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Copper Complexes of Imidazole-2-carbaldehyde N(4)-Substituted Thiosemicarbazones: Synthesis, Characterization and Antimicrobial Activity

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Imidazole-2-carbaldehyde N(4)-pyrrolidinyl, N(4)-piperidinyl, N(4)-morpholinyl and N(4)-piperazinyl thiosemicarbazones and their copper(II) complexes have been synthesized. The compounds were characterized by NMR, IR, UV-visible, ESR spectroscopy and ESI mass spectrometry. The stoichiometry, spectroscopic and mass spectrometry data indicates thiosemicarbazone coordination to Cu(II) in neutral form with NNS donors. The coordination spheres of the metal ion are completed by chlorine atoms in approximately square pyramidal geometry. The *in vitro* antimicrobial properties of the compounds in broth culture exhibited a moderate inhibitory effect on the microbial proliferation. Some copper(II) complexes exhibited a moderate inhibitory activity, better than that of the corresponding free thiosemicarbazone.

Keywords: Copper complex, Imidazole, Thiosemicarbazone, Antimicrobial properties.

INTRODUCTION

α-(N)-Heterocyclic thiosemicarbazones exhibit broad therapeutic properties such as antitumor, antibacterial, antiviral, antimalarial, antifilarial, antifungal and antileishmaniasis activities [1]. First successful report of thiosemicarbazone as drug against tuberculosis and leprosy appeared in 1950 [2,3]. The potential biological activities of thiosemicarbazones are due to their ability to form chelates with metal in biological system [1]. Metal complexes of thiosemicarbazones may be more active, reduce long term side effects, or serve as the vehicle for biological activation [4].

Recently, 3-aminopyridine-2-carboxaldehyde thiosemicarbazone and 5-aminopyridine-2-carboxaldehyde thiosemicarbazone have received much importance because of their potential anticancer activity [5,6]. On the other hand imidazole derivatives have shown a wide pharmacological activity such as antibacterial, antifungal as well as antitumor activity [7]. Some copper complexes of thiosemicarbazones have been found biologically more potent than their corresponding free thiosemicarbazones [8].

We report here the synthesis and characterization of 2-formyl-imidazole N(4)-pyrrolidinyl, N(4)-piperidinyl N(4)-morpholinyl, N(4)-piperazinyl thiosemicarbazones (Fig. 1), their Cu(II) complexes and *in vitro* antimicrobial properties.

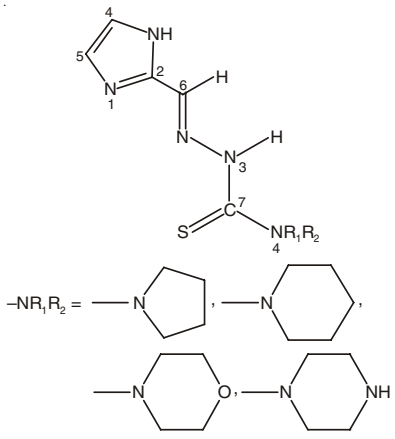

Fig. 1. Imidazole-2-carbaldehyde N(4)-substituted thiosemicarbazones

EXPERIMENTAL

Imidazole-2-carbaldehyde was commercially available from Sigma-Aldrich. Other chemicals like carbon disulfide, N-methyl aniline, sodium chloroacetate, hydrazine hydrate (98 %), acetonitrile were purchased from Himedia, Loba, S.D. fine chemical companies and used without further purification. $CuCl_2$ was purchased from Merck. Other solvents were purchased from Merck, Glaxo, BDH, Qualigens and Ranbaxy chemical companies and used without further purification.

