

Magnetic and Spectral Studies on Cobalt Complexes of Thiosemicarbazones

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Abstract

In the field of coordination chemistry, extensive studies have been carried out on metal complexes formed by ligands having dual sites for coordination. Of these, thiosemicarbazides having N and S as donor atoms deserve a special mention. Interest in thiosemicarbazones (derivatives of thiosemicarbazides) as ligands mainly developed due to their flexibility which led to extremely variable behaviour in their reactions with transition and non-transition metals. Literature studies show that thiosemicarbazones exhibit a wide range of stereochemistry on complexation with transition metal ions. Technological advances have led to the development of sophisticated and sensitive instrumentations which provide avenues to probe into the structure and bonding in the complexes. Hence new metal complexes have been synthesised using chloride salt of Cobalt and thiosemicarbazone obtained by variation of the parent carbonyl compound. Magnetic and spectral studies have been carried out to obtain information regarding effect of coordination on the central metal ion (oxidation state in particular) and stereochemistry exhibited by these complexes.

Key words: metal complexes, thiosemicarbazide, thiosemicarbazones, stereochemistry.

Introduction

Literature studies¹ show that thiosemicarbazones exhibit a wide range of stereochemistry on complexation with transition metal ions, of which few have been adequately studied. The enormous upsurge of interest in the field of coordination chemistry is mainly due to the development of theories which have been successful in explaining the various properties associated with transition complexes.

A large number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide. Depending upon the type of aldehyde or ketone used for condensation, thiosemicarbazones act as unidentate, bidentate or multidentate chelating agents for metal ions, producing highly coloured complexes. These coloured complexes have been used in selective and sensitive determination of metal ions and find a variety of analytical applications.

The stereochemistry adopted by thiosemicarbazone ligands while interacting with transition metal ions depends on two factors – i) charge on the ligand ii) presence of an additional coordinating centre in the ligand moiety. The charge on the ligand is influenced by thione-thiol equilibrium. In solution, thiosemicarbazones consist of an equilibrium mixture of thione and thiol tautomers.² Thione form acts as

neutral bidentate ligand. Loss of a proton from thiol tautomers gives a singly charged bidentate ligand. Depending upon the pH of the medium, cationic, anionic or neutral complexes are formed. When an additional coordinating group is present, the ligands act as tridentate species, giving polymeric complexes.

Coordination chemistry of Cobalt3

Cobalt has atomic number 27 with ground state electronic configuration $3d^7 4s^2$. It exhibits wide range of oxidation states, Co(I) to Co(V) of which Co(II) and Co(III) are most common.

Cobalt (II) complexes are observed with coordination numbers four, five and six, the stereochemistry exhibited being tetrahedral or square planar, trigonal bipyramidal and octahedral. Of these, tetrahedral and octahedral configurations are most common and are distinguished by their color, electronic spectra and magnetic moments. Tetrahedral cobalt (II) complexes have intense blue color whereas octahedral cobalt (II) complexes are pale red or purple. In tetrahedral systems the visible transition is intense and observed at low energies whereas in octahedral systems the transition occurs in the near infrared region. Effective magnetic moments for tetrahedral complexes fall in the range of 4.5 – 4.7 BM whereas for octahedral complexes, due to orbital contribution magnetic moment values between 4.7 and 5.5 BM are observed.

Cobalt (III) complexes generally show octahedral stereochemistry and are diamagnetic. Co (III) generally shows marked affinity towards nitrogen donors.

Materials and Methods

Syntheses of the Thiosemicarbazones

Cyclohexanone thiosemicarbazone (CHTSC) was prepared by the method reported by Sah and Daniel⁴. Cyclopentanone thiosemicarbazone (CPTSC) was prepared by the method reported by Sah and Daniel⁴. Diacetyl Monoxime thiosemicarbazone (DMTSC) was prepared by the method reported by Ablov and Belichuk⁵. Pyridine-2-carboxaldehyde thiosemicarbazone (PCTSC) was prepared by the method reported by Fukujiro et al⁶. 2-Acetylpyridine thiosemicarbazone (APTSC) was prepared by the method reported by Anderson et al⁷.

