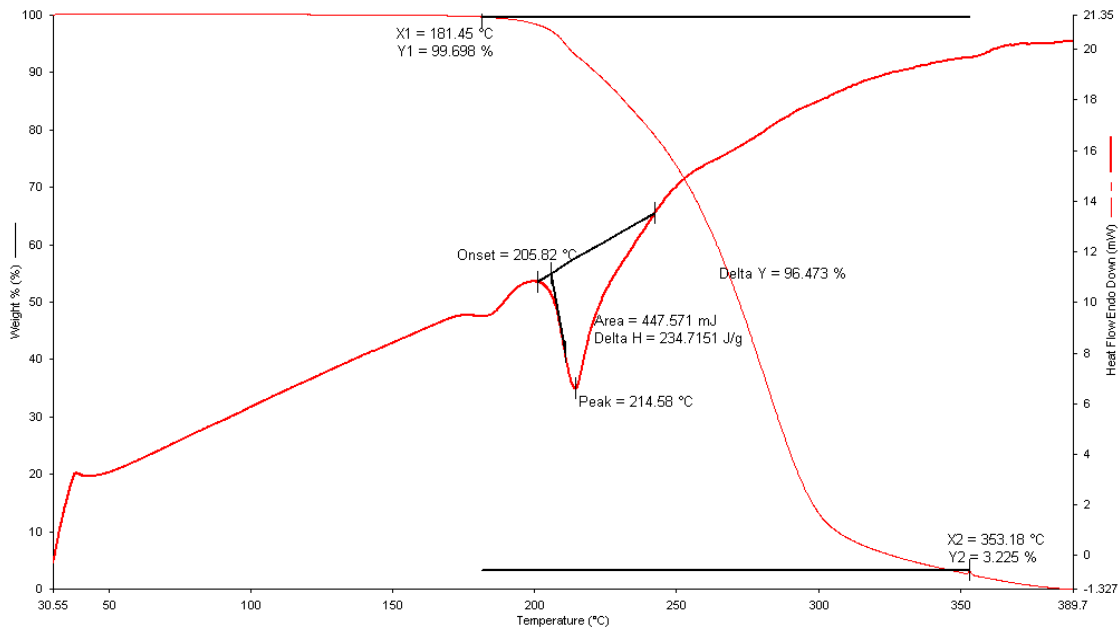


Fig. 9: TG-DTA Curve for  $[Cu(TSCDAB)_2](NO_3)_2$

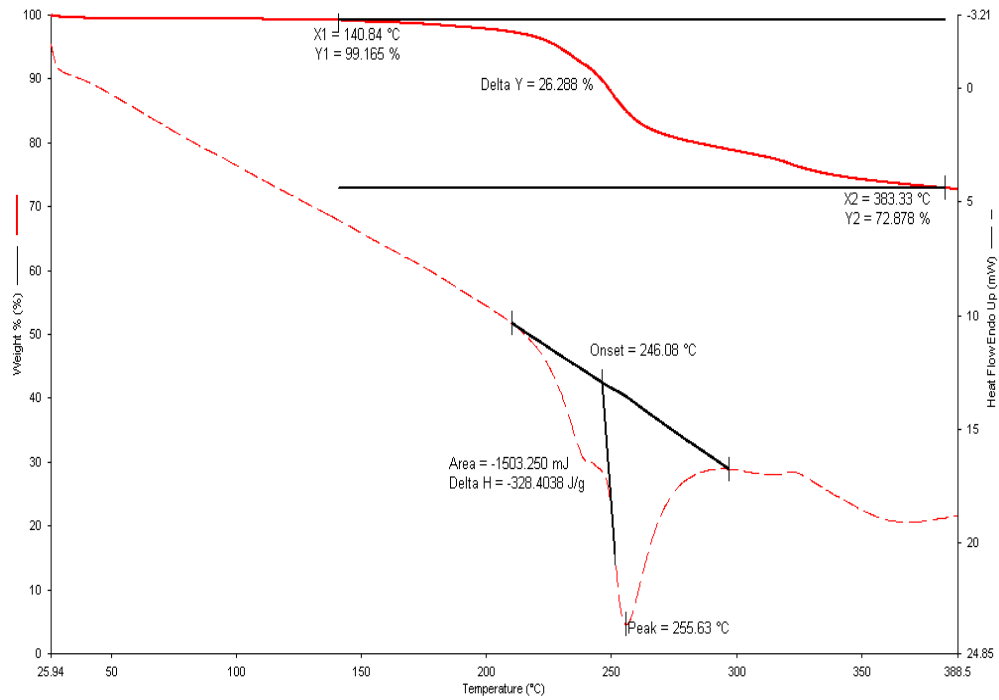


Fig. 10: TG-DTA Curve for  $[Ni(SCDAB)_2](Cl)_2$



**ANTIOXIDANT ACTIVITY**

**Assay of initiation of Lipid Peroxidation**

The details of the assay procedure are described earlier (Raj et. al., 1998). The reaction mixture in a final volume of 2 mL consisted of Tris-HCl (0.025 M, pH 7.5), microsomes (equivalent to 1 mg protein which were assayed by the method of Lowry, Lowery et. al., 1951) which were taken from the laboratory of Prof. HG Raj, Department of Biochemistry, VP Chest Institute and were prepared by adopting the method of Ernster and Nordenbrand (Ernster and Nordenbrand, 1967), ADP (3 mM) and FeCl<sub>3</sub> (0.15 mM). The tubes were pre-incubated for 10 min at 37 °C followed by the addition of the test compounds (metal complexes) added at a concentration of 100 µM in 0.2 mL of DMSO and then again incubated for 10 min at 37 °C. The reaction was started by the addition of 0.5 mM NADPH for initiation of enzymatic lipid peroxidation and incubated for different intervals. The reaction was terminated by the addition of 0.2 mL of 50% TCA, followed by addition of 0.2mL of 5N HCl and 1.6 mL of 30% TBA. The tubes were heated in an oil bath at 95°C for 30 min, cooled and centrifuged at 3000 rpm. The intensity of the colour of the thiobarbituric acid reactive substance (TBRS) formed was read at 535 nm. The lipid peroxidation was found to be linear upto 15 min under the conditions described here. The results (Table 3) illustrate the influence of ligands and metal complexes on the initiation of lipid peroxidation enzymatically. These results clearly indicate that metal complexes have higher antioxidant activities as compared to the Schiff base ligands. Thiosemicarbazone metal complexes show higher antioxidant activities than semicarbazone metal complexes. Moreover, nickel metal complexes show higher antioxidant activities than copper metal complexes.

**Table 3: Influence of ligands and metal complexes on the initiation of lipid peroxidation**

Ligands / Complexes	Percent of control
SCDAB	97
[Cu(SCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	81
[Cu(SCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	79
[Ni(SCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	69
[Ni(SCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	73
TSCDAB	98
[Cu(TSCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	75
[Cu(TSCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	71
