

# Synthesis, Characterization and spectroscopic study of new NNS Schiff base and its Cu(II), Cd (II) and Zn(II) metal complexes

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## Abstract

Novel copper(II), cadmium(II) and zinc(II) complexes of general formula,  $[M(NNS)_2]$  (NNS = uninegatively charged tridentate ligands formed by condensation of 6-methyl pyridine-2-carbaldehyde with 2-methylbenzyl hydrazinecarbodithioate) have been synthesized and characterized using different physico-chemical techniques. The complexes have tetrahedral geometry for Zn(II) and Cd(II) complexes while Cu(II) expected to has square planner structure with the ligands coordinated to the metal ions as uninegatively charged tridentate chelating agents *via* the pyridine nitrogen, the azomethine nitrogen and the mercaptide sulphur atoms. The new compounds expected to shows bioactivity against bacteria, fungi and against cancer cells.

## Introduction

There has been a considerable interest shown to the thiocarbazic acid and to the ligands derived from it especially those having NNS donor sequences <sup>[1]</sup>. These compounds warrant additional and further study due to their interesting properties which can be greatly modified by introducing different organic substituents, by which they can shows variation in donor properties. Interacting these ligands with metal ions to give structures of different geometry and properties and they are often biologically active <sup>[2,3]</sup>. To date, reports of the biological properties of these metal- dithiocarbazato complexes are still lacking since previous studies concentrated on synthesis and characterization <sup>[4-6]</sup>. The presence of both hard nitrogen and soft sulphur donor atoms permits coordination with a wide range of transition and non-transition metal ions yielding stable and colored metal complexes, some of which have exhibited interesting physico-chemical <sup>[7-11]</sup> and potentially beneficial chemotherapeutic properties <sup>[12-15]</sup>.

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A new Schiff base benzyl 2-methylbenzyl -2-[(6-methylpyridin-2-yl)methylidene] hydrazinecarbodithioate (NNS) from the condensation reaction of 6-methyl pyridine-2-carbaldehyde with 2-methylbenzyl hydrazinecarbodithioate. The three new metal complexes were prepared using copper(II) acetate trihydrate, nickel(II) acetate and zinc(II) acetate. The new compounds were characterized using various physico-chemical and spectroscopic techniques.

## Material and Methods

### - Material

All chemicals were used as supplied without any further purification: hydrazine hydrate (Fluka), potassium hydroxide (BDH), 2-methylbenzyl chloride (Acros), carbon disulphide (BDH), 6-methyl pyridine-2-carbaldehyde (BDH), Copper(II) acetate trihydrate (BDH), Zinc(II) acetate (fluka) and Cadmium(II) acetate. Dimethyl sulphoxide (DMSO) (99% BDH), Diethyl ether (fluka) and absolute ethanol (99.99%, BDH).

## Methods

### - Physical measurements

The melting point of each sample was determined using an Electrothermal digital melting point apparatus. Magnetic Susceptibility of metal complexes was measured using a Sherwood Auto Magnetic Susceptibility Balance at 298 K. The value obtained was then used to calculate the value of  $\mu_{\text{eff}}$ . Only copper complexes ( $d^9$ ) were done using this method as act as paramagnetic. Molar conductance of  $1 \times 10^{-3}$  molar solutions of the metal complexes in dimethyl sulphoxide (DMSO) was measured at 30°C using a 4310 Jenway Conductivity Meter and a dip-cell with platinized electrodes. The complexes were dissolved in DMSO, and the measurements were done on a Shimadzu UV-2501 PC Spectrophotometer for the range of (200–1100)  $\text{cm}^{-1}$  for solutions of  $10^{-3}$  M and  $10^{-4}$  M.

Infrared spectra were recorded as KBr discs on a FT-IR Perkin Elmer 1750X instrument. All the spectra were run in the range of 400 – 4000  $\text{cm}^{-1}$  at room temperature. Approximately 5mg of Schiff base which dissolved in DMSO was analyzed using a Jeol JNM (400 MHz) NMR spectrometer. Analysis of carbon, hydrogen, nitrogen and sulphur were carried out using a LECO CHNS-932 instrument. All the metal complexes were prepared in concentration of 10 ppm. Miligrams of sample was dissolved in 2-5 ml of nitric acid (65%) and left for 2 days before doing the dilution using the distilled water. The prepared 10 ppm solution of metal complexes were then been characterized using the Perkin Elmer Plasma 1000 Atomic Emission Spectrometer.

