A STUDY ON TERNARY COMPLEXES OF SOME TRANSITION AND INNER TRANSITION METAL IONS WITH BIOLOGICALLY HETEROCYCLIC THIOHDRAZONES

Jagadish Chandra Pati*[1], Dr. Hemant Sharma [2]
[1,2] Sri Satya Sai University of Technology & Medical Sciences, Sehore, MP

Abstract

A major class of sulfur-containing compounds as an essential component obtained by the condensation of thiohydrazide and a carbonyl compound are called thiohydrazones. Thiohydrazones consist of a group CSNHN = CH- bound to an aromatic or heterocyclic ring. It is reported that a broad spectrum of biological activity is associated with several heterocyclic compounds. In addition to the ability of sulfur donors, their presence in compounds has been shown to increase their therapeutic value. 2-Formylpyridinthiosemicarbazone, the first compound to be tested for biological activity, showed mild anti-leukemic activity against L-1210 tumor in mice at drug levels that produced significant toxicity. Some sulfur-containing reagents have proven to be the most sensitive in the photometric determination of osmium.

Introduction

Heterocyclic compounds are the major class of organic substrates that contain at least two different types of atoms in the ring. The mixed rings without any carbon atoms are inorganic heterocyclics and ring with one or more carbon atoms and heteroatoms (N, O & S) are organic heterocyclics. Over half of all known chemical compounds incorporate at least one heterocyclic moiety which makes them the largest class of compounds in organic chemistry. The presence of heteroatom gives heterocyclic compounds many significant physical and chemical properties. Heterocycles are abundant in nature and are of great importance to human life because their structural subunits exist in many natural products such as vitamins, hormones, antibiotics and pigments. Thus these derivatives have attracted considerable attentions in the design of biologically active molecules. The nitrogen containing heterocyclics are synthetically challenging models for a number of physiologically active natural products. Modern society is dependent on synthetic heterocycles for many purposes such as drugs, pesticides, dyes, plastics, cosmetics, information storage, solvents, antioxidants and vulcanization accerlators. Synthetic heterocycles have widespread therapeutic uses such as antibacterial, antifungal, antimycobacterial, trypanocidal, anti-HIV, antileishmanial, genotoxic, antitubercular, antimalarial, herbicidal, analgesic, anti-

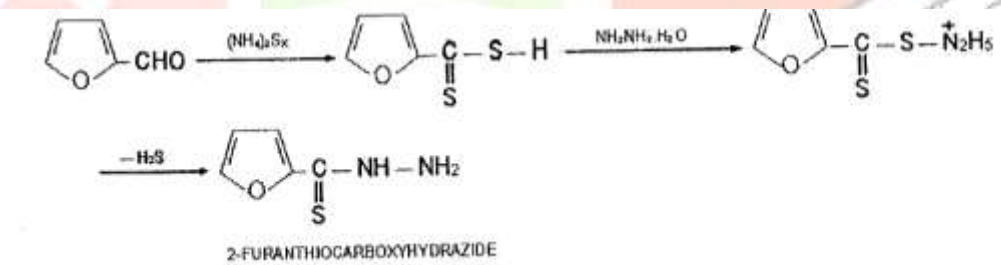
inflammatory, muscle relaxants, anticonvulsant, anticancer, lipid peroxidation inhibitor, hypnotics, antidepressant, antitumoral, antihelmintic and insecticidal activities.

HETEROCYCLIC THIOHYDRAZONES

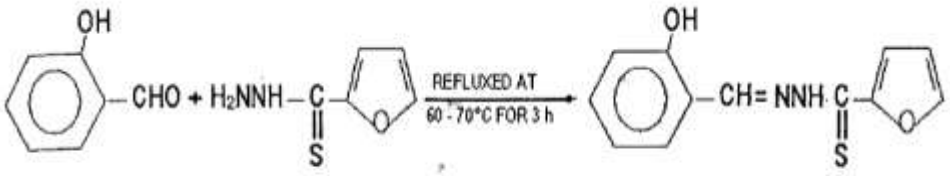
(i) HYDROXYBENZENE-2-CARBOXYALDEHYDE-FURANTHIO CAR-BOXYHYDRAZONE, (HFTLI)

For the preparation of the ligand, 2-furanthiocarboxyhydrazide was first obtained by the following procedure

A solution of furfural (30g) in ethanol (90ml) is heated to 60°C and 132ml of a solution of ammonium polysulphide, prepared according to the directions of Bost and Shealyl, is added. The solution is heated to boiling for ten minute, filtered off and cooled in ice. After addition of 150ml of ether, concentrated HCI is added with stirring until all the dithio acid has been liberated. The dark red ethereal solution is separated end washed with water and then treated several times with 10% aqueous solution of hydrazine hydrate. The deep red- brown colored solution of the hydraziniurn salt is kept for 60 minutes. The colour of the solution fades and a grayish crystalline product separated out. The solution is acidified with acetic acid and filtered off. The thiohydrazide is recrystallized from benzene with the addition of active carbon. The product is soluble in boiling water. Yield 45%; melting point l32±1°C.



