Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **5(3),** 49-52, March **(2015)** *Res. J. Chem. Sci.*

Synthesis, Spectroscopic and Physico chemical Characterization of Cu (II), Ni(II), Co(II) and Mn(II) Coordination compounds with 4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemi-carbazone (4-MSCST)

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Available online at: www.isca.in, www.isca.me
Received 15th September 2014, revised 14th February 2015, accepted 11th March 2015

Abstract

The synthesis and characterization of copper (II), nickel (II), cobalt (II) and manganese (II) coordination compounds of 4-methoxy salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone (4-MSCST) have been presented. The prepared metal complexes are ML_2 type. (M= Cu, Ni, Co and Mn; L= 4-MSCST). The IR spectrum suggests that the thiosemicarbazones coordinate in their neutral form and they act as [Metal, N] bidentate chelating ligand. Magnetic properties and UV-visible spectra indicate the octahedral geometries of the 4-MSCST metal complexes. In this work we have proposed the possible structures of the formulated complexes using TGA studies. All the prepared compounds have been tested for their antimicrobial activities.

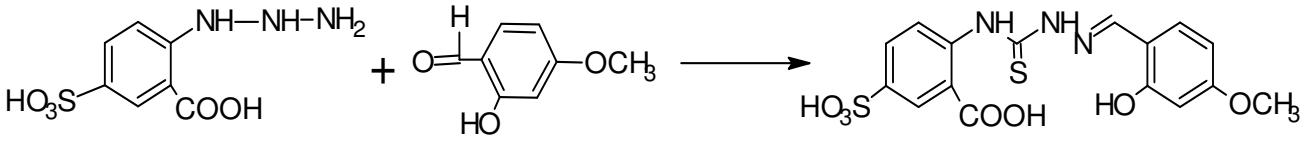
Keywords: Metal complexes, thiosemicarbazone, antibacterial activity.

Introduction

A number of review articles[1-6] has shown on various complexes of thiosemicarbazones and its metal-coordination. In current era a number of researches have worked on some transition metal coordination complexes of thiosemicarbazones[7-14] and reported in authentic journal. In this present work we have reported the synthesis, physico chemical properties and bacterial activity of copper (II), Nickel(II), cobalt(II) and Manganese (II) complexes of 4-methoxy salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl) -3-thiosemicarbazone (4-MSCST). Thiosemicarbazones and their metal complexes are known for their biological applications and the great medicinal value including antibacterial, antifungal, antimalarial, antitumor and antiviral activity[15-19].

Material and Methods

Melting points of the synthesized compounds were taken in open ended glass capillary on "Stuart SMP10" melting point instruments. Chemical reaction was monitored by thin layer chromatography (TLC). Magnetic susceptibilities were done at room temperature using Gouy balance. The IR spectra of the ligand and complexes were taken using KBr disc with a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H-NMR spectra (δ, ppm) of ligands were taken in DMSO using "Bruker-Advance 400 MHz spectrometer". Elemental analyses were done on ECS 4010 CHN Elemental analyser. All the chemicals used throughout in this work were of Analytical grade purity.

