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Complexes of Fe(II), Co(II) & Ni(II) with o-Mercapto benzophenone thiocarbohydrazone

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Abstract

Complexes of the type $K_2[ML_2]$ [where, M = Fe(II), Co(II) & Ni(II); L = o-mercapto benzophenone thiocarbohydrazone] have been isolated by a metal ion catalysed template synthesis. The synthetic method involves the reaction of ethanolic solution of the metal salts, o-mercaptobenzophenone and thiocarbohydrazide in the molar ratio 1:4:2. The compounds have been characterized on the basis of analytical, infrared and electronic spectral, magnetic moment and molar conductivity data. Infrared spectral data show that o-mercapto benzophenone thiocarbohydrazide acts as a tridentate bi negative ligand coordinating through all the three sulphur donor atoms present in it as the corresponding thiophenolic SH bands present in the spectrum of ligand are absent in the spectra of metal complexes as well as C=S band is shifted from it's position. NMR spectra also support coordination through thio-phenolic sulphur donor atoms as the peak at 2.8 ppm present in the spectrum of the ligand is absent from the spectra of complexes. The nitrogen donor atoms, azomethinic as well as amidic ones remain unutilised in coordination as the corresponding bands remain unshifted. Molar conductivity of the complexes measured in nitrobenzene has been found to lie in the range 35 - 45 S cm^2 mol^{-1} which indicate complexes to be electrolytic in nature of the type 2:1. Magnetic data indicate Fe(II) and Ni(II) complexes to be spin paired diamagnetic whereas Co(II) complexes are low spin. On the basis of above mentioned data, complexes have been proposed to possess hexacoordinated structure with metal ions present in square planar stereochemical environment.

Keywords: Metal complexes, Schiff base ligands, Fe(II), Co(II), Ni(II), spectral studies.

Introduction

Uses of metal dihydrazone complexes for the synthesis of a series of novel macrocyclic complexes have gained interest during the later half of the last century[1-6]. However such investigations were confined to biacetyldihydrazone. Very recently, works on synthesis, characterization and biochemical study using thiosemicarbazones and thiocarbohydrazones have been presented in a review article[7] which has sparked an upsurge in research activity in the field. Consequently, present studies to synthesize and characterize a series of transition metal complexes with o-mercapto benzophenone thiocarbohydrazone have been undertaken. The

present paper deals with the synthesis, characterization and structure elucidation of iron(II), cobalt(II) and nickel(II) complexes on the basis of spectral , magnetic and conductivity studies.

Experimental

All the metal salts and solvents such as ethanol, methanol, acetone, nitrobenzene, DMF, DMSO used in the present study were of analytical grade. These chemicals were purchased from CDH or Merck and used as such. All the complexes were prepared under similar experimental conditions by an in situ method. A typical preparation is described here. Bis (o-mercapto benzophenone thiocarbohydrazone) nickel(II) chloride O-mercapto benzophenone (0.04 mol) in ethanol, thiocarbo-hydrazide (0.02 mol) also in ethanol was treated drop wise with an ethanolic solution of nickel chloride hexahydrate (0.01 mol). The resulting mixture was heated to boiling with constant stirring when a light green precipitate readily formed. It was refluxed over a water bath for nearly 2 hours. The compound obtained was cooled, filtered, washed successively with ethanol and ether and dried at room temperature. Yields were almost quantitative in each case.

In addition to in situ method complexes have also been prepared by traditional method as well by preparing the ligand and then mixing the ethanolic solution of the ligand with ethanolic solution of metal salts in molar ratio 2:1 followed by refluxing the mixture solution for 2 hours. The pH of the reaction mixture was maintained strongly basic by adding KOH.

Ligand preparation

Decimolar solution of ortho mercapto benzophenone was prepared by dissolving 0.321 g of it in 15 ml of methanol. On the other hand 0.05 molar solution of thiocarbohydrazide was prepared by dissolving 0.132 g of it in 25 ml of water. Equal volumes of both the freshly prepared solutions were mixed with vigorous shaking. The reaction began with the separation of yellowish precipitate. The reaction mixture was refluxed on a steam bath for an hour and then cooled to room temperature. The product was filtered off and recrystallised to get a white shining crystals. The purity of ligand was checked by elemental analysis and melting point (184^0 c). It was also characterized by infrared and nmr spectral studies.

The yield was slightly lower in this case. The coloured precipitate thus obtained was filtered, washed and analysed.

The compounds were analysed by standard procedures[8]. Magnetic susceptibilities were measured using a Guoy balance at room temperature. The analytical, colour, magnetic moment and molar conductivity data are recorded in Table-1. The infrared spectra of the complexes were recorded on a Beckman IR-20 spectrophotometer. The reflectance spectra were recorded in nujol on a Beckman spectrophotometer.