Syntheses of Cobalt(II) and Cobalt(III) chloride complexes of Thiosemicarbazones

2 mmol of the thiosemicarbazone was dissolved in 50 cm³ of methanol by stirring for thirty minutes. A methanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1mmol in 40 cm³) was slowly added to the ligand solution. The reaction mixture was stirred at room temperature for twenty four hours. The precipitate of the complex was filtered and recrystallized using suitable solvent. The following complexes were synthesized $[\text{Co}(\text{CHTSC})_2]\text{Cl}_2$, $[\text{Co}(\text{CPTSC})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{DMTSC})(\text{DMTSC-H})]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{PCTSC})(\text{PCTSC-H})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{APTSC})(\text{APTSC-H})]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

The complexes have been characterized by IR, NMR and UV-visible spectroscopy. The oxidation states of cobalt in these complexes were determined by magnetic studies.

Results and Discussion

Infrared spectra

The infrared spectra of the complexes have been recorded in the range 4000 to 200 cm^{-1} region. Positions of selective bands corresponding to characteristic group frequencies are given in Table 1. The NH stretching frequencies observed in the ligands⁸, remains almost unchanged in the complexes indicating non-participation of the NH_2 and NH group of the ligand in coordination. The C-N stretching and NH deformation vibrations^{8,9,10} observed in the ligands, show a shift to the higher frequency region accompanied by splitting in the complexes. Coordination to the metal by introducing more double bond character in the C-N bond adjacent to sulphur, explains this shift^{11,12,13}. The C-S and C-N stretching vibrations observed in the ligands show a shift to the lower and higher frequencies respectively in the complexes. The shift to the higher frequency is due to large increase in bond order brought about by coordination⁸. In the ligands the C-S stretching frequency coupled with N-C-N stretching vibration^{14,15} shows shift to the higher frequency region in the complexes, indicating increase in the multiplicity of the C-N bond. In the complexes the most marked shift is observed for the C-S stretching frequency¹ due to the change in bond order caused by the formation of the M-S bond.

Table: 1 – Infrared Spectral Data (Bands In Cm^{-1}) Of The Ligands And Complexes of Cobalt

LIGAND/COMPLEX	$\nu(\text{C}=\text{N})$ + $\delta(\text{NH}_2)$	$\nu(\text{C}=\text{S})$ + $\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{C}-\text{N})$	$\nu(\text{C}=\text{S})$	In and out of plane pyridine ring deformation	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$
CHTSC	1588	1460, 1350	1125	770	-	-	-
$[\text{Co}(\text{CHTSC})_2]\text{Cl}_2$	1605	1430, 1370	1135	740	-	345	304
CPTSC	1590	1460	1085	820	-	-	-
$[\text{Co}(\text{CPTSC})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	1622	1420	1140	745	-	379	301
DMTSC	1605	1470	1150	785	-	-	-
$[\text{Co}(\text{DMTSC})(\text{DMTSC}-\text{H})\text{Cl}_2] \cdot \text{H}_2\text{O}$	1630	1440	1160	740	-	380	306
PCTSC	1610	1470, 1370	1140	780	610, 415	-	-
$[\text{Co}(\text{PCTSC})(\text{PCTSC}-\text{H})\text{Cl}_2] \cdot \text{H}_2\text{O}$	1635	1450, 1380	1160	740	625, 421	349	302
APTSC	1615	1465, 1366	1150	790	570, 409	-	-
$[\text{Co}(\text{APTSC})(\text{APTSC}-\text{H})\text{Cl}_2] \cdot \text{H}_2\text{O}$	1630	1447	1165	730	583, 430	385	309

For the DMTSC complex, absence of band corresponding to $-\text{OH}$ stretching frequency in the ligand suggests that binding occurs through this additional site. Shifts in the pyridine ring deformation bands for the PCTSC complex, suggests the involvement of the pyridine Nitrogen, in coordination¹⁶. In the far

infrared spectral region, characteristic M-S and M-N stretching frequencies^{16,17} are observed which further confirms the binding sites.

