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SYNTHESIS AND SPECTRAL STUDIES OF SOME TRANSITION METAL COMPLEXES

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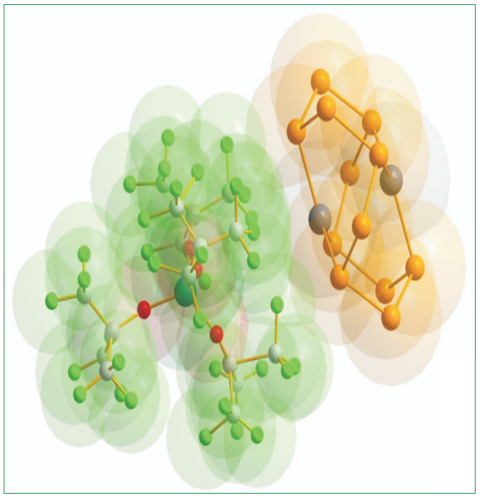
ABSTRACT

Thiocarbohydrazide are an important class of compounds which possess applications in many fields. The Chemistry of Thiocarbohydrazide has gained increased interest in both Inorganic Chemistry and biological fields and has considerable value in many useful applications such as the assessment process of the three-dimensional ultra structure examination techniques of interphase nuclei and tissues, besides their therapeutic importance. They are also described for use as fogging agents and are considered as safe, storable, and cool-burning pyrotechnic compounds for dissemination of smoke, chemical warfare agents. On the other hand, thiocarbohydrazide are used in performing a highly selective heavy metal ion adsorbent and as complexing agents for the solvent extraction separation methods. The present review covers the literature up to date for the synthesis, reactions and applications of such compounds.



KEYWORDS :*Thiosemicarbzide Zinc(II),Mercury(II),Cadmium(II) complexes determination, Ethanol, Thiosemicarbazide,Sodium acetate.*

INTRODUCTION

Thiosemicarbazide (TSC)

Coordination compounds have been a challenge to inorganic chemist since they were identified in the 19th century. They defy the usual rules of valence at that time and hence called complexes. Schiff bases have often been used as chelating ligands in the field of coordination Chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules

[1].They play vital role in our lives. Transitions metal complexes with soft or hard donor groups have been used extensively in coordination and organometallic Chemistry. These ligands have two donor atoms S and N through which they can coordinate with the metal ions. They are capable of forming three dimensional networks like structure and extensive hydrogen bonding in the complex enhancing the nonlinearity. In most complexes thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazinicNitrogen atoms, although in a few cases they behave as unidentate ligands and bond through only sulphur atom2-4. Moreover, thiosemicarbazones have found their way into almost every branch of chemistry; commercially they are used as dyes, photographic films, plastic and in textile industry. Keeping in mind various biomedical application of these class of compounds, we report the synthesis and characterization of Cd(II), Hg(II), Zn(II) complexes of thiosemicarbazide derivatives. The synthesis and structural investigations of thiosemicarbazone and their metal complexes are of considerable centre of attention because of their potentially beneficial pharmacological properties and a wide variation in their modes of bonding and stereochemistry1–3. Interest in metal complexes with thiosemicarbazone and semicarbazone ligands has been stimulated because biological activities are often enhanced on complexation. The variety of possible Schiff base metal complexes with wide choice of ligands, and coordination environments, has prompted us to undertake research in this area [2] There is substantial interest in the coordination Chemistry of cadmium complexes because of the toxic environmental impact of cadmium. As a part of our continuing work on dissymmetry tetradentate Schiff base complexes containing N, S and O donor atoms [3-4] and in light of the importance of Hg, Cd and Zn ion metals, we now report the synthesis and characterization of Mercury(II), Zinc (II) and cadmium(II)complexes of the tetradentate unsymmetric elements.

EXPERIMENTAL SECTION

All the Chemicals and solvents used for the synthesis were of reagent grade and were obtained commercially from Merck Company with the exception of the cadmium nitrate, which was obtained from Aldrich. The solvents were purified by standard methods [5]

I. SYNTHESIS OF THIOSEMICARBAZIDE LIGAND

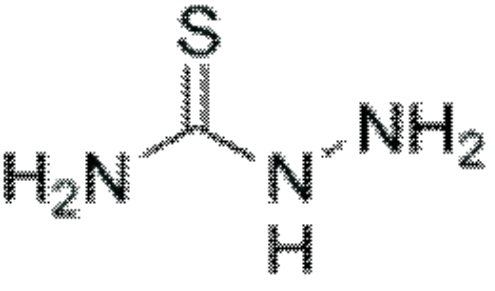
The compound prepared by treating urea with hydrazines

$OC(NH_2)_2 + N_2H_4 \rightarrow OC(NH_2)(N_2H_3) + NH_3$

A further reaction can occur to give carbohydrazide:

$OC(NH_2)(N_2H_3) + N_2H_4 \rightarrow OC(N_2H_3)_2 + NH_3$

Semicarbazones are derived by the condensation reaction between a ketone (or aldehyde) and a semicarbazide.Semicarbazide products (semicarbazones and thiosemicarbazones).



