



Synthesis and Characterization of Divalent Transition Metal Complexes Containing Thiosemicarbazone Ligands

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ABSTRACT

Complexes of divalent transition metals Co(II), Ni (II) and Cu(II) with ligand 2 – hydroxy – 4 – nitro acetophenone thiosemicarbazone have been synthesized. The complexes were characterized on the basis of elemental analysis, magnetic studies, electrical conductance and IR and electronic spectra. The complexes of Co(II) and Ni(II) were found to be octahedral where as Cu(II) complexes has square planer geometry.

Key words: Thiosemicarbazone, Schiff's bases, Transition metals, complex compounds.

INTRODUCTION

Thiosemicarbazones possess considerable biological properties and have medicinal applications such as anti T.B. and leprosy¹⁻², antiviral properties³, antitumour⁴, anticancer^{5,6}. Literature survey reveals that the presence of a metal ion increases the activity of or mitigate the side effects of the parent organic compounds⁷⁻¹⁰.

In continuation of our previous work in this communication we are going to report synthesis and characterization of complexes of Co(II), Ni(II) and Cu(II) with ligands containing thio semicarbazone of substituted aromatic ketones.

EXPERIMENTAL

Preparation of Ligand

4.8g of 2-hydroxy – 4 nitro – acetophenone was dissolved in methanol and treated with a solution containing 3.8 g BDH Anal R grade thio semicarbazide hydrochloride in water.

The mixture was stirred well and refluxed for half an hour on a water bath and cooled. Pale yellow crystals were separated. The crude yellow product was recrystallised from alcohol as colourless needles. Melting point of the compound was determined by Kjeldahl's method and was found to be 491 K. The pure and dried compound was chemically analysed. It is slightly soluble in alcohol but highly soluble in DMF but insoluble in water.

Preparation of complexes

Calculated quantity of metal salts (0.482 g cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was dissolved in methanol while the ligand (HNAPTS) was dissolved in DMF. Both the solution were mixed together and 1.0 g sodium acetate was added to it. The solution was refluxed for about three hours and left overnight. The grey precipitate was obtained. It is filtered and washed with methanol and ice cold water. The pure complexes was dried in air.

0.520g of nickel (II) chloride was dissolved in water while 0.820 g ligand was dissolved in DMF. Both the solution were mixed. 1.0 g sodium acetate was added and refluxed for about three hours and left to stand for an hour. The red coloured precipitate was obtained. It was filtered and washed with water and ethanol and dried in air.

An ammoniacal solution of 0.256 g copper (II) chloride was treated with a solution of 0.348 g ligand (HNAPTS) dissolved in DMF. The red coloured precipitate separated was digested on the water bath for two hours and then left to stand for an hour. It was filtered washed with water and dried in air. All the three complexes were analysed chemically.

RESULTS AND DISCUSSION

Probable structure of ligand 2-hydroxy-4-nitroacetophenone thiosemicarbazone (HNAPTS)

The interpretation of I. R. spectra is quite complicated due to the presence of various similar groups and hence presence of many absorption bands. However, comparison of the spectral bands of the ligand (HNAPTS), with those of its complexes

gives some important information regarding the nature of the ligand as well as the co-ordination sites through which metal ion has co-ordinated with the ligand.

The band at 3195 cm^{-1} in the ligand assignable to phenolic O – H (hydrogen bonded) stretching frequency¹¹ disappears in the Ni(II), Co (II) complexes showing deprotonation of phenolic proton. The ligand also shows strong band at 1260 cm^{-1} which may be attributed to the phenolic C – O vibration. A shift of this band to higher frequency ($\sim 1300 \text{ cm}^{-1}$) in the complexes indicate chelation of the ligand to metal ion through phenolic oxygen.

The sharp band at 1580 cm^{-1} in the free ligand due to $\nu_{\text{C=N}}$ of Schiff's base residue shifts to the lower frequency at ($\sim 1565 \text{ cm}^{-1}$) in the complexes showing co-ordination through the nitrogen atom. The lowering may be very small in some cases. The ligand band at 1165 cm^{-1} may be assigned to $\nu_{\text{C=S}}$ group and shows downward shifting in metal complexes, indicating participation of this group in co-ordination.

The absorption band at 3380 cm^{-1} due to $\nu_{\text{N-H}}$ group in the free ligand remains unaltered in the complexes, indicating non-participation of this group in co-ordination.

A band present at 1385 cm^{-1} in the I. R. spectra of the ligand is assigned¹² to $\nu_{\text{C-N}}$ group due to nitro group. This band remains unchanged in all the complexes, suggesting non – participation of nitro group in co-ordination.