UV-visible electronic spectra in DMF (concentration 5 × 10^{-5} mol/L) were recorded on Perkin Elimer Lamba 40 UV/VIS spectrometer at the Department of Medicine Management, Babarmahal, Kathmandu. Elemental analysis (C, H and N) measurement was performed on CHN recorder MT-5 instrument at IIT Chennai, India. ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 solution on FT-500 NMR spectrometer at IIT, Chennai, India. IR spectra were recorded using KBr medium on Shimadzu FTIR-200 spectrometer at the Department of Botany, Thapathali, Kathmandu. Mass spectra were recorded in DMF on ESI instrument: Thermo LTQ at Department of Chemistry, Tufts University, USA. The parameters used are capillary temperature = 200 °C, capillary voltage = 140 V, flow = 20 µL/min. ESR spectra were recorded on Bruker BioSpin Corp. (EMX series) Model: A 200-9.5/12B/S at Sogang University, Seoul, Korea. The melting points were determined by using melting point apparatus (Philip Harrish).

Chlorine content was determined potentiometrically using Osaw Digital Potentiometer (cat no: 30067, Osaw India). The base of the dried Ni-crucible was covered with Na_2CO_3 and about 0.025 g of Cu(II) complex was spread over it. The compound was covered again with a little Na_2CO_3 and then kept in furnace at 900 °C for 1 h. After cooling, the complex was dissolved with 2 N HNO_3 (50-60 mL). These solutions were titrated against 0.02 N $AgNO_3$ solution using salt bridge of Agar/Agar and KNO_3 (1:5).

Synthesis of thiosemicarbazone: Thiosemicarbazides were synthesized following the procedure reported in the literature [9].

Synthesis of imidazole-2-carbaldehyde N(4)-pyrrolidinyl thiosemicarbazone (Him4pyrd): Him4pyrd was synthesized by refluxing a 1:1 molar mixture of imidazole-2-carbaldehyde and N(4)-pyrrolidinyl thiosemicarbazide in 60 % ethanol for about 8 h. The product was recrystallized in ethanol water solution [10].

Him4pyrd **(1)**: Grayish white solid. Yield: 67 %, m.p. 212 °C. Anal. found C, 48.05; H, 5.29; N, 31.40; Calcd. for $C_9H_{13}N_5S$: C, 48.41; H, 5.87; N, 31.36;. Electronic spectrum (cm^{-1}): 34482s (1.608).

Synthesis of imidazole-2-carbaldehyde N(4)-piperidinyl (Him4pipe), N(4)-morpholinyl (Him4morp) and N(4)-piperazinyl thiosemicarbazone (Him4piprz): These ligands (Him4pipe, Him4morp and Him4piprz) were synthesized by following the procedure reported in the literature [9] by refluxing a equimolar mixture of 4-methyl-4-phenyl-3-thiosemicarbazide, corresponding base and imidazole-2-carbaldehyde in MeCN for about 45 min. The product was collected and recrystallized in MeOH.

Him4pipe (2): Creamy white solid. Yield: 73 %, m.p. 171 °C. Anal. found C, 50.0; H, 6.42; N, 29.50; Calcd. for $C_{10}H_{15}N_5S$: C, 50.61; H, 6.37; N, 29.51. Electronic spectrum (cm^{-1}): 34482s (1.778).

Him4morp (3): White solid. Yield: 58 %. m.p. 163-167 °C. Anal. found C, 45.05; H, 5.35; N, 28.95; Calcd. for $C_9H_{13}N_5SO$: C, 45.17; H, 5.48; N, 29.27. Electronic spectrum (cm^{-1}): 34482s (1.143).

Him4piprz (4): Pale cream solid. Yield: 56 %. m.p. 187-189 °C. Anal. found C, 45.02; H, 5.25; N, 34.92; Calcd. for $C_9H_{14}N_6S$: C, 45.36; H, 5.92; N, 35.26. Electronic spectrum (cm^{-1}): 34482s (2.210).

Synthesis of Cu(II) complexes: Copper(II) complexes were prepared by refluxing an ethanol suspension of $CuCl_2{\cdot}5H_2O$ and the corresponding thiosemicarbazone for 5-7 h. The complex was filtered and washed with ethanol and ether and dried at 40-50 °C for 3 h and then at 80-90 °C for 2 h.