## Preparation of 2-methylbenzyl hydrazinecarbodithioate

This compound was prepared by dissolving potassium hydroxide 5.7 g (0.1 mole) in 90% of 35ml ethanol<sup>[16]</sup>. Hydrazine hydrate ( $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ ) 5 g

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(4.864ml) was added. 7.6 g of Carbon disulfide (6.017 ml) was then added dropwise using a burette. During this time, two layers formed. The lower light brown oil layer was separated using a separating funnel and dissolved in previously cooled 40% ethanol (30ml). 2-methylbenzyl chloride (0.1 mole) was added slowly into the mixture with vigorous stirring. After the complete addition of 2-methylbenzyl chloride, stirring was continued until the white product formed. The product was collected and kept in the freezer.

## Preparation of Schiff base

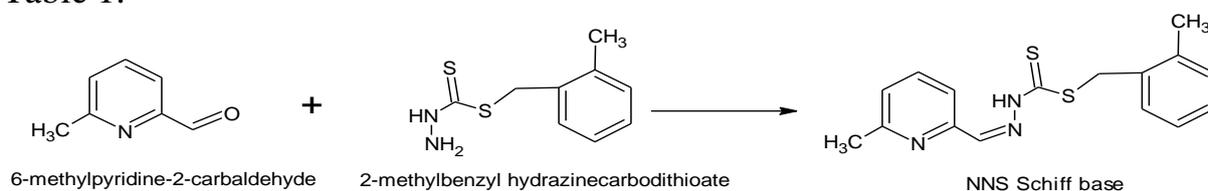
0.1 mol of 2-methylbenzylhydrazinecarbodithioate was dissolved in acetonitrile (100 ml). To this solution, was added a solution of 6-methylpyridine (0.1 mole) in minimal volume of ethanol (~5 ml). The resultant mixture was heated to reduce the volume to approximately 50 ml. The mixture was cooled and kept in a freezer to get complete crystallization. The crystals formed were filtered and dried. The recrystallization process was done using acetonitrile.

## Preparation of Metal Complexes

Schiff base (0.001 mole) dissolved in 100 ml of acetonitrile. The mixture was heated while the undissolved compound was filtered. To this solution,  $M(ac)_2$  (0.001 mole) {M = Cu(II), Zn(II) and Cd(II)} in 95% ethanol. The resultant mixture was heated to reduce the volume to half. The metal complexes formed were kept in the freezer for a night and then filtered.

## Results and discussions

The synthesis reaction of the novel Schiff base is expressed in scheme 1, while the physical properties, CHNS data and the metal contents are shown in Table 1.



**Scheme 1: Synthesis equation of new NNS Schiff base**

**Table 1: : physical properties of the synthesized compounds**

Compound	Melting Point ( $\pm 1^\circ\text{C}$ )	Colour	%Found (Calculated)				%M
			%C	%H	%N	%S	
NNS	170	Yellow	58.55 (60.92)	4.93 (5.43)	12.76 (13.32)	18.59 (20.33)	-
[Cu(NNS)CH <sub>3</sub> COO]	298.0	dark green	47.03 (49.24)	4.19 (4.82)	8.93 (9.57)	12.23 (14.61)	12,75 (14.47)
[Cd(NNS)CH <sub>3</sub> COO]	203.0	Yellow	41.29 (44.31)	4.81 (4.34)	9.02 (8.61)	11.79 (13.14)	21.88 (23.04)
[Zn(NNS)CH <sub>3</sub> COO]	245.0	Yellow	52.11 (49.03)	4.29 (4.80)	8.94 (9.53)	12.70 (14.54)	13.65 (14.83)

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All analytical data obtained in Table 1 are in a good agreement with proposed structures, beside the presence of oxygen in the metal complexes was detected and approved using CHN apparatus; also the analytical values of percentage of metal in the metal complexes were found very close to the calculated value which indicates that the structures are similar as predicted.

### Molar Conductivity and Magnetic Susceptibility Analyses

The molar conductivities were determined for  $10^{-3}$  M solutions of the complexes in DMSO. The molar conductance data (Table 2) indicated that all complexes were non-electrolytes, suggesting that the complexes did not dissociate in solution.