Now, to obtain the desired ligand the above product, 2- furanthiocarboxy- hydrazide (21.3g), was refluxed on water bath at 60-70 °C with hydroxybenzene-2-carboxaldehyde (18.3g) in ethanol for three hours. On cooling the resulting solution, cream yellow crystals were produced. It was washed with acetone and dried. The ligand was recrystallized from DMF. The yield was 78%, melting point 184±1°C.

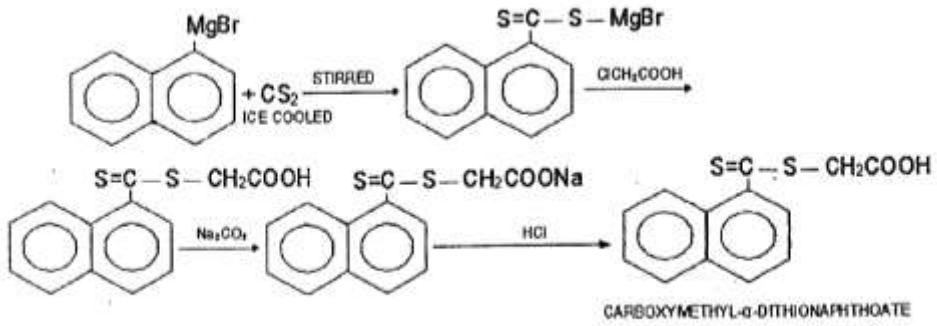


HYDROXYBENZENE-2-CARBOXALDEHYDE-2'-FURANTHIOCARBOXYHYDRAZONE

PYRIDINE-2-CARBOXALDEHYDE-1'-THIONAPHTHOYL HYDRA- ZONE, (PTNH)

For the preparation of the ligand, Carboxymethyl- a-dithionaphthoate was first obtained by the following procedure:

To a solution of a-naphthylmagnesium bromide, prepared from a- bromonaphthaline (51.25g) and magnesium (6.0g) in 300ml of ether, was added with ice-cooling and stirring, 14.3ml of carbon disulphide. The mixture was kept overnight at room temperature. Ice was added and the ether layer was separated. To the aqueous layer, was added a solution of chloroacetic acid (23.7g), neutralized with sodium carbonate, after standing for a 24 h at room temperature, the mixture was acidified with concentrated HCL The carboxymethylester separated as brownish crystals, which were washed with water and dried. It was recrystallized from benzene. Yield 55%, melting point136±1°C.



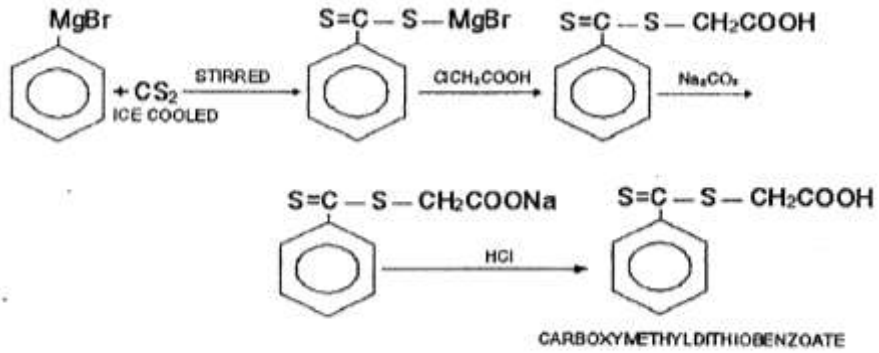
CARBOXYMETHYL-α-DITHIONAPHTHOATE

(iii) PYRIDINE-2-CARBOXALDEHYDE THIOBENZOYLHYDRA ZONE, (PTBH)

For the preparation of the ligand, carboxymethyldithiobenzoate was first obtained by the following procedure:

