

Synthesis, Spectroscopic, and Antimicrobial Studies of the Bivalent Nickel, and Copper Complexes of Thiosemicarbazide

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A series of metal complexes of Ni(II), and Cu(II) having the general composition $[M(L)_2X_2]$ with thiosemicarbazide have been prepared and characterized by elemental chemical analysis, molar conductance, magnetic susceptibility measurements, mass, IR, electron paramagnetic resonance, and electronic spectral studies. The IR spectral data suggest the involvement of sulfur and terminal amino nitrogen in coordination to the central metal ion. On the basis of spectral studies, an octahedral geometry has been assigned for the Ni(II) complexes whereas tetragonal geometry for Cu(II) complexes. Thiosemicarbazide and its metal complexes have been tested *in vitro* against a number of microorganisms in order to assess their antimicrobial properties.

Key words thiosemicarbazide; nickel(II); copper(II); antibacterial activity; antifungal activity

Sulfur compounds have been the subject of interest in coordination chemistry. Thiosemicarbazide-based compounds have been extensively studied over the last couple of decades.^{1–3} The various schiff bases of thiosemicarbazide (thiosemicarbazones) have attracted much attention because of the large number of potentially useful biological properties such as antibacterial, antifungal, antitumor, antimalarial, antiviral, radioprotective, trypanocidal and anti-inflammatory activities.^{4–15} Their activity has frequently been thought to be due to their ability to chelate metals. It is well known that the compounds containing $>C=S$ moiety have a strong ability to form metal complexes. Although many structures of thiosemicarbazone complexes have been reported, there are a few for complexes of the precursor thiosemicarbazide.¹⁶ Thiosemicarbazide usually acts as a chelating ligand for transition metal ions by bonding through the sulfur and terminal amino nitrogen atom, although in some cases they behave as monodentate ligands where bond through sulfur only.¹⁷

It is interesting to note that in the literature reported, Ni(II) and Cu(II) complexes of thiosemicarbazide reflect higher tendency to exhibit square planar geometry.¹⁸ A variety of colored compounds containing thiosemicarbazide can be obtained depending on the method of preparation and also on the anion used.¹⁹ The control of the geometry around a metal ion is important for controlling the properties of a compound. Although Ni(II) and Cu(II) complexes of thiosemicarbazide are reported in literature,^{20–22} antimicrobial properties of these complexes are not adequately reported. Thus, it was considered desirable to study the structure of Ni(II) and Cu(II) thiosemicarbazide metal complexes to evaluate their tendency to exhibit antimicrobial properties.

In view of the above applications, in this paper we report the synthesis, spectroscopic, and antimicrobial studies of the Ni(II) and Cu(II) complexes of thiosemicarbazide.

Experimental

Instrumentation and Materials The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured with the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as callibrant. Diamagnetic corrections were made using Pascal's constants. The electronic impact mass spectrum was recorded on a JEOL, JMS-DX-303 mass spectrometer. IR spectra (KBr) were recorded on a FTIR spectrum

BX-II spectrophotometer. The electronic spectra were recorded in dimethyl sulfoxide (DMSO) on a Shimadzu UV mini-1240 spectrophotometer. The electron paramagnetic resonance (EPR) spectra of the complexes were recorded as polycrystalline sample, at room temperature for Cu(II) complexes on a E₄-EPR spectrometer using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) as the g-marker. The molecular weights of the complexes were determined cryoscopically in benzene.

All the chemicals were of analytical grade and were procured from Sigma Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

Preparation of Complexes A hot ethanolic solution (20 ml) of thiosemicarbazide (1.8 g, 0.02 mol) and a hot ethanolic solution (20 ml) of the corresponding metal salt (0.01 mol) were refluxed for 3–4 h at 60 °C. On cooling colored complexes were precipitated out. They were filtered off, washed with 50% ethanol, and dried under vacuum over P_4O_{10} .

[Ni(L)₂Cl₂]: Green powder. Yield 59%. mp 300 °C. MS *m/z*: 314 (M⁺). *Anal.* Calcd for C₂H₁₀N₆S₂Cl₂Ni: C, 7.70; H, 3.21, N, 26.94; Ni, 18.84. Found: C, 7.54; H, 3.16; N, 26.71; Ni, 18.61.