The room temperature magnetic moments of the complexes (Table 2) indicate that Cu(II) complex is paramagnetic with magnetic moments of 1.60 B.M. The structure of the Cu(II) complex is proposed to be square planar <sup>[17]</sup>. The remaining complexes are diamagnetic with the zinc (II) and cadmium(II) complexes are tetrahedral species <sup>[18]</sup>.

**Table 2: Molar conductivity and magnetic data for the new compounds**

Compound	Molar Conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ )	$\mu_{\text{eff}}$ (B . M)
NNS	1.60	-
[Cu(NNS)CH <sub>3</sub> COO]	2.39	1.65
[Cd(NNS)CH <sub>3</sub> COO]	5.24	Diamagnetic
[Zn(NNS)CH <sub>3</sub> COO]	2.01	Diamagnetic

### Electronic Spectral Analyses

The electronic spectra of the complexes exhibit intra-ligand bands at *ca.* 250 nm and from 300 nm to 400 nm corresponding to n to  $\pi^*$  and  $\pi$  to  $\pi^*$  transitions within the ligand (the Schiff base) itself. NNS Schiff base spectra have band at 354 nm indicating the transition of n to  $\pi^*$ . The electronic spectra of the copper complex shows bands at 659 nm, and 624 nm which are characteristic of square planar stereochemistry of Cu(II) complex <sup>[19]</sup>. Because the  $d^9$  configuration can be thought of as an inversion of  $d^1$ , relatively simple spectra consisting of a single broad band are expected for  $d^9$  complexes <sup>[20]</sup>. A great majority of Cu(II) complexes are blue or green because of a single broad absorption band in the region of 600 to 900 nm <sup>[21]</sup>. For the Cd(II) and Zn(II) complexes, there were no d-d transitions observed as the diamagnetic nature of the complexes with the spectra exhibit similarly to the Schiff bases as the complexes showed bands that were caused by the charge transfer <sup>[22]</sup>. The significant electronic spectral of the Schiff bases and their complexes is shown in Table 3.

**Table 3: Electronic Spectral Analyses Data**

Compound	UV-Vis Spectra ( $\lambda_{\max}$ (nm))
NNS	354 (4.6)
[Cu(NNS)CH <sub>3</sub> COO]	656(1.9), 624(1.9)
[Cd(NNS)CH <sub>3</sub> COO]	436(3.5)
[Zn(NNS)CH <sub>3</sub> COO]	409(3.6)

### Infrared Analyses

The IR Spectra of the Schiff base given in Table 4 shown strong bands at 3089 cm<sup>-1</sup>, this attributed to the secondary amine  $\nu$ (N-H) mode of the free ligand. The disappearance of  $\nu$ (N-H) bands in the IR spectra of the metal complexes suggest deprotonation and consequent coordination through the thiolate anions. The Schiff base also showed strong bands at 1538 cm<sup>-1</sup>, this assigned to the  $\nu$ (C=N) modes for the free ligand. In the metal complexes, this stretching band shifted to higher frequencies, due to the lowering of the C=N bond order as a result of the metal-nitrogen bond formation [23].

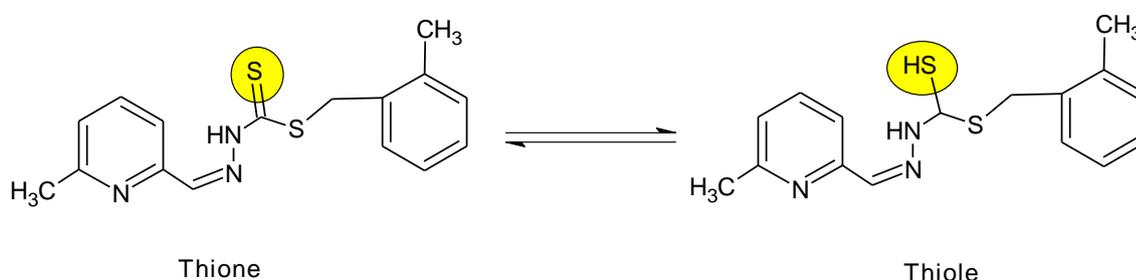
For the hydrazinic,  $\nu$ (N-N) band shifts to lower values in the spectra of the metal complexes relative to the free ligands, because of the reduction in the repulsion between the lone pairs of electrons on the nitrogen atoms as a result of coordination through the azomethine nitrogen atom. The ring deformation mode of pyridine in the spectrum of the ligand shifts to higher values in the spectra of the complexes indicating coordination through the pyridine nitrogen atom [24]. The presence of new  $\nu$ (C-S) bands in the metal complexes spectra attributable to the bond formation through the sulfur atom [23, 24]. The absence of  $\nu$ (S-H) absorbance at ca. 2570 cm<sup>-1</sup> in the spectrum of Schiff bases indicates that in solid states, they exist primarily in the thione form. These thione groups are relatively unstable in the monomeric form and tend to convert to the more stable thiolo forms by enethiolization in solution (Ali, 2004). Selected infrared absorption bands for the ligand and its metal complexes of Zn(II), Cu(II) and Cd(II) is shown in Table 4.

