

Synthesis, structure and physico-chemical studies of Mn (II) complexes of salicylaldehyde derived semicarbazone and thiosemicarbazone

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ABSTRACT

Complexes of semicarbazone and thiosemicarbazone of salicylaldehyde with Mn(II) have been synthesized by ethanolic solution of 0.05 mole of $MnCl_2 \cdot 4H_2O$ and 0.1 mole of corresponding ligand (ie, semi and thiosemicarbazone). Crystal data are reported with variable coordination modes. The complexes have been characterized by various physico-chemical techniques, viz. magnetic susceptibility measurement, electronic, infra-red and electron spin resonance spectral studies. These complexes are found of the type of $Mn(\text{ligand})_2X_2$ {X = Cl^- , Br, SO_4^{2-} and SCN^- }. All the complexes show a very good agreement with standard magnetic moment value of complexes having five unpaired spins at room temperature. They show magnetic moments in the range of 5.93 – 6.03 BM at room temperature. Electronic spectra of the complexes display weak absorption bands in the range $18200-20400\text{ cm}^{-1}$, $21060-25100\text{ cm}^{-1}$, $24870-29860\text{ cm}^{-1}$, $31300-33350\text{ cm}^{-1}$ which are characteristics of octahedral geometry.

Key words: Semicarbazone, thiosemicarbazone Ligand,
Magnetic susceptibility electronic spectra IR, ESR.

INTRODUCTION

Semicarbazide ($H_2N.NHCONH_2$) is a reagent for identification of aldehyde and ketones and has application in medicine as a lathyrogenic¹⁻⁵ and a teratogenic⁶. It forms complexes with polynucleotides⁷ and enhances growth of polio⁸, rubella viruses⁹. The possibility for semicarbazide to act as a bidentate ligand has been suggested¹⁰. Thiosemicarbazone and their metal complexes have received considerable attention because of their antibacterial, antifungal, antitumor, antiamebic and antimalarial, antiviral, radio-protective, trypanocidal and anti-inflammatory activities¹¹⁻²².

Among the various class of biologically active co-ordination compound complex with heterocyclic thiones as ligands play an important role in biological process and they are used to an effective plant protecting agents²³.

Theoretical details

Mode of Coordination

(2a) Bonding in Semicarbazone Complexes

The semicarbazide may act as a monodentate or bidentate chelating agent. Crystal structure of some semicarbazide complex studies and showed that semicarbazide is a bidentate. Crystal structure of some semicarbazide

complexes, eg. $\text{Cu}(\text{Sem})_2\text{Cl}_2$ and $\text{Zn}(\text{Sem})_2\text{Cl}_2$ has shown that each metal atom is surrounded by a trans-planar arrangement of two oxygen and two hydrazinic nitrogen which are found at the corners of a distorted square.

Coordination is completed by two chlorine on opposite sites of the square such an octahedral coordination more or less is likely to be found in the cd complexes and in other disemicarbazide compound as well.²⁴.

(2b) Bonding in Thiosemicarbazone complexes

The chemistry of transition metal complexes of thiosemicarbazone has been receiving considerable attention largely because of their pharmacological properties. In the solid state, these thiosemicarbazones exist in the thione form fig (i) In solution however they are known to tautomerize into the thiol fig.(ii) form complexation usually takes place via dissociation of the acidic proton resulting in the formation of a five membered chelate ring fig.(iii) When an additional donor site d is incorporated in such ligands linked to the Carbonylic carbon via one or two intervening atoms, D,N,S tri coordination fig. (iv) usually takes place.²⁵

A very large number of metal complexes involving thiosemicarbazide derivative as ligands have been prepared and studied²⁶⁻³¹ including also mixed macrocyclic complexes containing crown ether moieties.

These type of ligands are interesting because of their ability to form hepta-coordinated – bipyramidal (PBP) complexes even with some 3d elements which characteristically do not form such complexes.³¹⁻³² these planar pentadentate ligands occupy the equatorial plane while the PBP surrounding of the metal is completed with two monodentate ligands at the axial position.

It has been shown³³ that the thiosemicarbazide molecule itself exists in the trans-configuration and when complexing in this configuration it behave as a monodentate ligand bonding only through the sulphur atom.

They shown that³⁴ monodentate nature bonding may also occur through the hydrazinic

nitrogen in fig (1a) and fig(1b) showing bidentate nature bonding through hydrazinic nitrogen and amide nitrogen if any radical is attached with sulphur center..