[Ni(L)₂(NO₃)₂]: Brown powder. Yield 55%. mp 240 °C. MS *m/z*: 364 (M⁺). *Anal.* Calcd for C₂H₁₀N₈S₂O₆Ni: C, 6.58; H, 2.73; N, 23.01; Ni, 16.08. Found: C, 6.53; H, 2.95; N, 23.17; Ni, 16.23.

[Ni(L)₂(CH₃COO)₂]: Brown powder. Yield 60%. mp 190 °C. MS *m/z*: 361 (M⁺). *Anal.* Calcd for C₆H₁₆N₆S₂O₄Ni: C, 20.07; H, 4.45; N, 23.39; Ni, 16.35. Found: C, 20.34; H, 4.09; N, 23.52; Ni, 16.49.

[Cu(L)₂Cl₂]: Brown powder. Yield 57%. mp 190 °C. MS *m/z*: 315 (M⁺). *Anal.* Calcd for C₂H₁₀N₆S₂Cl₂Cu: C, 7.59; H, 3.16; N, 26.55; Cu, 20.08. Found: C, 7.36; H, 3.03; N, 26.76; Cu, 20.32.

[Cu(L)₂(NO₃)₂]: Brown powder. Yield 61%. mp >350 °C. MS *m/z*: 372 (M⁺). *Anal.* Calcd for C₂H₁₀N₈S₂O₆Cu: C, 6.49; H, 2.70; N, 22.71; Cu, 17.18. Found: C, 6.52; H, 2.79; N, 22.92; Cu, 17.02.

[Cu(L)₂(CH₃COO)₂]: Brown powder. Yield 55%. mp 180 °C. MS *m/z*: 365 (M⁺). *Anal.* Calcd for C₆H₁₆N₆S₂O₄Cu: C, 6.60; H, 2.74; N, 23.08; Cu, 17.46. Found: C, 6.49; H, 2.92; N, 23.15; Cu, 17.33.

Antimicrobial Screening *In vitro* antimicrobial screening was performed by the agar disc diffusion method.^{23,24} All the test organisms were obtained from Microbial Type Culture Collection and Gene Bank (MTCC) (Institute of Microbial Technology, Chandigarh, India). Nutrient agar growth media was prepared according to the instructions of MTCC. Twenty-five milliliter nutrient agar media was poured in each petriplate of 90 mm diameter. The inoculum was spread on the top of solidified media. Sterile discs of Whatman No. 1 filter paper having a diameter of 6 mm, impregnated with the test compounds were placed at four equidistant places on the inoculated petriplates. The zone of inhibition was calculated in millimeters.

The antibacterial activity of thiosemicarbazide and its metal complexes were tested against Gram-positive (*Staphylococcus aureus* and *Staphylococcus epidermidis*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) pathogenic bacteria at a concentration of 100 μg disc⁻¹. Nutrient agar media was prepared by using peptone, beef extract, yeast extract, NaCl, agar-agar, and distilled water. Bacterial cultures were adjusted to 0.5 McFarland turbidity standard and inoculated onto the nutrient agar plates.²⁵ The discs were carefully transferred onto the seeded agar plates. Filter paper

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disc treated with DMSO served as control and Amikacin ($30 \mu\text{g disc}^{-1}$) was used as a standard drug. All determinations were made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. The petriplates were incubated at 37°C for 24 h. The zone of inhibition was calculated.

The antifungal activity of thiosemicarbazide and its metal complexes was tested against two pathogenic fungi, *Candida albicans* and *Aspergillus niger* at a concentration of $200 \mu\text{g disc}^{-1}$ for each. Nystatin ($200 \mu\text{g disc}^{-1}$) was used as standard fungicide and DMSO served as a means of control. For *Candida albicans* nutrient agar media was prepared using yeast extract, peptone dextrose, agar-agar and distilled water. Inoculum suspension in normal saline was prepared from fresh, mature (3–5 d old) cultures grown on nutrient agar slants. Using spectrophotometry at 530 nm, turbidity was measured and adjusted to match a 0.5 McFarland density standard resulting in an inoculum containing 1×10^6 to 5×10^6 fungal cells/ml.²⁶ This suspension was used to directly inoculate agar plates.