**Table 4: Significant IR bands of the Schiff bases and their complexes**

Compound	$\nu$ (N-H)	$\nu$ (C=N)	$\nu$ (N-N)	$\nu$ (C=S)	$\nu$ (C-S)
NNS	3089	1538	1048	790	-
[Cu(NNS)CH <sub>3</sub> COO]	-	1595	968	-	864
[Cd(NNS)CH <sub>3</sub> COO]	-	1567	1061	-	951
[Zn(NNS)CH <sub>3</sub> COO]	-	1559	1068	-	967

### <sup>1</sup>H NMR Analyses

The <sup>1</sup>H NMR data for the Schiff base shows that the absence of ν(S-H) absorbance at ca. 2570 cm<sup>-1</sup> in the spectrum of Schiff base indicates that in the solid state, it exists primarily in the thione form. Therefore, the <sup>1</sup>H NMR spectrum of NNS in DMSO do not show any peak at approximately δ 4.0 ppm attributable to the S-H proton proving that the thiole tautomer was not present in solution, scheme 2 shows thione thiole tautomerism. The multiplet in the range of δ 7.67–7.73 ppm is assigned to the resonance peaks associated with the aromatic groups in NNS. The signals at 7.07 ppm is attributed to the N-H group of NNS Schiff base. The Schiff base containing a methyl group on the pyridine ring showed a peak δ 2.35 ppm attributed to the methyl hydrogen while the methyl group on the benzene ring appears at δ 2.55 ppm [25-27].



**Scheme 2: Thione thiole tautomerism**

### Conclusion

New NNS Schiff base was synthesized. Copper (II), Zinc (II) and Cadmium (II) complexes of the Schiff base above were prepared. All of these compounds were characterized by various physic-chemical techniques. The preparation of the complexes from the Schiff base was very successful due to the high yield percentage of the metal complexes obtained. The NNS Schiff base was tridentate, uninegatively charged ligand through the pyridine nitrogen, the azomethine nitrogen and thiole sulfur atoms. The new compounds expected to show bioactivity against bacteria, fungi and against cancer cells.

### References

1. Tarafder, M.T.H., Chew, K.B., Crouse, K.A., Ali, A.M., Yamin, B.M. and Fun, H.K. 2002. Synthesis and Characterization of Cu(II), Ni(II) and Zn(II) Metal Complexes of Bidentate NS Isomeric Schiff Bases Derived From S-methyldithiocarbamate (SMDTC): Bioactivity of The Bidentate NS Isomeric Schiff Bases, Some of Their Cu(II), Ni(II) and Zn(II) complexes and The X-ray Structure of The Bis[S-methyl-β-N-(2-furylmethyl)methylenedithiocarbazato] Zinc(II)Complex. *Polyhedron* 21: 2683-2690.
2. Tarafder, M.T.H., Asmadi A., Talib M. S S., Ali A.M. and Crouse K.A 2001. Studies on coordination chemistry of a nitrogen-sulfur donor ligand with lighter and heavier metal ions and biological activities of its complexes. *Transition Metal Chemistry* 26: 170-174.
3. Ali, M.A., Mirza, A.H., Iran, M.S.H., Burcher, R.J., Tarafder, M.T.H., Keat, T.B. and Ali, A.M. 2002. Magnetic, spectroscopic and biological properties of copper(II) complexes of the tridentate ligand, α-N-methyl-S-methyl-β-N-(2-