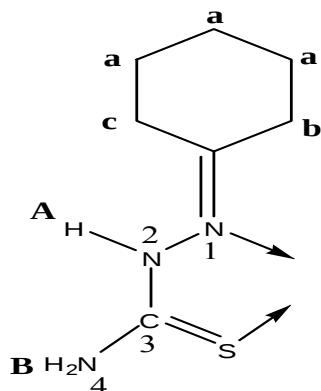
From the infrared spectral data, one comes to the following conclusions – CHTSC and CPTSC behave as bidentate chelating agents and coordinate through the nitrogen atom of the C=N group and the sulphur atom of the C=S group of thiosemicarbazide moiety. DMTSC, PCTSC and APTSC behave as tridentate chelating agents with additional binding site, oxime group in DMTSC and nitrogen atom of pyridine ring in PCTSC and APTSC.

¹H NMR spectra

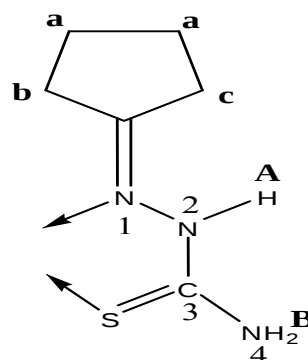
The ¹H NMR spectra of the ligands and the complexes have been recorded in DMSO – d₆. The proton chemical shifts (δ) have been referenced in ppm from tetramethyl silane (TMS) signal and are given in Table 2. Structure and numbering scheme of the ligand protons indicating potential binding sites are given in figs. A to E.

TABLE – 2: ¹H NMR SPECTRAL DATA OF THE LIGANDS AND COMPLEXES OF COBALT

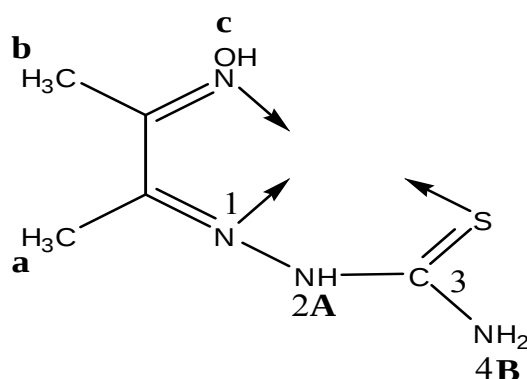
LIGAND/COMPLEX	CHEMICAL SHIFTS IN δ ppm RELATIVE TO TMS							
	H _C	H _A	H _B	H _D	H _d	H _c	H _b	H _a
CHTSC	-	10.1	7.92 7.5	-	-	2.4	2.22	1.56
[Co(CHTSC) ₂]Cl ₂	-	9.62	8.62 7.36	-	-	2.58	2.28	1.62
CPTSC	-	9.82	7.95 7.48	-	-	2.38	2.32	1.72
[Co(CPTSC) ₂]Cl ₂ .H ₂ O	-	9.4	8.0 7.8	-	-	2.64	2.5	1.82
DMTSC	11.49	10.14	8.37 7.69	-	-	-	2.09	1.99
[Co(DMTSC)(DMTSC-H)Cl ₂]H ₂ O	-		6.82	-	-	-	2.34	2.20
PCTSC	-	11.64	8.36	8.28	8.56	8.18	7.82	7.37
[Co(PCTSC)(PCTSC-H)Cl ₂ .H ₂ O	-	-	8.68	8.07	8.11	8.05	7.8	7.36
APTSC	-	10.29	8.5 8.43	2.42	8.69	8.15	7.83	7.43
[Co(APTSC)(APTSC-H)Cl ₂ .H ₂ O	-	-	8.72	2.5	8.11	8.05	7.93	7.44



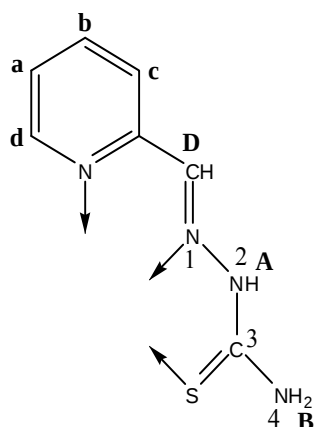
CHTSC (A)