[Cu((Him4pyrd)Cl_2] (5): Green solid. Yield: 79 %. m.p. 225 °C. Anal. Found C, 30.12; H, 2.81; N, 18.75; Cl, 19.49 Calcd. for $C_9H_{13}N_5SCuCl_2$: C, 30.22,; H, 3.66; N, 19.58; Cl, 19. 82. Electronic spectrum (cm^{-1}): 24509b (0.972), 34722s (1.249). Mass spectrum (*m/z*): 358.00 $[M]^+$ (cal. 357.75).

[Cu((Him4pipe)Cl_2] (6): Green solid. Yield: 78 %. m.p. 202 °C. Anal. Found C, 33.28; H, 2.94; N, 19.0; Cl, 18. 54 Calcd. for $C_{10}H_{15}N_5SCuCl_2$: C, 32.31,; H, 4.07; N, 18.84; Cl, 19. 07.. Electronic spectrum (cm^{-1}): 24752b ((0.946), 34722s (3.292). Mass spectrum (*m/z*): 372.00 $[M]^+$ (cal. 371.78).

[Cu((Him4morp)Cl_2] (7): Green solid, Yield: 65 %, m.p. 184 °C. Anal. Found C, 28.72; H, 3.21; N, 18.53; Cl, 18.55 Calcd. for $C_9H_{13}N_5SOCuCl_2$: C, 28.92,; H, 3.51; N, 18.74; Cl, 18. 97. Electronic spectrum (cm^{-1}): 24630b (0.914), 34722s (2.362). Mass spectrum (*m/z*): 374.09 $[M]^+$, (cal. 373.75).

[Cu((Him4piprz)Cl_2] (8): Greenish brown solid. Yield: 65 %, m.p. 255 °C. Anal. Found C, 28.98; H, 3.21; N, 22.32; Cl, 18.49 Calcd. for $C_9H_{14}N_6SCuCl_2$: C, 29.00; H, 3.79; N, 22.55; Cl, 19. 02. Electronic spectrum (cm^{-1}): 25380b (0.204), 34722s (1.089). Mass spectrum (*m/z*): 373.00 $[M]^+$, (cal. 372.76).

Antimicrobial assay: The antimicrobial evaluation of synthesized thiosemicarbazones and its copper complexes was carried out following established protocol [11]. Four pathogenic bacteria *S. aureus* KCTC 1621*, B. subtilis* QST713*, K. pneumoniae, Enterobacter* were used as test organism.

Thiosemicarbazones and their Cu(II) complexes were dissolved in dimethyl sulfoxide by mild sonication in a sonicator bath for few minutes and stock solution of concentration of 3000 µg/mL was prepared. Sample was used in different concentrations ranging from 1-300 µg/mL.

Mueller Hinton agar M173 (MHA) and Mueller Hinton broth M391-500G (MHB, Hi-media), were used as the culture medium for bacteria. Test inoculums of bacteria were maintained at 5 × 10^4 cells per mL after 24 h growth in MHB. Bioassay was done for each organism at 1, 10, 20, 30, 40, 50, 100, 200 and 300 µg/mL concentrations of each compound. Determination of minimum inhibitory concentration (MIC) of each sample on all four microorganisms was carried out by macrobroth dilution method [12] in MHB. Control is used as MHB having no test compound with 1 % DMSO, which is the minimum concentration of compound that inhibits the microbial growth. Visual method was used to detect the minimum inhibitory concentration (MIC) after 24 h incubation at 37 °C. The culture tubes ranging from MICs up to highest concentration was taken to determine minimum bactericidal concentration (MBC) which is the concentration of compound at which no growth of microorganism occurs. 100 µL cultures from MIC experiment were taken and spread on Mueller Hinton agar (MHA). Observations were done in different time period comparing with positive control that contained pure culture of all respective microorganisms. The experiment was triplicate for confirmation.