For *Aspergillus niger*, nutrient agar media was prepared using czapek concentrate (NaNO_3 , KCl , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and distilled water), K_2HPO_4 , yeast extract, sucrose, agar-agar and distilled water. Seven days old colonies were covered with approximately 1 ml of sterile 0.85% saline and the suspensions were made by gently probing the colonies. The resulting mixture of conidia and hyphal fragments was withdrawn and transferred to sterile tube. After heavy particles were allowed to settle for 3–5 min, the upper homogenous suspensions were collected. The densities of the conidial suspensions were read and adjusted to an optical density (OD) that ranged from 0.09–0.11 (80 to 82% transmittance) at 530 nm.²⁷ The sterile discs impregnated with the test compounds were placed on the already seeded plates at 30°C for 48 h. A clearing zone around the disc indicated the inhibition activity of the test compounds on the pathogenic fungi.

Results and Discussion

The complexes were synthesized by reacting thiosemicarbazide with the metal ions in 2 : 1 molar ratio in an ethanolic medium. Thiosemicarbazide behaves as bidentate and coordinates through the terminal amino N and S atoms. The analytical data, magnetic susceptibility, and spectral analysis agree well with the proposed composition of Ni(II) and Cu(II) complexes of thiosemicarbazide. The molar conductance of the complexes in *N,N*-dimethylformamide (DMF) lies in the range of $10\text{--}20 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their nonelectrolyte behaviour. Thus, the complexes may be formulated as $[\text{M}(\text{L})_2\text{X}_2]$, (where $\text{M}=\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$; $\text{L}=\text{thiosemicarbazide}$; $\text{X}=\text{Cl}^-$, NO_3^- and CH_3COO^-). Complexes containing Cl^- and CH_3COO^- are produced in *trans* form while *cis* form is obtained when NO_3^- is the anion as shown in Figs. 1A, B.

Magnetic Susceptibility As shown in the Table 2, magnetic moment observed for the Ni(II) complexes lies in the range of 2.91–2.95 BM which is consistent with the octahedral stereochemistry of the complexes while the room temperature magnetic moment of the Cu(II) complexes lies in the range 1.77–1.83 BM, corresponding to one unpaired electron.

IR Spectra The assignments of the significant IR spec-

tral bands of thiosemicarbazide and its metal complexes are presented in Table 1. The 3365 cm^{-1} band in thiosemicarbazide due to $\nu_{\text{as}}(\text{NH}_2)$ is shifted to lower frequencies in the complexes. Thiosemicarbazide has two bands at 1642 and 1619 cm^{-1} . The former is the deformation mode, $\delta(\text{NH}_2)$, of the amine in the hydrazine residue, and the latter is the amide (II) band of primary amine. These bands shift towards lower frequencies due to the involvement of one of the NH_2 group in coordination. Strong evidence is the appearance of the $430\text{--}459 \text{ cm}^{-1}$ band due to $\nu(\text{M-N})$. Strong band at 800 cm^{-1} assigned to $\text{C}=\text{S}$ stretching vibration shifts to lower frequencies in the complexes, indicating the involvement of thioketo sulfur in complex formation. In each complex, two thiosemicarbazide ligands coordinate to the central metal ion through two terminal hydrazine N atoms and two S atoms. Thus, it is concluded that the ligand acts as bidentate chelating agent. The infrared spectra of *trans* and *cis* complexes show marked differences in certain regions of the spectrum. For the region around $3400\text{--}3000 \text{ cm}^{-1}$, where NH_2 stretching frequencies are observed, the *trans* isomers show two sharp strong bands. The corresponding *cis* isomers show only broad bands throughout this range. In the region around 1600 cm^{-1} , corresponding to NH_2 bending modes, two sharp bands are observed for the *trans* isomer, while a single broad band is observed for *cis* isomer.¹⁹

The presence of bands at 1458–1412, 1320–1299 and $1056\text{--}1012 \text{ cm}^{-1}$, in the IR spectra of metal complexes of Ni(II) and Cu(II), suggests that both the nitrate groups are coordinated to the central metal ion in a unidentate fashion. In the IR spectra of chloro complexes, bands corresponding to $\nu(\text{M-Cl})$ are observed at $345\text{--}320 \text{ cm}^{-1}$ indicating the presence of M-Cl bond. The IR spectra of Ni(II) and Cu(II) of acetato complexes show the medium intensity bands at 1620 and $1332\text{--}1320 \text{ cm}^{-1}$, assigned to $\nu_{\text{a}}(\text{C-O})$ and $\nu_{\text{s}}(\text{C-O})$, respectively. The difference between these two frequencies is *ca.* 289 cm^{-1} , which is greater than that for uncoordinated acetate ions by *ca.* 145 cm^{-1} and that for bidentate