Table 1: Elemental analysis data of ligand and complexes

Compound	% Observed (calculated)					
	C	H	N	O	M	
HNAPTS						
$[\text{Co}(\text{HNAPTS})_2]$	37.98 (38.23)	3.76 (3.16)	20.05 (19.83)	16.73 (17.0)	11.16 (11.38)	10.32 (10.40)
$[\text{Ni}(\text{HNAPTS})_2]$	38.43 (38.25)	3.28 (3.18)	19.47 (19.84)	17.83 (16.97)	17.83 (16.97)	10.16 (10.38)
$[\text{Cu}(\text{HNAPTS})\text{NH}_3]$	31.80 (32.36)	3.95 (3.60)	20.18 (20.97)	15.96 (14.40)	15.96 (14.40)	18.96 (19.40)

Thus, we come to a conclusion that the ligand, 2 – Hydroxy – 4 – nitro acetophenone thiosemicarbazone (HNAPTS) behaves as a tridentate ligand for the metal ions, co-ordinating through (i) phenolic oxygen (C – O), (ii) nitrogen atom of (C = N), of azomethine group and (iii) ketonic sulphur of C = S, as enolic group. Similar kind of situation has been reported by S. K. Thampy.¹³ This ligand is monoprotic in all the cases except Ni(II) and Cu (II) at higher pH (pH = 9). It has been observed that in these cases a band present at 1165 cm⁻¹ in the free ligand disappears, perhaps due to deprotonation of the C = S (enolic) proton.

Many workers¹⁴⁻²⁰ have prepared complexes with Schiff's base derived from substituted salicylaldehyde and reported non-participation of the substituents in the co-ordination. However, stability of the complex is certainly influenced by the presence of the substituents. These results are in

good agreement with our previous observation¹⁷⁻²⁴. The ligand may be assumed to be tautomer of the following two probable structures.

Structure of complexes

The molar conductance values of complexes 18.78 for Co(II), 16.80 for Ni(II) and 18.6 for Cu(II) suggest non-electrolytic nature of all the complexes [Co(HNAPTS)₂], [Ni(HNAPTS)₂] and [Cu(HNAPTS)NH₃].

Electronic Spectra

These Ni (II) complexes show four bands in their reflectance spectra favouring an octahedral stereochemistry²⁵. Out of these four bands, three can be assigned to spin allowed d – d transition, eg. ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{1g}(P). The fourth band near 10750 cm⁻¹ is probably spin forbidden²⁵ and may be assigned to ²B_{1g} → ²E_g transition.

Table 2: Melting point, Decomposition temperature, magnetic moment & electrical conductivity data of complexes

Compounds	M. P(K)	D.T. (K)	μ_{eff} (BM)	\wedge_M^0 Ohm cm ² mol ⁻¹
HNAPTS	491	-	-	-
[Co(HNAPTS) ₂]	-	473	4.15	18.78
[Ni(HNAPTS) ₂]	-	533	3.05	16.80
[Cu(HNAPTS)NH ₃]	503	513	1.83	18.6

* M.P - Melting point;D.T. - Decomposition temperature ,

μ_{eff} =Magnetic moment \wedge_M^0 = molar conductivity

Table 3: Electronic spectral data of complexes and their assignment

Compound	$\bar{\nu}$ (in cm ⁻¹)	Assignment
[Co(HNAPTS) ₂]	9390	⁴ T _{1g} → ⁴ T _{2g} (F)
	19900	⁴ T _{1g} → ⁴ A _{2g} (F)
	22085	⁴ T _{1g} → ⁴ T _{1g} (P)
[Ni(HNAPTS) ₂]	11560	³ A _{2g} → ³ T _{2g} (F)
	17380	³ A _{2g} (F) → ³ T _{1g} (F)
	26864	³ A _{2g} (F) → ³ T _{1g} (F)
	11385	Spin forbidden
[Cu(HNAPTS)NH ₃]	20,000	² B _{1g} → ² A _{1g} , ² E _g

Table 4: IR Spectral bands (cm⁻¹) of ligand and complexes

Ligand HNAPTS	Complexes			Assignment
	[Co(HNAPTS) ₂]	[Ni(HNAPTS) ₂]	[Cu(HNAPTS)NH ₃]	
3380	3380	3385	3380	N – H stretching
3195				O – H (H- bonded)
3090	3105	3100	3105	C – H stretching
1580	1575	1570	1580	C=N stretching
1405	1415	1400	1410	N – H bending
1385	1395	1390	1395	C – N stretching
1260	1305	1285	1285	C – O (phenolic)
1195			1205	Skeletal in plane vibrations
1175			1175	
1155	1145	1140	1135	C=S stretching
1135	1065	1130	1125	Characteristic vibration of 1,2,4 – trisubstituted benzene ring
1045	1050	1040	1030	
910-920	920-930	915-925	910-920	C – N bending
820	820	820	820	Skeletal vibrations
	530	540	535	M – N bond
	505	480	495	M – O bond
	375	330	285	M – S bond

Copper (II) has d⁹ configuration which makes Cu (II) subject to John – Teller distortion, if placed in an environment of cubic like regular octahedral or tetrahedral symmetry and this has a profound effect on all its stereochemistry²⁷.