RESULTS AND DISCUSSION

The reaction of thiosemicarbazone and $CuCl_2$ in ethanol produced green colour copper(II)-complexes in good yield of 65-80 %. The colour of the complexes were more intense than the corresponding thiosemicarbazones because of the charge transfer from ligand to Cu(II) centre. The micro analytical data were consistent with 1:1 metal to ligand ratio in the complexes $[Cu(HL)Cl_2]$. The spectroscopic properties (^1H, ^{13}C NMR, IR and UV-visible) as well as mass spectrometry result were consistent with the proposed structure of the complexes with neutral ligand in coordination. The complexes were stable in air and moisture, slightly soluble in H_2O, MeOH, EtOH, MeCN and more soluble in DMF and DMSO.

NMR studies: The assignment of ^1H NMR peaks (Table-1) were in general agreement with the previous work on imidazole-2-carbaldehyde N(4)-substituted thiosemicarbazones [13]. The ^1H NMR spectral result indicate hydrogen bonding by the thiosemicarbazone moiety's N(3) proton to a imadazole ring nitrogen for Him4pyrd, Him4pipe, Him4morp and Him4piprz. In case of 2-acetylpyridine [14] or acetylpyrazine thiosemicarbazones [15] with N(4) substitution with two alkyl groups or a ring down field shift of N(3) proton of thiosemicarbazone moiety above 14 ppm have been observed because of its hydrogen bonding to ring nitrogen. The resonance of N(3) proton for Him4pyrd (13.72), Him4pipe (13.80), Him4morp (13.88) and Him4piprz (13.96) reveals that it predominantly exist in the form of *Z*-isomer.

Down field shift of imidazole proton of Him4pyrd (12.92s), Him4pipe (12.93b), Him4morp (12.97b) and Him4piprz (12.96b) may be due to its hydrogen bonding to solvent DMSO [13]. Both C(4)-H and C(5)-H show up field shift than C(6)-H for the thiosemicarbazones due to bonding of later carbon with azomethine nitrogen [11,13,16].

In the ^{13}C NMR, pair of peaks for C(2), C(4), C(5) and C=S are present for most of the thiosemicarbazones (Table-2) due to the presence of hydrogen bonding isomers. All assignments were made taking into account reports on related ligands [13]. ^{13}C NMR resonance for C=S in case of Him4morp (180.90, 181.10) and Him4piprz (180.46, 180.83) are down field shifted compare to N(4)-mono or di-substituted alkyl thiosemicatbazones [13]. Azomethine carbon (C=N) for Him4morp (119.08) and Him4piprz (119.07) also show the same trend of down field shift compare to its N(4)- mono or di-substituted analogue. Among all the carbon nuclei C(4) has suffered more down field shift influenced by N(4) substitution [11,13,16].

IR studies: The diagnostic IR bands are compiled in Table-3. The spectra of the free ligands show a broad band in 3163-3120 cm^{-1} region which includes the stretching vibration of the NH group which is involved in hydrogen bonding. However, the position of ν(NH) bands are slightly shifted to the higher energy range (3255-3151 cm^{-1}) in the complexes and splitted into several bands. The strong bands in the range 1600-1558 cm^{-1} for the free thiosemicarbazones are assigned to ν(C=N) stretch which are often coupled with δ(NH) to give broad bands. These bands are shifted to lower energy in the complexes (1579-1546 cm^{-1}) which indicate coordination through azomethine nitrogen. Its coordination is consistent with the presence of band at 486-447 cm^{-1} assignable to ν(Cu-N) stretch for the complexes. Bands at 871-806 cm^{-1} in the free thiosemicarbazones correspond to ν(C=S) stretch which are shifted to lower frequency (821-780 cm^{-1}) in the complexes. Small decrease in energy of the ν(C=S) band is attributed to coordination through thione sulphur. Its coordination is further supported by the presence of band at 374 cm^{-1} of medium to weak strength in the complexes due to ν(Cu-S) stretch [13].