SYNTHESIS OF METAL COMPLEXES

REQUIERD CHEMICALS

- Ethanol
- Thiosemicarbazide
- Sodium acetate

PROCEDURE

Take ligand and metals salts in ratio 1:2.Dissolve ligand TSC in 50ml of ethanol taken in 250ml round bottom flask. Solution is refluxed for 1hr. To the refluxing solution add metals salts of (Zn, Cd , Hg dissolve in 10-15ml of distilled water)solution .Continue the reflux for 2hrs.Formation of complex takes place, if not add 1gm sodium acetate. Then filter the solution and dry the complex at room temperature.

REACTION:

1.$ZnSO_4+2NH_2NH(CS)NH_2 \rightarrow [Zn(NH_2—NHCSNH_2)2].SO_4$

2. $HgCl_2+2NH_2NH(CS)NH_2 \rightarrow [Hg(NH_2—NHCSNH_2)_2].Cl_2$

3. $CdCl_2+2NH_2NH(CS)NH_2 \rightarrow [Cd(NH_2—NHCSNH_2)_2].Cl_2$

II. Methods of elemental analyses

Metal estimations of the complexes were carried out according to the standard method reported in the literature [6]. The percentage of carbon, hydrogen and nitrogen were estimated by using Tru spec LECO CHN analyzer, USA made.

A) Estimation of Mercury.

A sample solution containing 4–85 mg of mercury (II) and varying amounts of diverse metal ions, an excess of 0.04 M EDTA was added and the solution was diluted with 25 ml of distilled water. The pH of the solution was adjusted to 5–6 by adding solid hexamine. The surplus EDTA was back titrated with standard zinc sulphate solution to a sharp color change of xylenol orange from yellow to red. To this, a freshly prepared 0.3 % solution of ethanethiol was added in the required amount. The contents were mixed well and allowed to stand for 5 min in order to ensure the quantitative release of EDTA. The liberated EDTA was then titrated with the standard zinc sulphate solution as before. The second titrate value is equivalent to the amount of mercury (II) present in the aliquot.

B) Estimation of Zinc.

The accurately weighed 0.2 g of metal complex was decomposed with concentrated nitric acid (10 ml) and concentrated hydrochloric acid (15 ml). The residue obtained was dissolved in 100 ml of water. The pH of the solution was raised to 10 by aq. Ammonia and Ammonium chloride buffer solution was titrated with standard 0.001M EDTA solution using Erichrome black T as an indicator. The amount of zinc present was evaluated.

C) Estimation of Cadmium

Take 100ml of sample in a pyrex Erlinmeyer flask, add 0.1N ml conc.H_2SO_4 and evaporate to dense white fumes and then add conc.HNO_3 to fuming liquid drop by drop till the solution clears and becomes colourless .Repeat addition of HNO_3 and fuming to remove excess HNO_3 and chlorides which

interfere. Neutrilise with metal-free NH_4OH solution is about 0.18M $(NH_4)_2SO_4$ boil to remove excess NH_4OH.filter and fuming to remove excess HNO_3 and chlorides which interfere. transfer the sample to the polarographic cell .add 10mg gelatin to suppress maxima .connect the cell to the polarograph .bubble N_2 through the solution for 5 minutes. Run a pologram 0.00 to 1.6volts. add sufficient NH_4OH to make the solution about 0.4M in NH_3.agin run a pologram add 300mg of EDTA and repeat.

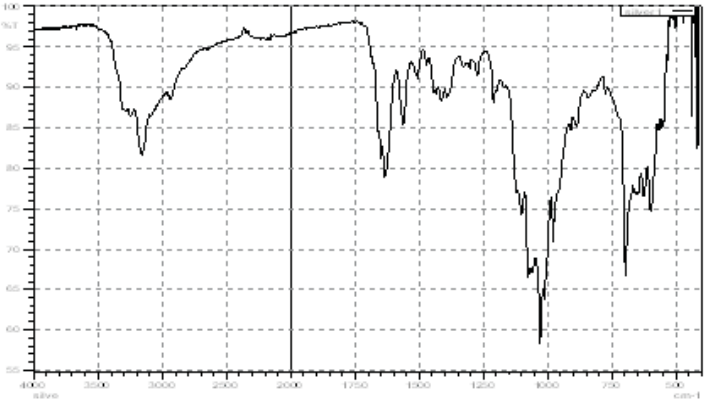
D) Estimation of chloride

Adjust PH of 100ml sample (in a250ml conical flask)to 7to10ml with H_2SO_4 and 1ml of 5% K_2CrO_4 solution (indicator),stir well and titrate with 0.0282N $AgNO_3$ solution (282ml of 0.1N $AgNO_3$ diluted to 1litre) to a permanent reddish tinge