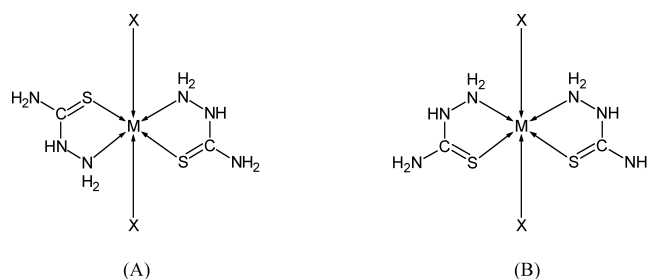


Fig. 1. Suggested Structure of the Complexes

(A) *trans*- $[\text{M}(\text{L})_2\text{X}_2]$, where $\text{M}=\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and $\text{X}=\text{Cl}^-$ and CH_3COO^- . (B) *cis*- $[\text{M}(\text{L})_2\text{X}_2]$, where $\text{M}=\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and $\text{X}=\text{NO}_3^-$.

Table 1. Important IR Spectral Bands of Thiosemicarbazide and Its Complexes (cm^{-1})

Compounds	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_{\text{s}}(\text{NH}_2)$	$\delta(\text{NH}_2)$	$\nu(\text{C}=\text{S})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$
$\text{CH}_3\text{N}_3\text{S}$ (L)	3365	3263	1642	800	—	—
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	3349	3256	1638	703	436	330
$[\text{Ni}(\text{L})_2(\text{NO}_3)_2]$	3317	3153	1633	697	431	317
$[\text{Ni}(\text{L})_2(\text{CH}_3\text{COO})_2]$	3344	3176	1620	701	439	355
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	3338	3247	1633	784	430	330
$[\text{Cu}(\text{L})_2(\text{NO}_3)_2]$	3320	3244	1635	779	452	346
$[\text{Cu}(\text{L})_2(\text{CH}_3\text{COO})_2]$	3302	3243	1632	708	459	361

Table 2. Electronic, EPR Spectral Data and Magnetic Moment for Thiosemicarbazide Complexes

Complexes	λ_{\max} (cm ⁻¹)	g_{\parallel}	g_{\perp}	g_{iso}	G	μ_{eff} BM
[Ni(L) ₂ Cl ₂]	9337, 14124, 24100	—	—	—	—	2.92
[Ni(L) ₂ (NO ₃) ₂]	9765, 14350, 24200	—	—	—	—	2.91
[Ni(L) ₂ (CH ₃ COO) ₂]	9870, 14577, 25700	—	—	—	—	2.95
[Cu(L) ₂ Cl ₂]	14562, 20190, 23903	2.27	2.08	2.14	3.37	1.77
[Cu(L) ₂ (NO ₃) ₂]	14800, 20480, 24180	2.13	2.05	2.07	2.60	1.80
[Cu(L) ₂ (CH ₃ COO) ₂]	15625, 21048, 24248	2.24	2.07	2.12	3.42	1.83

Table 3. Antibacterial Activity of Thiosemicarbazide and Its Complexes

Compounds	Diameter of zone of inhibition (mm)			
	<i>Staphylococcus aureus</i>	<i>Staphylococcus epidermidis</i>	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>
CH ₃ N ₃ S (L)	—	—	—	—
[Ni(L) ₂ Cl ₂]	—	—	—	—
[Ni(L) ₂ (NO ₃) ₂]	—	—	—	—
[Ni(L) ₂ (CH ₃ COO) ₂]	—	—	—	—
[Cu(L) ₂ Cl ₂]	12	12	11	10
[Cu(L) ₂ (NO ₃) ₂]	13	12	10	9
[Cu(L) ₂ (CH ₃ COO) ₂]	10	11	10	8
Amikacin	26	22	21	20

acetate ion by *ca.* 219 cm⁻¹. It is strongly supported that both the acetate ions are coordinated to the metal ion in a unidentate fashion.^{28–30}