Ring deformation modes of imidazole (756-675 cm^{-1}) on coordination in its neutral form were found at higher frequency (775-694 cm^{-1}) in the complexes. This also attributes to slightly higher energy shift of ring ν(NH) compare to the free thiosemicarbazones. The band corresponding to ν(Cu-N, imidazole) is expected in the range 400-300 cm^{-1} and in the complexes there are weak to medium bands in this region. The same region includes ν(Cu-Cl) stretch [13,16] consistent with the five-coordinated nature of the complexes with neutral ligand having two assignable ν(Cu-Cl) bands. Therefore, the most plausible

TABLE-1
^1H NMR SPECTRAL DATA OF THE COMPOUNDS

Assignment (ppm)	Compound **1**	Compound **2**	Compound **3**	Compound **4**
N(3)H	13.72s	13.80s	13.88s	13.96s
N(imz)H	12.92s	12.93b	12.97b	12.96b
C(4)H	7.31s	7.29s	7.31s	7.33s
C(5)H	7.37s	7.36s	7.39s	7.35s
C(6)H	7.41s	7.41s	7.42s	7.42s
N(4)CH	3.75b, 3.71b, 1.87s, 2.01b	3.95t, 3.85t, 1.66t, 1.60d	3.69t, 3.66t 3.92t, 3.97t	3.35b, 4.08s, 4.13s, 4.19s, 2.79t (H-Piprz)

TABLE-2
^{13}C NMR SPECTRAL DATA OF THE COMPOUNDS

Assignment (ppm)	Compound **1**	Compound **2**	Compound **3**	Compound **4**
C(2)	142.00, 143.03	141.84, 142.91	141.70, 142.75	141.77, 142.85
C(4)	129.56, 130.15	129.54	136.28	135.77, 135.89
C(5)	127.03	126.93	127.49, 129.67	127.14, 127.81, 12 7.68, 129.66
C=N	118.82	118.96	119.08	119.07
C=S	176.80	179.94, 180.60	180.90, 181.10	180.46, 180.83
N(4)C		51.56, 50.62, 24.38, 25.94, 26.08	49.83, 51.06, 66.22, 66. 43	49.31, 51.83, 45.84, 45.92, 48.05, 47.59, 50.90, 49.64

TABLE-3
KEY IR SPECTRAL (cm^{-1}) BANDS OF THE COMPOUNDS

Assignment (cm^{-1})	Compounds							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
ν(NH)	3120s, b	3132s	3163s	3140s 3093s, b	3061s, b	3032s, b	3151s, 3055s, b	3255s, 3120b
ν(C=N) + δ(NH)	1600s, 1556s, b	1573s	1581s, b	1558s, b	1579s, 1556s	1550s, 1516	1573s, 1546s,	1546m, 1492s,
ν(ring) + ν(CNS)	1523m, 1438s, 1411m	1481m 1435s 1411m	1435m	1435s	1458m 1446m, 1433m	1427m, 1377w	1381w	1388s, 1462, 1442
ν(CS)	806s	810m	871s	864s, b	790m	780m	813w	821m
ρ(OP)	686m	675m	725s	756s	704m	694m	775s	771s
ν(CuN)					468m	447w	470w	486w
ν(CuS)					374m	374w	374w.	374m

structures, based on the above spectroscopic results for the complexes are square pyramidal [17].

UV-visible studies: The thiosemicarbazones have sharp band at 34482 cm^{-1} with weak shoulder at slightly lower energy due to n→π* transition of the imidazole ring and thiosemicarbazone moiety, respectively. Usually thiosemicarbazones show n→π* bands below 30,000 cm^{-1} involving transitions within C=N and C=S group of the thiosemicarbazon moiety. These bands were found merged with the n→π* transition of the imidazole ring. In the spectra of complexes low energy bands due to L→M charge transfer transitions indicate the coordination of thiosemicarbazone with Cu(II) centre [18,19]. These bands below 30,000 cm^{-1} include S ⟶ Cu (II) and N→Cu(II) band and Cu(II) *d-d* transition band. These bands may have also contribution from Cl→Cu(II) charge transfer transition [13,18]. In DMF solution the number of *d-d* bands is reduced to one and the single ligand band (imidazole ring and thiosemicarbazone moiety) is shifted to higher energy suggesting weak interaction with the solvent. The electronic absorption spectra of the complexes consist a clear *d-d* band in the visible region at about 25000 cm^{-1}.