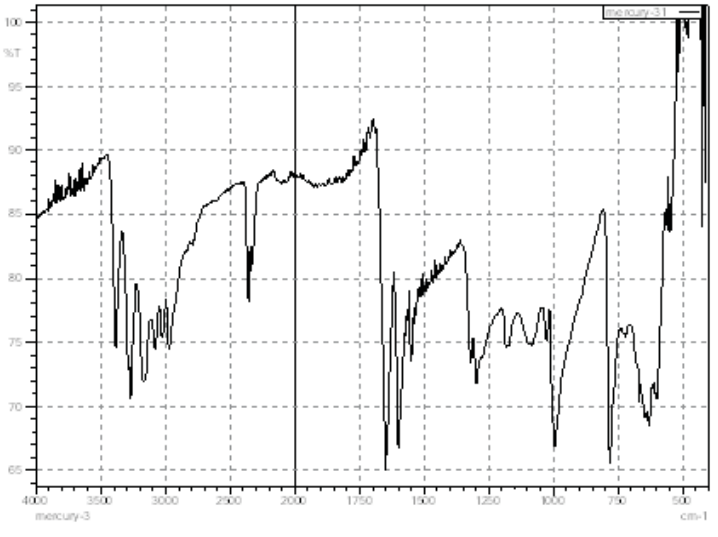
III.PHYSICO-CHEMICAL TECHNIQUES

1.Infrared Spectral Studies

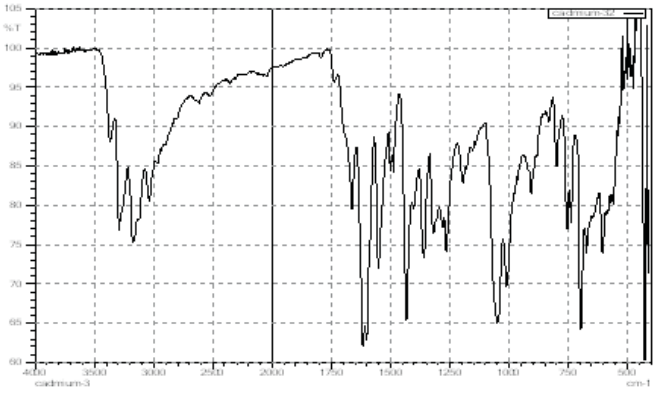
The Spectra of ligand and its metal complexes were obtained on a Shimadzu 8400-S, Japan, in the region 4000-400 cm^{-1}.



IR Spectra of Zinc Thiosemicarbazide complex



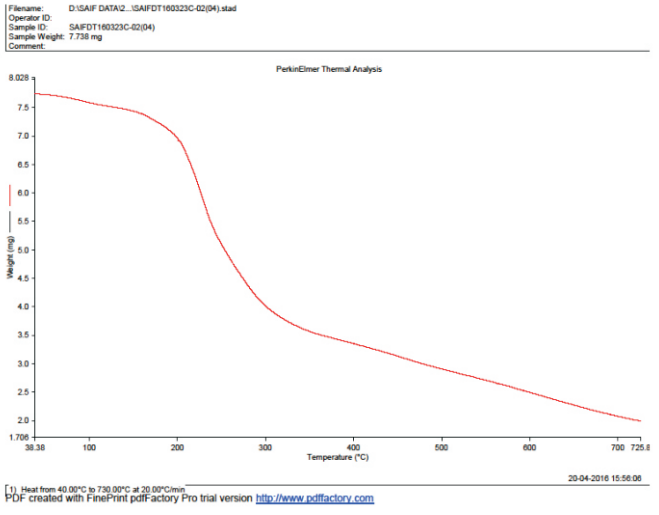
IR Spectra of MercuryThiosemicarbazide complex



IR Spectra of CadmiumThiosemicarbazide complex

2.Thermal studies

In the present investigation, thermogravimetric analysis(TGA) and derivative thermogravimetry(DTG) techniques have been used to study the thermal behavior of the metal complexes. Thermo analytical method involves the measurement of various properties of compounds subjected to dynamically changing environment under pre determined continuous change of heating rate, temperature range and gaseous atmosphere or vaccum.



CONCLUSION

The bonding of ligand to metal ion is confirmed by the analytical, spectral and thermal studies, all the above studies indicate that the complexes are high spin tetrahedral geometry.

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