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Arabic Summary ١

List of Abbreviations

S_1	Thiocarbohydrazide
S2	4-Amino-3-methyl-5-mercapto-1,2,4-triazole
CT	Charge Transfer
DMF	N,N-Dimethyformamide, $HCON(CH_3)_2$
DMSO	Dimethylsulfoxide,$(CH_3)_2SO$
g	Gram(s)
LMCT	Ligand to metal charge transfer transition
MLCT	Metal to ligand charge transger transition
m.p.	Melting point
ppm	Parts per million
s	singlet
d	Doublet
t	triplet
q	quartet
UV	Ultraviolt
UV-Vis	Ultraviolt-Visible
IR	Infrared spectra
^{1}H-NMR	Proton NMR
ESR	Electron spin resonance
μg/L	Micro gram per liter
λ_{max}	Maximum wavelength
%T	Transmittance
No.	Number

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Aim of the Work

Inorganic chemistry plays a very important role in our life. It can solve a lot of problems that our world is suffered. It has applications in every aspect of the chemical industry–including catalysis, materials science, pigments, surfactants, coatings, medicine, fuel, and agriculture.

Schiff bases are important class of ligands in coordination chemistry and their complexing ability containing different donor atom is widely reported. The chemistry of transition metal complexes containing heterocyclic donor continues to be of interest on account of their biological importance. There is a growing interest in the studies on the metal complexes of Schiff bases derived from triazoles and its derivatives which are biologically important ligands. The triazole Schiff bases constitute one of the most important classes of O, N, and S donor atoms.

Our work aimed to:

1. Preparing new triazole Schiff base ligands.
2. Characterizing the newly prepared ligands using melting point, elemental analysis, IR spectrum, ^{1}H-NMR spectrum, the spectral behavior of it in buffer solutions and the determination of their acid ionization constants.
3. Spectrophotometric, potentiometric and conductometric studies on these ligands with some transition metal cations in solution.
4. Characterizing the newly neutral solid complexes using elemental analysis, infrared spectrum, electronic absorption spectrum, molar conductance and electron spin resonance spectroscopy

Summary

The Schiff base acts as a bidentate monobasic donor for Cu(II), Ni(II), Cd(II), Cr(III) and Fe(III) and prominent sites of coordination are nitrogen of the azomethine group and oxygen of the hydroxyl group. Thus the present study describes the synthetic and structural studies of bivalent and trivalent transition metal ions Cu(II), Ni(II), Cd(II), Cr(III) and Fe(III) complexes of Schiff base derived from 4-Amino-3-methyl-5-mercapto-1,2,4- triazole with some aldehyde derivatives.

This thesis which entitled **"Physico Chemical Studies on Transition Metal Chelates of Some Mercapto Compounds"** includes three chapters; introduction, experimental and results and discussion (characterization of the organic ligands, studies of complexes in solution and studies of solid complexes).

1- **Chapter 1** includes a literature survey of the previous studies on Schiff bases and their complexes with different metal ions. This survey includes spectrophotometric, conductometric and potentiometric study on Schiff base complexes.

2- The experimental part **Chapter 2** includes the preparation and purification of the seven triazole schiff base ligands under investigation; these ligands were prepared through three steps to give the percentage yields about 76%. The preparation of schiff bases ligand complexes with some transition metal ions. It comprises also information about the instruments and measurements which were used for UV-Vis spectrophotometic, conductometric, potentiometric, IR, ^{1}HNMR and ESR.

3- **Chapter 3 (Part A)** include the results of the studies on characterization of the organic ligands, the melting point, elemental analysis and the spectral behavior of ligands under consideration in buffer solutions is considered to determine their acid ionization constants using three different methods. It was found that some ligands have an isosbestic point indicating the presence of acid-base equilibrium occurred between the non-ionized and ionized species, as in ligand I the isosbestic point at 350 nm and ligand VII showed up isosbestic point at 240 nm.

The IR spectra of ligands under investigation are studied and the different functional groups are assigned like ν_{OH}, ν_{NH} , $\nu_{C=N}$ and $\nu_{C=S.}$ On the other hand, the ^{1}H-NMR spectra for different types of hydrogens expected for ligands under investigation can be numerated determined and correlated to the molecular structure of the ligands.

4- **Chapter 3 (Part B)** contains studies of complexes in solution where three different points were discussed.

a) The conductometric titrations which were done to determine the stoichiometric ratio of the complexes formed using diluted concentration of ligands (1×10^{-3} M) and it reveled that the stoichiometric ratio of the type (1:1), (1:2) and (2:3) (M:L) are detected.

b) The potetiometric titrations which studied and done by using 0.1 M HCl and 1.0 M KCl of ionic strength at 25 ± 1 ºC; I = 2.2. From the data obtained, the ionization constants of ligands and formation constants pK_H of the complexes formed were obtained. The half interpolation is applied to determine the proton-ligand stability constants, and both the stepwise formation constants pK, and the overall formation constants of the produced chelates. It was found that the ligand I have two protonated hydrogen (ionized hydrogen ions of the thionyl and hydroxyl group), pK_1^H and pK_2^H but ligands II-VII have one ionizable proton (ionized hydrogen ion of the thionyl group in compounds, pK_1^H.

c) The spectrophotometric studies of metal complexes were also performed to determine the optimium conditions for each complex and after that the stability constant of such complexes were calculated using two different spectrophotometric methods which indicated that the stoichiometric ratio (L:M) is found to be (1:1). Also Beer's law, the least square methods and Ringbom methods and were performed for determination of the metal ion concentration.

The average of stability constants calculated by the molar ratio and continuous variation methods was found in the range between 6.05-8.75, and as a representative example for the stability constant for Ni^{2+} complexes deceases in the order V > I > IV > III > II.

5- **Chapter 3 (Part C)** includes studies of the solid chelates by elemental analysis, determination of molar conductance, infrared spectrum, electron spin resonance spectra and electronic absorption spectra in DMF and nujol mull. The molar conductivities for Ni^{2+}, Cu^{2+} and Cd^{2+} metal ions complexes of ligands I-VII indicates the non-electrolytic nature and neutral character of such complexes while the values of the molar conductivity for Fe^{3+} and Cr^{3+} complexes with ligands I-VII indicates the electrolytic nature and each molecule ionizes in solution into two ions. The IR absorption spectra of the solid complexes produced from the reaction of the newely prepared Schiff bases (I-VII) with Cr^{+3}, Fe^{+3}, Ni^{+2}, Cu^{+2} and Cd^{+2} ions of stoichiometric ratio (1:1) and (1:2) (M:L) are studied and compared to those of the free ligands.