Mass spectrometry (ESI-MS): The ESI mass spectra of the complexes [Cu(Him4pyrd)Cl_2], [Cu(Him4pipe)Cl_2], [Cu(Him4morp)Cl_2] and [Cu(Him4piprz)Cl_2] were recorded using DMF as a solvent and a small amount of methanol as a co-solvent. The peak observed for the complexes [Cu(Him4pyrd)Cl_2], [Cu(Him4pipe)Cl_2], [Cu(Him4morp)Cl_2] and [Cu(Him4piprz)Cl_2] at *m/z* 358.00, 372.00, 374.09 and 373.00 respectively were due to the molecular ion $[M]^+$ fragment [20]. The molecular ion peak suggests that the ligands act in the neutral form [20]. The mass spectra of the metal complexes also show a series of peaks corresponding to various fragments and also some strong peaks beyond the molecular ion peak due to chloro bridged $[2M\text{-}3Cl\text{-}2H]^+$ dimer.

Electron paramagnetic resonance spectra: In order to get insight into the structure of Cu(II)-complexes we next performed solid state EPR experiments. The EPR spectra of all the solid state Cu-complexes are shown in Fig. 2. No hyperfine structure is observed except in [Cu((Him4pipe)Cl_2]. The absence of hyperfine splitting in $g_{\|}$ region, due to the interaction of nuclear spin (I = 3/2) with electron spin (S = 1/2), of other three Cu(II)-complexes ([Cu(Him4pyrd)Cl_2], [Cu(Him4morp)Cl_2] and [Cu(Him4piprz)Cl_2]) indicates the

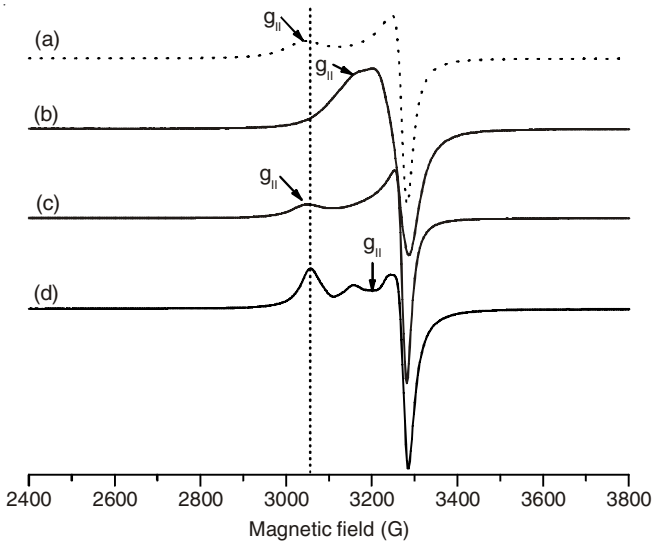

Fig. 2. Solid state EPR spectra (9.388 GHz) of (a) [Cu(Him4pyrd)Cl_2] (b) [Cu(Him4piprz)Cl_2] (c) [Cu(Him4morp)Cl_2] (d) [Cu((Him4pipe)Cl_2] at room temperature

coupling between two Cu(II) ions in polycrystalline solid sample [21]. The hyperfine splitting in [Cu((Him4pipe)Cl_2] is also non homogenous and this is probably due to the dipolar broadening from incomplete separation of paramagnetic Cu(II) centers or $g_{\|}$ overlapped with the $g_{\perp}$ signal.