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- pyridyl)methylenedithiocarbamate(NNS) and the X-ray crystal structure of the [Cu(NNS)<sub>2</sub>] complex, *Transition Metal Chemistry* 27: 262–267.
4. Ali, M.A., Haroon, C.M., Uddin, M.N., Majumder, S.M.H., Tarafder, M.T.H. and Khair, M .A. 1992. Synthesis, characterization and biological activities of some new nickel(II), zinc(II) and cadmium(II) complexes of quadridentate SNNS ligands. *Transition Metal Chemistry* 17: 133-136.
  5. Ali, M.A., Hj Ibrahim, N.E., Butcher, R.J., Jasinski, J.P., Jasinski, J.M. and J.C. Bryan. 1998. Synthesis and Characterization of Some Four- and Five-Coordinate Copper(II) Complexes of 6-methyl-2-formylpyridinethiosemicarbazone (HNNS) and the X-ray Crystal Structures of the [Cu(NNS)(CH<sub>3</sub>COO)(H<sub>2</sub>O)] and [Cu(HNNS)(H<sub>2</sub>O)(SO<sub>4</sub>)]·H<sub>2</sub>O Complexes. *Polyhedron*, 17: 1803-1809.
  6. Ali, M.A., Ghausul, H.S.M., Majumder, S.M., Nazim, U. M. and Tarafder, T.H. 1987. Synthesis and characterization of some new nickel(II), zinc(II) and cadmium(II) complexes of quadridentate SNNS ligands. *Polyhedron* 6(8): 1653-1656.
  7. Tian, Y-P, Chun-Y.D., Cun-Yuan Z., Xiao-Zeng Y., Thomas C.W.M. and Ze-Ying Z. 1997. Synthesis, Crystal Structure, and Second-Order Optical Nonlinearity of Bis(2-Chlorobenzaldehyde Thiosemicarbazone) Cadmium Halides (CdL<sub>2</sub>X<sub>2</sub>; X = Br, I). *Inorganic Chemistry* vol.36, pp.1247-1252. USA.
  8. Liu ZH, Duan CY, Hu J, You XZ. 1999. Design, Synthesis, and Crystal Structure of a cis-Configuration N(2)S(2)-Coordinated Palladium(II) Complex: Role of the Intra- and Intermolecular Aromatic-Ring Stacking Interaction. *Inorganic Chemistry*. 38(8): 1719-1724.
  9. Liu, Z.H., Yang, S.R., Duan, C.Y. and You, X.Z. 1999. A Novel Macrocyclic Tetranuclear Copper(II)-Copper(I) Mixed-Valence Complex. *Chem. Lett. Jpn.*10: 1063-1064.
  10. Tian, Y.-P., Duan, C.Y., You, X.-Z., Mak, T.C.W., Luo, Q. and Zhou, J.-Y. 1998. Crystal structures, spectroscopic and nonlinear optical properties of metal complexes of Schiff-base ligands containing nitrogen and sulfur donors. *Transition Metal Chemistry*. 23: 17-20.
  11. Abu-Raqabah, A., Geoffrey D., Mohamed A., Ahmed El-Toukhy, Shahid N. and Jon Z. 1992. Transmetalation of tetranuclear copper complexes with tin transmetalators. Molecular structure of *cis*-dichloro-bis(*trans*-S-methyl isopropylidenehydrazine carbodithioato)tin(IV) and consideration of transmetalation mechanisms. *Inorganica Chimica Acta*. Volume 193(1, 2): 43-56.
  12. Crouse, K.A., Chew, K.B., Tarafder, M.T.H., Kasbollah, A., Yamin, A.M. and Fun, H-K. 2004. Synthesis, characterization and bio-activity of S-2-picolylidithiocarbamate (S2PDTC), some of its Schiff bases and their Ni(II) complexes and the X-ray crystal structure of S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbamate. *Polyhedron* 23: 161-168, and references therein.
  13. West D.X., Liberta A.E., Padhye S.B., Chikate R.C., Sonawane P.B., Kumbhar A.S., Yerande R.G. 1993. Thiosemicarbazone complexes of copper(II): Structural and biological studies. *Coordination Chemistry Reviews*, 123 (1-2): 49-71.
  14. Kasuga NC, Sekino K, Ishikawa M, Honda A, Yokoyama M, Nakano S, Shimada N, Koumo C, Nomiya K. 2003. Synthesis, structural characterization and antimicrobial activities of 12 zinc(II) complexes with four thiosemicarbazone and two semicarbazone ligands. *Journal of Inorganic Biochemistry*. 96(2-3): 298-31.
  15. Liberta AE, West DX. 1992. Antifungal and antitumor activity of heterocyclic thiosemicarbazones and their metal complexes: current status. *Biometals*. 5(2):121-6.
  16. Isam H.T. Al-Karkhi. 2011. Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy.