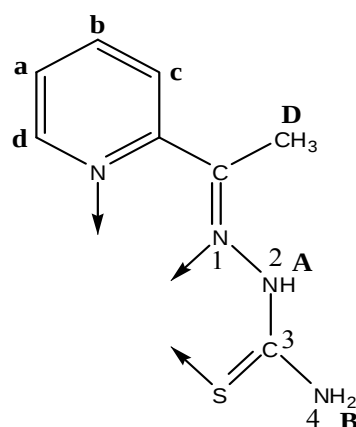
CPTSC (B)



DMTSC (C)



PCTSC (D)



APTSC (E)

Figures (A) to (E) – Structures of Ligands (Arrows indicate points of potential bonding between ligand, atoms and metal)

The ^1H NMR spectra of CHTSC and CPTSC (fig) show two resonances for the NH_2 protons (B) indicating the non-equivalent nature of these protons due to the partial double bond character in the $\text{C}(\text{S})\text{-NH}_2$ bond and hence a hindered rotation about this bond¹⁸. X-ray crystallographic data for several thiosemicarbazones have shown that $\text{C}(3)\text{-N}(2)$ and $\text{C}(3)\text{-N}(4)$ bonds are shorter than single bonds¹⁹. The

NH proton (A), since it is bonded to two unsaturated nuclei absorb at lower fields. The two methylene protons (c,b) of the cyclohexyl ring in CHTSC and of the cyclopentyl ring in CPTSC, adjacent to the substituent carbon (the carbon double bonded to nitrogen) absorb as triplet peaks. The other protons (a) of the methylene group, (the β – and γ methylene protons) absorb as a peak of high intensity²⁰ in CHTSC and CPTSC. The ¹H NMR spectra of cobalt complexes of CHTSC and CPTSC show broad peaks due to the paramagnetic nature of these complexes.

The ¹H NMR spectrum of DMTSC exhibits resonance at low fields due to proton (C) of the hydroxyl group²⁰. The NH proton (A) absorbs at low field as it is bound to two unsaturated nuclei. The NH₂ protons exhibits two resonances indicating their non-equivalent nature due to the partial double bond character, and hence the hindered rotation about the –C(S)-NH₂ bond¹⁸. The methyl protons (a and b) exhibit two resonances showing non-equivalence due to different environments²⁰ (oxime group and thiosemicarbazide moiety). In the cobalt complex of DMTSC the signal due to oxime proton (C) disappears indicating that binding to the metal occurs through this site. The disappearance of the NH proton (A) signal indicates that thiol form of ligand is involved in coordination. The methyl protons (a,b) exhibit down-field shift in the complex.

In the ¹H NMR spectra of PCTSC and APTSC, the NH proton (A), being bonded to two unsaturated nuclei absorb at lowest fields. The NH₂ protons (B) absorb as two signals¹⁸. Of the ring protons, as in pyridine, the α protons (d) absorb at low fields, the β - protons (a) absorb at higher fields, while the γ - protons (b) absorb at intermediate fields. In the cobalt complexes of PCTSC and APTSC, absence of the NH proton (A) signal indicates the involvement of thiol form of ligand in coordination. The NH₂ protons (B) exhibit down-field shift whereas the ring protons show up-field shift due to the  delocalization in the pyridine ring.

Magnetic susceptibility measurements

The magnetic susceptibility of the polycrystalline complexes were measured at room temperature by the Guoy method. The magnetic moments of the complexes have been calculated and given in Table 3. The oxidation state of the metal ion in the complex has been ascertained from the magnetic moment values obtained. The complexes of CHTSC and CPTSC show magnetic moment values of 4.37 and 3.84 BM suggesting the cobalt ion to be in the +2 oxidation state, giving Co (II) complexes. The complexes of DMTSC, PCTSC and APTSC were found to be diamagnetic thereby suggesting the cobalt ion to be in the +3 oxidation state, giving Co (III) complexes.