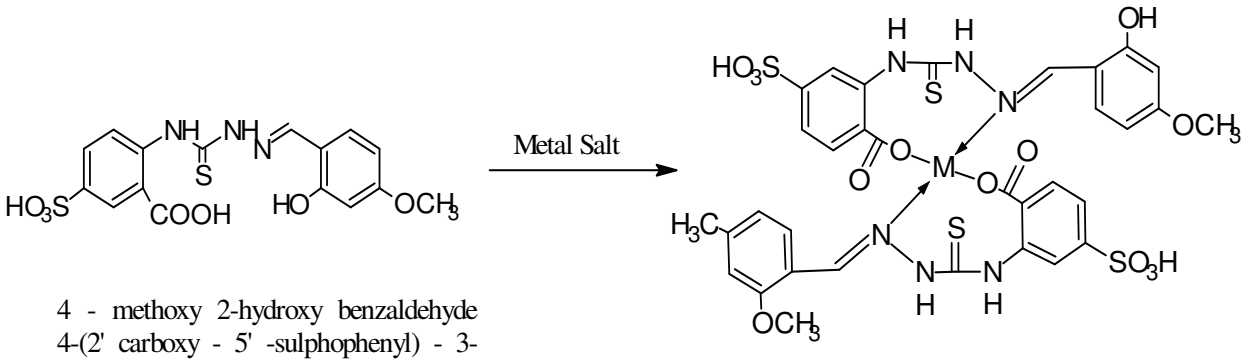


4-(2'-carboxy-5'-sulphophenyl) -3 -Thiosemicarbozide

4 - methoxy 2-hydroxy benzaldehyde

4 - methoxy 2-hydroxy benzaldehyde 4-(2' carboxy - 5' -sulphophenyl) - 3-thiosemicarbazone

Scheme –I
Experimental section



4 - methoxy 2-hydroxy benzaldehyde 4-(2' carboxy - 5' -sulphophenyl) - 3-thiosemicarbazone

Where M = Cu(II), Ni(II), Co(II) and Mn(II)

Scheme–II

Results and Discussion

Synthesis of 4-(2'-carboxy-5'-sulphophenyl) -3-thiosemicarbazide [CST]: The method for the preparation of 4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazide have been reported erliear by N C Patel and et al[20].

4-methoxy-salycylaldehyde-4- (2'-carboxy-5'-sulphophenyl)-3- thiosemicarbazone (4-MSCST): Thiosemicarbazide (0.01 mol) and 4-methoxy-salycylaldehyde (0.01 mol) were dissolved in ethanol (40 ml) and refluxed for 2 hr[21] then allowed to stand for overnight. 4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone formed was filtered, wash with ethanol and dried under vacuum and was recrystallized from water and DMF. Yield 71%. Characterization of ligand and its metal complexes were given below.

4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone (4-MSCST): Light yellow crystals; m.p. 221ºC; yield 86%; IR (KBr, cm^{-1}): 1567 (C-N), 1027 (C=S), 1215 (N-N), 1656 (C=O) , NMR (400.1 MHz, $CHCl_3$): δ_H 4.34 (s, -OH or -NH), 4.7 (s, 3H, -H), 6.64-7.80 (m, 7H,Ar-H), 8.7 (s, 1H, -NH); anal. calcd for: $C_{16}H_{15}N_3O_7S_2$ (425); found (C, 45.03; H, 3.26; N, 9.71; O, 15.03; S, 13.97 %); required (C, 45.17; H, 3.52; N, 9.88; O, 26.35; S, 15.05).

Synthesis of Complex: A general method adopted for the synthesis of the complexes. Hydrated metal salts (0.01 mol) and a 4-MSCST ligand (0.005 mol) were dissoled in ethanol (40 ml). The resulting reaction mixture was heated on water bath for 2 hrs and then filtered, wash with ethanol and dried under vacuum.

4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone: [Cu (II) -4-MSCST]: Pale yellow crystals; yield 62 %; IR (KBr, cm^{-1}): 1580 (C-N), 1049 (C=S), 1201 (N-N), 1612 (C=O), Anal. Calcd for: $C_{32}H_{28}N_6O_{14}S_4Cu$ (911.54); Found (C, 42.02; H, 3.15; N, 9.12; O, 24.48; S, 13.98 %); required (C, 42.12; H, 3.07; N, 9.21; O, 24.57; S, 14.04).

4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone: [Ni (II) -4-MSCST]: Pale yellow crystals; yield 68 %; IR (KBr, cm^{-1}): 1590 (C-N), 1049 (C=S), 1247 (N-N), 1613 (C=O), anal. calcd for: $C_{32}H_{28}N_6O_{14}S_4Ni$ (906.69); found (C, 42.23; H, 3.00; N, 9.22; O, 24.51; S, 14.02 %); required (C, 42.31; H, 3.08; N, 9.25; O, 24.68; S, 14.10).