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17. Tarafder, M.T.H., Saravanan, N., Weng, W.-Y., Kumar, S.K., Umar-Tsafe, N. and Crouse, K.A. 2000. Coordination Chemistry and Biological Activity of two Tridentate ONS and NNS Schiff bases derived from Sbenzylthiocarbazate. *Transition Metals Chemistry* 25: 295-298.
18. Cotton, F.A., Wilkinson, G., Murillo, C.A. and Bochmann, M. 1999. *Advanced Inorganic Chemistry*, sixth ed., New York: Wiley.
19. Ali, M.A., Mirza, A.H., Butcher, R.J., Tarafder, M.T.H. and Ali, M.A. 2001b. Synthetic, spectroscopic, biological and X-ray crystallographic structural studies on a novel pyridine-nitrogen-bridged dimeric nickel(II) complex of a pentadentate N<sub>3</sub>S<sub>2</sub> ligand. *Inorganica Chimica Acta* 320: 1-6.
20. Thahira B.S.A. Ravooof, Karen A. Crouse, M. Ibrahim M. Tahir, Andrew R. Cowley, M. Akbar Ali. 2007. Synthesis, characterization and bioactivity of mixed-ligand Cu(II) complexes containing Schiff bases derived from S-benzylthiocarbazate and saccharinate ligand and the X-ray crystal structure of the copper-saccharinate complex containing S-benzyl-β-N-(acetylpyrid-2-yl)\_\_\_\_\_methylenedithiocarbazate. *Polyhedron*, 26(6): 1159-1165.
21. Singh, J.; Hundal, G.; Corbella, M. and Gupta, R. Synthesis, Characterization and Structures of Copper(II) Complexes with Amide-Based Ligands: Unusual Formation of a Linear Trimer and a Zig-zag Chain and Their Contrast Magnetic Behaviour, *Polyhedron*, 2007, 26, 3893-3903.
22. Chan, M.H.E., Crouse, K.A., Tahir, M.I.M. and Rosli, R. 2008. Synthesis and characterization of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of benzyl N-[1-(thiophen-2-yl)ethylidene] hydrazine carbodithioate and benzyl N-[1-(thiophen-3-yl)ethylidene] hydrazine carbodithioate and the X-ray crystal structure of bis{benzyl N-[1-(thiophen-2-yl)ethylidene] hydrazine carbodithioate}nickel(II). *Polyhedron*. 27(4): 1141-1149.
23. Thahira, B.S.A.R., Crouse, K.A., Mohamed, .I.M.T., Cowley, A. and Ali M.A 2004. Synthesis, characterization and bioactivity of mixed-ligand Cu(II) complexes containing S-methylthiocarbazate derivatives and saccharinate ligands and the X-ray crystal structure of the copper-saccharinate complex containing S-methyl-B-N-(6-methylpyrid-2-yl)methylene dithiocarbazate. *Polyhedron* 23: 2491-2498.
24. Ali, M.A., Mirza, A.H., Keng, T.W. and Butcher, R.J. (2003). Palladium(II) and platinum(II) complexes of Schiff bases derived from 2,6-diacetylpyridine and S-methylthiocarbazate and the X-ray crystalstructure of the [Pd(mdapsme)Cl] complex. *Transition Metals of Chemistry*. 28: 241-245.
25. Ali, M.A., Mirza, A.H., Fatriaah, H.B., Malai, H., Hamid, S.A. and Paul V. B. 2006. Synthesis, characterization and X-ray crystallographic structural study of copper(II) and nickel(II) complexes of the 2-quinoline carboxaldehyde Schiff base of S-methylthiocarbazate (Hqaldsme). *Polyhedron* 25: 3245-3252.
26. Marisa, B-F., Franco, B., Giorgio, P., Silvana, P. and Perialberto, T. 2007. Synthesis, characterization, crystal structure and antiproliferative in vitro activity of long-chain aliphatic thiosemicarbazones and their Ni(II) complexes. *Polyhedron* 26: 5150-5161.
27. Neelam, B., Mannar, M., Fehmida, N., Alok, B., Sudha, B. and Amir, A. 2000. Palladium(II) complexes of NS donor ligands derived from S-methyl-dithiocarbazate, S-benzylthiocarbazate and thiosemicarbazide as antiamoebic *agents*. *European Journal of Medicinal Chemistry* 35: 481-486.