The EPR data show that all complexes display axial signal with two g-values ($g_{\|}$ and $g_{\perp}$). Both g values are greater than 2.01 (Table-4). The g_{av} (average) was calculated using the formula:

$$g = \frac{g_{\|} + 2g_{\perp}}{3}$$

The $g_{\|} > g_{\perp} > g_e$ suggests the unpaired electron of Cu(II) is in $d_{x^2-y^2}$ orbital and $d_{x^2-y^2}$ is the ground state. We do not see isotropic symmetry in the complexes (*i.e.* $g_1 = g_2 = g_3 = g$) or similar bond length for all associated ligands in square-

TABLE-4
EPR DATA OF Cu(II)-COMPLEXES

g-value	Cu-Pipe	Cu-Morp	Cu-Piprz	Cu-Pyrd
$g_{\perp}$	2.056	2.05	2.083	2.055
$g_{\|}$	2.079	2.186	2.11	2.191
$A_{\|}$	100 G	–	–	–
g_{av}	2.063	2.095	2.092	2.100

pyramid. We can ruled out the trigonal bi-pyramidal geometry of the complexes because in TBP geometry, the g values are reverse *i.e.* ($g_{\parallel} < g_{\perp}$) [22].

Antimicrobial studies: The thiosemicarbazones and their copper(II) complexes eventually checked for MIC and MBC, which showed their minimum inhibitory concentrations in concentrations ranging from 10 µg/mL. Concentration above 200 or 300 µg/mL showed almost strong inhibition by each compounds against all the test organism *S. aureus, B. subtilis, K. pneumonia* and *Enterobacter.* The result observed in MBC shows that bacteria takes longer time to grow at higher concentration (300 µg/mL) but after some time of incubation, bacterial growth again starts as quick as control. This response of the microorganism emphasized that the compounds are bacteriostatic against these organisms instead of bactericidal.

Copper complexes showed their activity more efficiently towards *Enterobacter* and *Klebsiella pneumoniae*. The growth of these bacteria was significantly inhibited (MIC) at concentration of 20-30 µg/mL, whereas a MIC value of 10 µg/mL was observed against *Enterobacter* by compound [Cu((Him4pipe)Cl_2]. Minimum bactericidal concentrations were not defined under experimental range which might even much more higher than MICs, evidencing that a bacteriostatic effect is involved. The stated results point out the wide and remarkable inhibitory effect against most of the tested strains (inhibited at concentrations ranging from 10 to 40 µg/mL). A good effectiveness is exhibited by Him4piprz which acts in the range 10 µg/mL to 20 µg/mL towards *S. aureus* and have bacteriostatic time of 1 h at 30-40 µg/mL whereas a more limited inhibition (50 µg/mL) of [Cu(Him4pyrd)Cl_2] was observed towards *Klebsiella pneumonia*. The result coincides with the report indicating the enhancement of antimicrobial activity of complexes due to their structure-activity relationship [8,11,23]. Free thiosemicarbazones also had MIC within the range that of Cu-complex (10-20 µg/mL) but they did not inhibit the growth of organism as compared to Cu-complexes. Copper complexes of the thiosemicarbazones with N(4)-pyrrolidinyl (four member ring) and N(4)-piperidinyl (five member ring) were found to be more effective to inhibit the growth of bacteria. The average bacteriostatic time towards Cu-complexes were found to be higher (about 4 h) than that of the free thiosemicarbazones.

Conclusion

Novel thiosemicarbazone ligands derived from imidazole-2-carbaldehyde and their Cu(II) complexes of the type [$CuHLCl_2$] (where HL is thiosemicarbazone) which have higher inhibitory activity against different pathogenic microorganisms have been synthesized and characterized. Imidazole-2-carbaldehyde thiosemicarbazones behave as neutral ligands and coordinate through N,N,S donors in these synthesized copper complexes. The coordination geometry around the copper centre can be described as square pyramidal with chloro ligands as in Fig. 3.

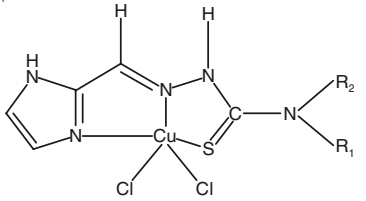

Fig. 3. Proposed structure of Cu(II) complexes

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