Table – 1

Analytical data, Found (Calc.), colour, M.P, Molar conductivity (Scm^2mol^{-1}), Magnetic moment(B.M).

Compounds	Colour	C	H	N	S	M	M.P, (°C)	Λ_m	μ_{eff}
$C_{27}H_{22}N_4S_3$	White	65.65 (65.06)	4.41 (4.42)	11.26 (11.24)	19.32 (19.28)	--	184	--	--
$K_2[Fe(C_{27}H_{20}N_4S_3)_2]$	Brown	57.73 (57.58)	3.56 (3.54)	6.96 (9.95)	17.31 (17.05	4.97 (4.96)	120	38.2	Dia
$K_2[Co(C_{27}H_{20}N_4S_3)_2]$	Pink	57.42 (57.39	3.53 (3.54)	9.94 (9.92)	17.02 (17.00)	5.23 (5.22)	135	35.5	2.42
$K_2[Ni(C_{27}H_{20}N_4S_3)_2]$	Green	57.41 (57.39)	3.52 (3.54)	9.93 (9.92)	17.03 (17.00)	5.21 (5.22)	155	43.9	Dia

Infrared spectral data are recorded in Table-2. NMR spectral data are presented in Table-3.

Table-2

Infrared spectral bands of ligand and metal complexes (in cm^{-1})

Compounds	ν_{S-H}	ν_{C-S}	ν_{C-S}	ν_{M-S}
H_2L	2600	740	730	……..
$K_2[Fe\ L_2]$	……..	620	690	355
$K_2[Co\ L_2]$	……..	660	700	395
$K_2[Ni\ L_2]$	……..	655	710	360

Table-3

Compound NMR spectral bands

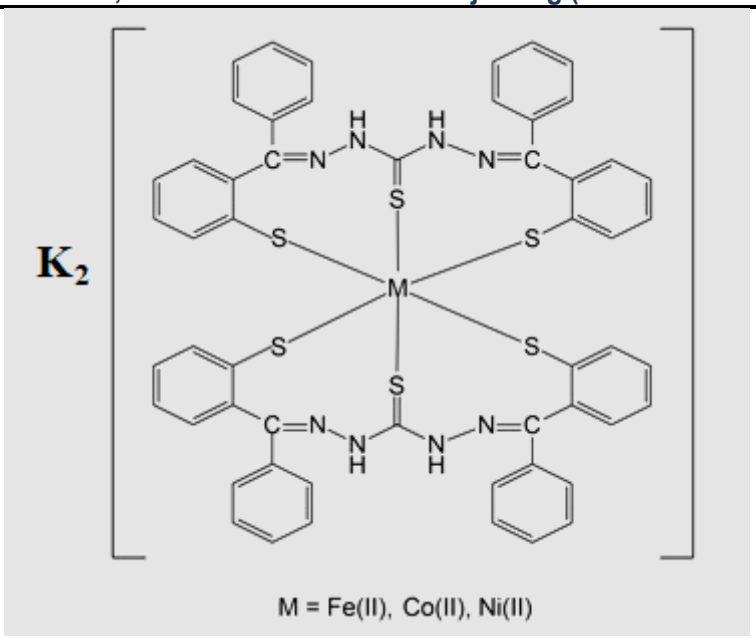
Compounds	δ_{SH}	$\delta_{NH\ (I)}$	δ_{ArH}	$\delta_{NH\ (II)}$
H_2L	3.8	4.2	7.45	5.2
$K_2[Fe\ L_2]$	-	4.0	7.40	5.4
$K_2[Co\ L_2]$	-	4.1	7.38	5.3
$K_2[Ni\ L_2]$	-	3.9	7.35	5.3

Results and discussion

On comparison of ir and nmr spectra of the ligand H_2L, ortho mercapto benzophenone thiocarbohydrazone and metal complexes valuable information regarding bonding mode are obtained. Position of azomethine and amidic bands remain unshifted whereas. Phenolic SH band disappear indicating coordination to take place through sulfur. Thionyl sulfur also takes part in co-ordination as C=S band is shifted. Appearance of new bands in far ir region due to metal sulfur stretching also support the mode of coordination.

Diamagnetic nature of iron and nickel complexes as well as low value of magnetic moment for cobalt complex is suggesting square planar environment of ligand around metal centres. Electronic spectra support this structure.

Molar conductivity data indicate electrolytic nature of complexes On the basis of above-mentioned consideration complexes have been assigned structure as shown below.



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