[Ni(TSCDAB) <sub>2</sub> ](Cl) <sub>2</sub>	60
[Ni(TSCDAB) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	62

**ANTIBACTERIAL ACTIVITY**

The antibacterial activities of the metal complexes were determined at different concentrations (30 µg/disc) against different pathogenic bacteria's by using disc diffusion technique and the results were compared with standard antibiotic, Kanamycin (30 µg/disc). It was found that the metal complexes were active against all of the test bacteria but the metal complexes [Cu(TSCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> and [Ni(TSCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> were most effective against all pathogenic bacteria's as shown in Table 4. The zones of inhibition of the complexes were however lesser as compared to standard Kanamycin. The metal complexes have higher antibacterial activities as compared to the Schiff base ligands. Thiosemicarbazone metal complexes show higher activities than semicarbazone metal complexes.

**Table 4: Antibacterial activity of ligands and metal complexes**

Test organism	Diameter of zones of inhibition (mm)										
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>	M <sub>5</sub>	M <sub>6</sub>	M <sub>7</sub>	M <sub>8</sub>	L <sub>1</sub>	L <sub>2</sub>	Kanamycin
Escherichia Coli	7	8	9	8	12	14	12	17	3	3	23
Klebsiella species	5	6	7	5	15	17	16	17	3	2	20
Shigella Sonnei	8	8	10	9	13	16	12	16	4	4	24
Sacillussubtilis	8	8	9	7	12	14	15	15	2	4	24

M<sub>1</sub>: [Cu(SCDAB)<sub>2</sub>](Cl)<sub>2</sub>; M<sub>2</sub>: [Cu(SCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>; M<sub>3</sub>: [Ni(SCDAB)<sub>2</sub>](Cl)<sub>2</sub>; M<sub>4</sub>: [Ni(SCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>; M<sub>5</sub>: [Cu(TSCDAB)<sub>2</sub>](Cl)<sub>2</sub>; M<sub>6</sub>: [Cu(TSCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>; M<sub>7</sub>: [Ni(TSCDAB)<sub>2</sub>](Cl)<sub>2</sub>; M<sub>8</sub>: [Ni(TSCDAB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>; L<sub>1</sub>: SCDAB; L<sub>2</sub>: TSCDAB

## CONCLUSION

The present work describes the facile synthesis of metal complexes with newly synthesized Schiff base ligands and their biological activity. The resulting metal complexes show higher antioxidant and antibacterial activities as compared to the ligands. The nickel complexes derived from p-dimethylaminobenzaldehyde thiosemicarbazone show remarkable antioxidant and antibacterial activities.

## ACKNOWLEDGEMENTS

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