Electronic Spectra The electronic spectra of Nickel(II) complexes display three absorption bands (Table 2) in the range 9870–9337, 14577–14124 and 25700–24100 cm⁻¹. The ground state of Ni(II) in an octahedral coordination is ³A_{2g}. Thus, these bands may be assigned to three spin-allowed transitions: ³A_{2g}(F)→³T_{2g}(F) (ν_1), ³A_{2g}(F)→³T_{1g}(F) (ν_2) and ³A_{2g}(F)→³T_{1g}(P) (ν_3), respectively. The position of the bands indicates that the Ni(II) complexes have six coordinate octahedral geometries.³¹ The electronic spectra of six coordinated Cu(II) complexes display bands in the range 15625–14592, 21048–20190 and 24248–23903 cm⁻¹ corresponding to following transitions: ²B_{1g}→²A_{1g} ($d_{x^2-y^2}$ → d_{z^2}) ν_1 , ²B_{1g}→²B_{2g} ($d_{x^2-y^2}$ → d_{xy}) ν_2 and ²B_{1g}→²E_g ($d_{x^2-y^2}$ → d_{xy}, d_{yz}) ν_3 , respectively. Therefore, the Cu(II) complex may be considered to possess a tetragonal geometry.^{32,33}

Electronic Paramagnetic Spectra Room temperature EPR spectra of Cu(II) complexes were recorded as polycrystalline sample, at frequency of 9.1 GHz under the magnetic field strength of 3000 G. The analysis of spectra gives g_{\parallel} =2.27–2.13, g_{\perp} =2.08–2.05 as shown in Table 2. The observed g_{\parallel} values for the complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{\parallel}>g_{\perp}>2.0023$ observed for the complexes indicates that unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are a characteristic of axial symmetry. Thus, a tetragonal geometry is confirmed for the aforesaid complexes.³⁴

$G=(g_{\parallel}-2)/(g_{\perp}-2)$, which measures the exchange interaction between the metal centres in a polycrystalline solid, has been calculated. According to Hathaway *et al.*,³⁵ if $G>4$, the exchange interaction is negligible, but $G<4$ indicates considerable exchange interaction in solid complexes. The complexes reported in this paper give the ' G ' value in the range 2.60–3.42, which is <4 , indicating the exchange interaction

in the solid complexes.

Antimicrobial Activity The antimicrobial screening data shows that thiosemicarbazide does not exhibit antimicrobial activity. Ni(II) complexes did not inhibit the growth of test organisms. However, they were found to be active against *Candida albicans*. Our results are in agreement with the earlier findings that 6-coordinate, paramagnetic Ni(II) complexes with two ligands do not inhibit growth of test organisms. Thus, in the Ni(II) complexes, the antimicrobial activity against the test organisms can correlate with their ligand-replacement abilities rather than solubility or hydrophobicity of the complexes.⁴ From the Table 3, it is clear that Cu(II) metal chelates exhibit effective antibacterial activities. The increased activity of the metal chelate can be explained on the basis of chelation theory. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agent, killing more of the bacteria than the ligand. It is observed that in a complex the positive charge of the metal is partially shared with the donor atoms present in the ligands and there may be π -electron delocalization over the whole chelating.³⁶ This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the bacterial membranes. There are other factors which also increase the activity, namely, solubility, conductivity, and bond length between the metal and ligand. The result of fungicidal screening as shown in Table 4 shows that Cu(II) complexes were active against pathogenic fungi, *Candida albicans* but showed no activity against *Aspergillus niger*.

The proposed study revealed an octahedral geometry in the Ni(II) complexes, whereas tetragonal geometry in Cu(II) complexes. Ligand acts as a bidentate chelating agent coordinating through the sulfur and terminal amino nitrogen atoms to form 5-membered chelate rings. The results of antimicrobial activity show that thiosemicarbazide itself does not exhibit antibacterial and antifungal activities. However it is important to note that Cu(II) complexes exhibited antimicrobial

Table 4. Antifungal Activity of Thiosemicarbazide and Its Complexes

Compounds	Diameter of zone of inhibition (mm)	
	<i>Candida albicans</i>	<i>Aspergillus niger</i>
CH ₃ N ₃ S (L)	—	—
[Ni(L) ₂ Cl ₂]	8	—
[Ni(L) ₂ (NO ₃) ₂]	8	—
[Ni(L) ₂ (CH ₃ COO) ₂]	8	—
[Cu(L) ₂ Cl ₂]	14	—
[Cu(L) ₂ (NO ₃) ₂]	10	—
[Cu(L) ₂ (CH ₃ COO) ₂]	9	—
Nystatin	26	18

activities. Cu(II) complexes showed more activity than the Ni(II) complexes. This may be due to the higher stability of Cu(II) complexes than the other complexes.³⁷⁾ It is interesting to know that 6-coordinate, paramagnetic Ni(II) complexes did not exhibit antibacterial activities. Their antifungal activities were also found to be much less compared to copper complexes. None of the complexes showed activity against *Aspergillus niger*.

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