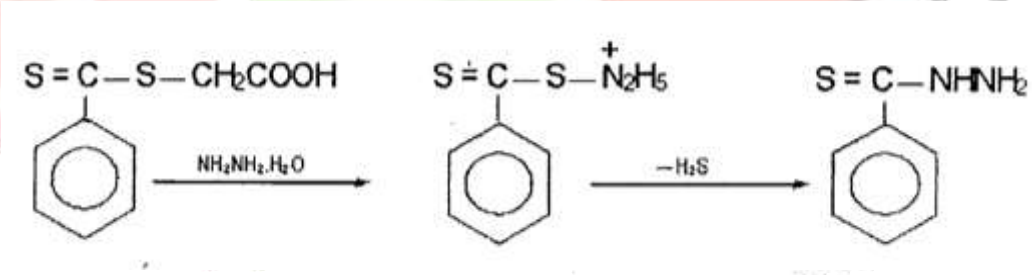
To a solution of phenyl magnesium bromide, prepared from phenyl bromide (39.25g) and magnesium (6.1g) in 300ml of ether, was added well cooled, 23.8ml of carbon disulphide with stirring. The mixture was kept overnight at room temperature. Ice was added and the ether layer was separated .To a aqueous layer, was added a solution of chloroacetic acid (23.9g), neutralized with sodium carbonate, after standing for twenty four hours

at room temperature , the mixture was acidified with concentrated HCI. The carboxyl methyl ester separated as crystals, which were washed with water and dried. It was recrystallized from benzene. Yield 55%

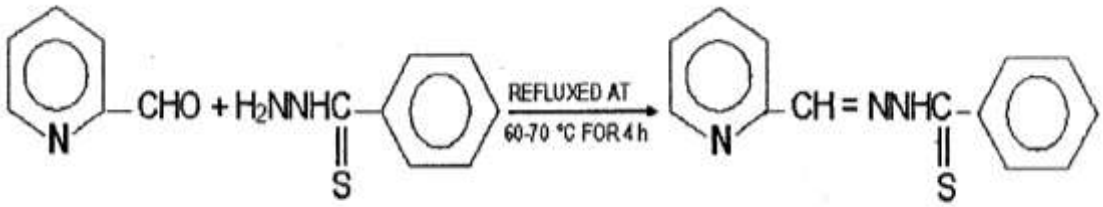


The conversion of carboxymethyldithiobenzoate into thiocarboxyhydrazide was carried out by adopting the literature procedure given below:

Carboxymethyldithiobenzoate (31g) was dissolved in N-NaOH (2001nl) and 200ml of water was added. Their solution was cooled in ice and hydrazine hydrate (11.5g) was added. The product separated out on standing the solution at room temperature for two hours. A little N-HCI was added to maintain pH between 5 and 6 and the mixture was kept in ice for one hour. The product was filtered off, washed with water and dried. The crude product was recrystallized from benzene. Yield 80%.



Now, benzenethiocarboxyhydrazide (15.2g) obtained as above, was refluxed on water bath at 60-70°C, with pyridine-2-carboxaldehyde (12.2g) in ethanol for four hours. On cooling the resulting solution, light yellow crystals were produced. It was washed with ethanol acetone and dried. The ligand was recrystallized from D. M.F. The yield was 80% melting point 138°C.



PYRIDINE-2-CARBOXALDEHYDETHIOBENZOYLHYDRAZONE

CHARACTERIZATION OF HETROCYCLIC THIOHYDRA ZONES AND LIGANDS

The heterocyclic thiohydrazones and azo ligands have been characterized on the basis of elemental analysis molecular weight determination and IR spectral studies.

IR STUDIES

A) HETEROCYCLIC THIOHYDRAZONES

IR spectra of the free thiohydrazones showed two strong bands at 1,530-1,500 cm^{-1} (s) and 1,305-1,290 cm^{-1} (m) (thioamide bands -I -II), characteristic vibrations of thioamide group. Further, the thiohydrazones, under study, displayed v(C=S) medium vibration due to thiocarbonyl group (thioamide band-IV) at 845-810 cm^{-1}. A band located at 960-950 cm^{-1} (In) in spectra of ligands may be due to v (N-N). The strong band appeared in the spectra of thiohydrazones at 3,190-3,195 cm^{-1} assignable to N-H stretching of amino group. The sharp bands appeared in region 3,030-3,015 cm^{-1} and 1,650-1,620 cm^{-1} in all the ligands, are characteristics of aromatic C-H stretching, and azomethine v(C=N) respectively. A group of three bands of medium intensity observed in the region 1,580-1,480 cm^{-1} is regarded as due to the aromatic C=Cvibrations.

In addition to the above bands, the ligand hydroylbenzene-2 carboxaldehyde-2' furanthiocarboxyhydrazone showed one strong broad band at 3,470 cm^{-1} due to -O-H stretching and another strong band at 1,280 cm-1 due to phenol C-O sym - stretching. Bands at 1,505 cm^{-1}, 880 cm^{-1} and 3 745 cm^{-1} are assigned to C-C skeletal vibrations -C-H out-of –plane deformation and v(C-O) of furan ring respectively.

Results and Disscussion

The complexes are quite stable at room temperature. They are non-hygroscopic. The complexes soluble in common organic solvents. Electrolytic conductance data of the complexes in their 10-3 M $PhNO_2$ solution are given. Molecular weights of the complexes have been measured by Rast Camphor method. colour, melting point, molar conductance, molecular weight and magnetic moment are reported.

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