4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone : [Co (II) -4-MSCST]: Pale yellow crystals; yield 62 %; IR (KBr, cm^{-1}): 1581 (C-N), 1047 (C=S), 1233 (N-N), 1645 (C=O) , anal. calcd for: $C_{32}H_{28}N_6O_{14}S_4Co$ (906.93); found (C, 42.20; H, 3.00; N, 9.09; O, 24.61 S, 13.99 %); required (C, 42.32; H, 3.07; N, 9.24; O, 24.67; S, 14.11).

4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone: [Mn (II) -4-MSCST]: Pale yellow crystals; yield 68 %; IR (KBr, cm^{-1}): 1505 (C-N), 1033 (C=S), 1230 (N-N), 1616 (C=O), anal. calcd for: $C_{32}H_{28}N_6O_{14}S_4Mn$ (902.93); found (C, 42.42; H, 3.21; N, 9.15; O, 24.62; S, 14.06 %); requires (C, 42.52; H, 3.10; N, 9.3; O, 24.8; S, 14.17).

Magnetic susceptibility: The magnetic property of the Copper (II) complex is around 3.8 BM which deduce the octahedral geometry of the complex. The nickel complexes were found to be diamagnetic which suggest square planner geometry four coordinate structure. The magnetic measurements of the Cobalt (II) complex is 4.8 BM suggests octahedral geometry and the present Manganese (II) complex having magnetic moment value is about 4.8 BM which also fevers octahedral geometry.

Infrared Spectra: The synthesis of 4-methoxy-salycylaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosem icarbazone [4-MSCST] was characterized by an IR spectra. The resulting 4-MSCST ligand was a pale yellow crystal. Ligands and its complexes found in agreement with their calculated values. The bands in the region 3078-3449 cm^{-1} indicating to N-H vibration. The IR spectrum of 4-MSCST comprises the important band showed at C=N band at 1590 cm^{-1}. The negative shift of 1580-1567 cm^{-1} band in the spectra of complexes

suggested the co-ordination of metal ion through C=N group. The C=O stretching frequency of the ligand observed at 1626 cm^{-1} shifts to 1616-1612 cm^{-1} in the complexes indicating coordination of –OH of carboxyl group in bond formation[22].

NMR Spectroscopy: The downward shift in C=O of 4-MSCST on complexation indicated the involvement of –OH of carboxyl group in bond formation. The NMR spectra of the ligand 4-MSCST gave the multiple between 6.5-8.2 δ ppm for aromatic protons, singlet at 3.8 δ ppm for ($-OCH_3$) and singlet at 11.4 δ ppm for –OH or –NH.

Thermogravimetric studies: Thermal analysis of the complexes is carried out using *Perkin Elmer* Instrument. The Thermogravimetric data of complexes has found informative with regard to the strength of bonding between the ligand and the metal ions. The TGA curves of the complex of thisemicarbazone ligand were carried out within a temperature range from room temperature up to 800ºC. The data from thermogravimetric analysis of complexes do not weight up to 130-150ºC clearly indicated that the absence of lattice as well as water molecule in compound. A gradual increase in temperature above 150ºC had been accompanied by continues loss in weight up to 300ºC; it indicated partial decomposition of ligand moiety till 300ºC. The strait line has been seen after 600 ºC and almost 90 % decomposition observed and it is equal to two moles of ligand indicating 1:2 composition of the complex. The Cu (II), Ni (II), Co (II) and Mn (II) complexes represents octahedral geometry and the structural formulas assigned to these are presented in figure-1. In the present investigations on the thermal behavior of the metal complexes of 4-MSCST and substituted and does not have any water molecules.