The typical distortion is an elongation along one four fold axis, so that there is planar array of four short Cu-L bonds with two trans long ones. In the limit of course, the elongation leads to a situation indistinguishable from square co – ordination as found in many discrete complexes of Cu (II) . Thus the cases of tetragonally distorted “Octahedral” co – ordination and square co - ordination cannot be sharply differentiated.

Because of the relatively low symmetry of the environments in which the Cu²⁺ ion is characteristically found, detailed interpretation of spectra and magnetic properties are somewhat complicated even though one is dealing with the equivalent of a one – electron case.

The molar conductance values suggest non – electrolytic nature of this complex while I.R. band near 655 cm⁻¹ suggests M – NH₃ bonding.

The magnetic moment of Cu (II) complex correspond well with the presence of one unpaired electron and gives on specific information about their stereochemistries. The μ_{eff} value of Co(II) complex (4.15 BM) indicate the presence of three unpaired electron in the complex whereas μ_{eff} for Ni(II) complex

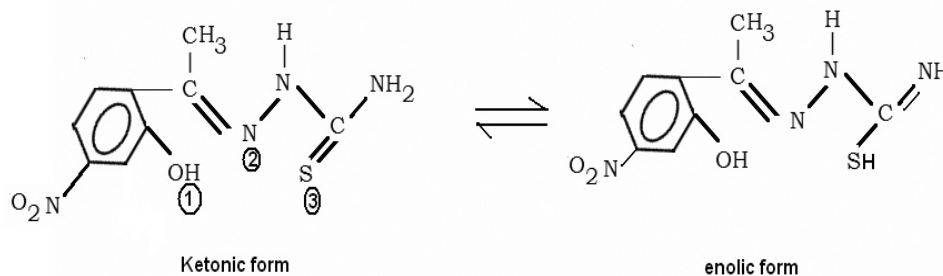


Fig. 1: 2 – Hydroxy – 4 – nitro aceto phenone thiosemicarbazone

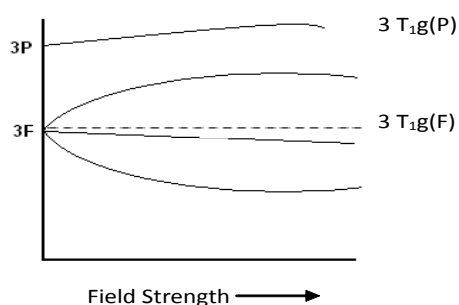


Fig. 2: Orgel diagram of Ni(II) complex

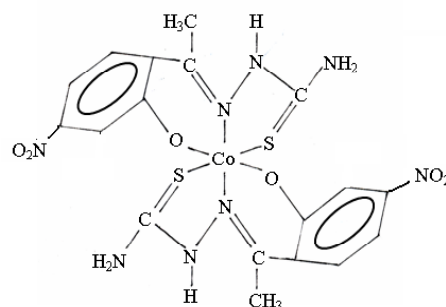


Fig. 3: Bis - (2- hydroxy - 4 - nitro acetophenone thio semicarbazone) Co (II)

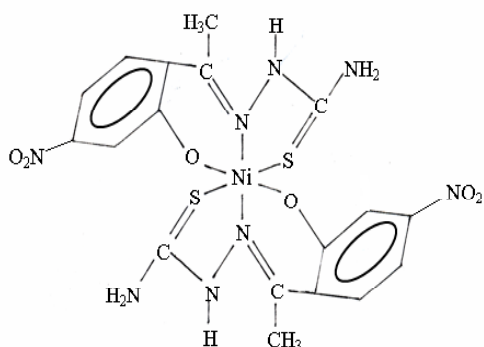


Fig. 4: Bis - (2- hydroxy - 4 - nitro acetophenone thio semicarbazone) Ni(II)

(3.05 BM) suggests presence of two unpaired electron in the complex.

Taking all these facts into consideration, along with their elemental analysis data the most probable structures of these complexes are given below in figure 3, 4 & 5.

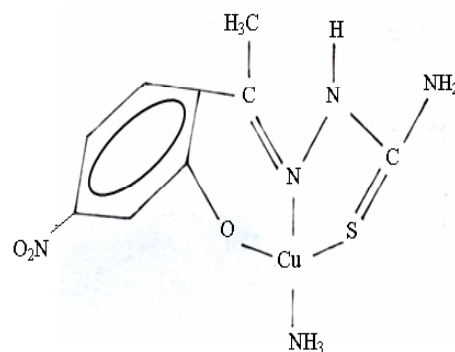


Fig. 5: Mono ammine 2- hydroxy - 4 - nitro acetophenone thio semicarbazone Cu(II)

CONCLUSION

Thiosemicarbazone metal complexes have been studied for a long time. The crystallographic data available to date is also very large but the study of the way thiosemicarbazone metal complexes interact with biological systems requires much attention. More light is needed on the grey zone between chemistry and molecular biology.

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