Table 3 Electronic Absorption Spectral and Magnetic Data of The Ligands and the Complexes of Cobalt

LIGAND/COMPLEX	BAND MAXIMA IN kK ^a	Magnetic Moment μ_{eff} (B.M.) (298K)
[Co(HTSC) ₂]Cl ₂	14.78 15.87 (sh) 16.43 16.81(sh) 17.86 (sh) 36.15	4.37
HTSC	36.2	-
[Co(CPTSC) ₂]Cl ₂ .H ₂ O	14.8 15.87 (sh) 16.41 16.75 (sh) 17.86 (sh) 35.84	3.84
CPTSC	36.15	-
[Co(DMTSC)(DMTSC-H)Cl ₂]H ₂ O	16.13 24.39 33.38	Diamagnetic
DMTSC	32.89	-
[Co(PCTSC)(PCTSC-H)]Cl ₂ .H ₂ O	23.54 28.15 32.32	Diamagnetic
PCTSC	30.9	-
[Co(APTSC)(APTSC-H)]Cl ₂ .H ₂ O	12.18 23.56 27.4 32.07	Diamagnetic
APTSC	31.37	-

a = kK is $1 \times 10^3 \text{ cm}^{-1}$, sh – shoulder

Electronic spectra

The electronic absorption spectra of the ligands and their complexes were recorded in DMF solution. Electronic absorption spectral studies combined with magnetic studies give an insight into the stereochemistry of the complexes – Table 3. The magnetic moment values of the cobalt complexes suggest them to be high-spin cobalt (II) complexes. The coordination number being four, and magnetic moment being high, a tetrahedral configuration has been suggested which is further supported by the electronic spectra²¹.

The electronic absorption spectra for these complexes show bands around 14 and 16 kK with low molar absorptivities, suggesting them to be d-d transitions. The $\Pi \rightarrow \Pi^*$ transition of the ligands is observed around 36kK. The diamagnetism exhibited by the complexes of DMTSC, PCTSC and APTSC suggest them to be cobalt (III) complexes. The coordination number being six, an octahedral geometry is suggested for these complexes, which is further substantiated by the electronic absorption spectra²¹.

The electronic absorption spectrum of the Co (III) complex of DMTSC exhibits bands at 16.13 and 24.39kK, suggesting them to be d-d transitions usually observed in octahedral Co (III) complexes. The

intensity of these d-d bands is high for an octahedral complex which due to symmetry conditions generally show low molar absorptivity values. It has therefore been suggested that there is an overlap of the d-d band with the charge –transfer band. The $\Pi\text{-}\Pi^*$ transition of the ligand is observed at 33.38kK.

The electronic absorption spectrum of the diamagnetic cobalt (III) complex of PCTSC shows intense bands at 23.54 and 28.15 kK which may be due to the overlap of the charge-transfer band over the d-d transition. The intra-ligand $\Pi\text{-}\Pi^*$ transition is observed at 32.32kK. The coordination number being six, an octahedral geometry is suggested for this complex.

The electronic spectrum of the cobalt (III) complex of APTSC shows a weak d-d transition at 12.18 kK. The high intensity of the bands at 23.56 and 27.4 kK is due to overlap of these d-d transitions by the charge transfer transitions. The intra- ligand $\Pi\text{-}\Pi^*$ transition for this octahedral Co (III) complex is observed at 32.07kK.

Conclusions

The influence of the parent ligand moiety on the final geometry of the complex is evident from the interaction of cobalt (II) chloride with potentially bidentate and tridentate thiosemicarbazones. Presence of large alkyl substituents in the thiosemicarbazone generally stabilize the divalent state of cobalt as indicated by the formation of the paramagnetic complexes, $[\text{Co}(\text{CHTSC})_2]\text{Cl}_2$ and $[\text{Co}(\text{CPTSC})_2]\text{Cl}_2\cdot\text{H}_2\text{O}$ which have tetrahedral stereochemistry. In these complexes, the ligands behave as bidentate chelating agents and coordinate to the metal ion through the ‘N’ and ‘S’ of the C=N and C=S of the thiosemicarbazide moiety.

Presence of an additional coordinating site in the ligands DMTSC, PCTSC and APTSC has led to the formation of diamagnetic cobalt (III) complexes having octahedral stereochemistry. This could be due to thiol form of the ligand coordinating to the metal. It is also known that cobalt (III) shows a marked affinity for nitrogen donors. In these cobalt (III) complexes, the ligands behave as tridentate chelating agents and bind through the ‘N’ and ‘S’ of the thiosemicarbazide moiety and the ‘N’ of the oxime group in DMTSC and ‘N’ of the pyridine ring in PCTSC and APTSC.

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