Biological properties: Four pathogenic microorganisms' bacteria have been selected for microbial study of ligands and their complexes in this research. Out of them two are gram positive bacteria (Staphylococcus aureus- ATCC 9144, Bacillus subtilis-ATCC 6051) and remaining two are gram negative bacteria (Escherichia coli- ATCC 25922, Pseudomonas aeruginosa- ATCC 35032). A number of workers[5,9,23-26] was interested in finding the biological application of ligand and metal complexes. Figure-1 showed the results obtained for zone of inhibition of the growth of bacteria of the tested compounds and under similar condition using ciprofloxacin as a standard for comparison. The zones of inhibition formed were measured for determination of MIC the highest dilution which inhibits the growth was recovered. In the present work, Kirby-Bauer method[27] was used for antibacterial study of complex and standard drugs and it shows slightly better against the Staphylococcus aureus and Pseudomonas aeruginosa. All four complexes having good activity against the Escherichia coli.

Conclusion

Analysis and spectral studies suggested ML_2 type of complex and the octahedral geometry for all the complexes. The activity of the Co (II) complex display good activity as compare to the other complexes[28-29] and it has been point out that ligand having less activity against *Escherichia coli*. The proposed octahedral structure of copper, nickel, cobalt and manganese complexes with 4-methoxy-salycylaldehyde -4- (2'-carboxy-5'-sulphophenyl) -3-thiosemicarbazone has been shown in figure-2.

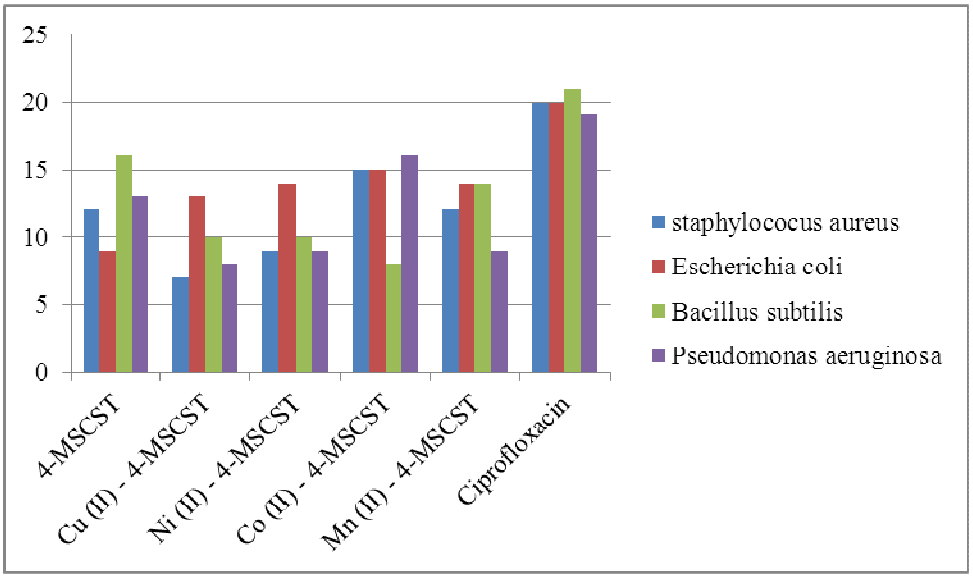
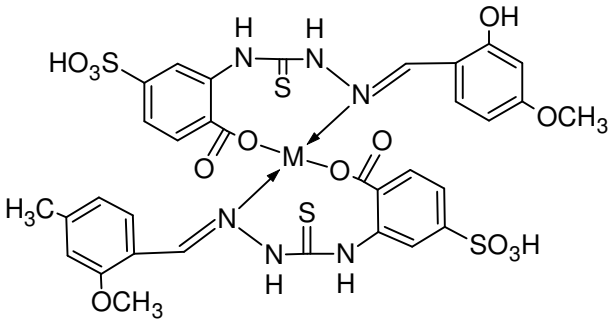


Figure-1
Antibacterial activity of 4-MSCST ligands and its metal chelates



Where M = Cu (II), Ni (II), Co (II) and Mn (II)

Figure-2
Probable structure of Metal complex

Acknowledgments

The authors would like to thank to Navyug Science College Surat, affiliated to VNSGU, Surat for providing research facilities and also thanks to Atul limited for provide library facilities.

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