EXPERIMENTAL

Present Work

Preparation of Complexes

$\text{Mn}(\text{ligand})_2\text{Cl}_2$

Ethanol solution of 0.05 mole of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.1 mole of corresponding ligand (ie, semi and thiosemicarbazone) was mixed and then the mixture was refluxed on water bath for 1½ hours. On cooling, light pink to cream coloured complex was separated out. The complex was filtered, washed with ethanol and dried over P_4O_{10} .

$\text{Mn}(\text{ligand})_2\text{X}_2$ (X=Br or SCN)

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.05 mole) and KX (X=Br or SCN^-) (0.1 mole) were dissolved in 30 ml ethanol. To this 0.1 mole ethanol solution of corresponding ligand (ie, semi and thiosemicarbazone) was added. The mixture was refluxed on water bath for one hour. On cooling, camel to cream coloured complex was separated out. The complex was filtered, washed with ethanol and dried over P_4O_{10} .

$\text{Mn}(\text{ligand})_2\text{SO}_4$

Ethanol solution of 0.05 mole of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.1 mole of corresponding ligand (ie, semi and thiosemicarbazone) was mixed and then the mixture was refluxed on water bath for two hours. On cooling, camel to light pink coloured complex was separated out. The complex was filtered, washed with ethanol and dried over P_4O_{10} .

RESULTS AND DISCUSSION

All the complexes have composition $\text{Mn}(\text{ligand})_2\text{X}_2$ [X= Cl^- , Br, SO_4^{2-} and $(\text{SCN})^-$] show a very good agreement with standard magnetic moment value of complexes having five unpaired spins at room temperature as in Table 1. In the high spin octahedrally coordinated Mn^{2+} complexes, the lowest configuration $(t_{2g})^3 (e_g)^2$ gives rise to the ground state ${}^6\text{A}_{1g}$. Since this is the only sextet level present, all the absorption bands³⁵ must therefore, be spin forbidden transitions.

Electronic spectra of the complexes display weak absorption bands in the range 18200-20400 cm^{-1} , 21060-25100 cm^{-1} , 24870-29860 cm^{-1} , 31300-33350 cm^{-1} which are characteristics of octahedral geometry. These bands may be assigned as ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (4G) ($10B+5C$), ${}^6A_{1g} \rightarrow {}^4E_g$ (4G) ($10B+5C$), ${}^6A_{1g} \rightarrow {}^4E_g$ (4D) ($17B+5C$) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4P) ($7B+7C$) transitions, respectively

(Table 2). The experimentally observed transition energies and calculated values for parameters B,C, Dq and b are shown in Table 3. For the parameter C, the transition ${}^6A_{1g} \rightarrow {}^4E_g$ (4G) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4P), has negative value which has no physical significance, while these transitions yield absurd values for parameter B and hence these values are not included in the table 3. The best set of the value

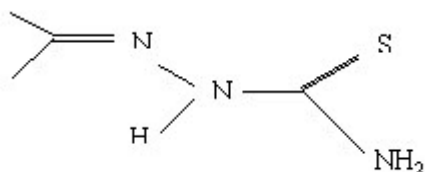


Fig. 1: Thione

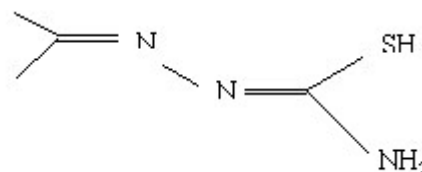


Fig. 2: Thiol

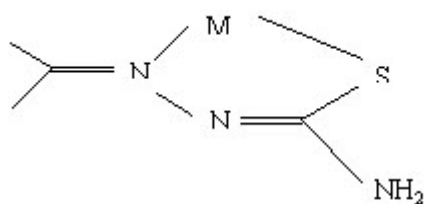


Fig. 3: Five membered chelate ring

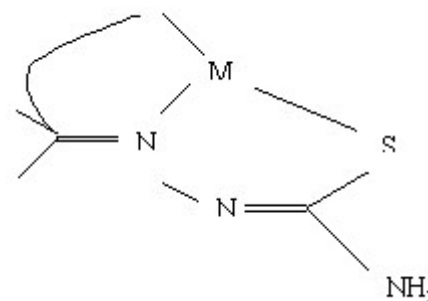


Fig. 4: D,N,S Tricoordination

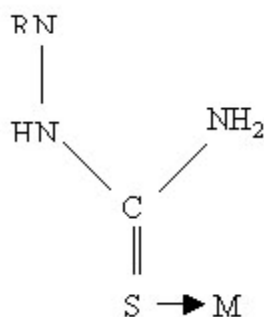


Fig. 1(a)

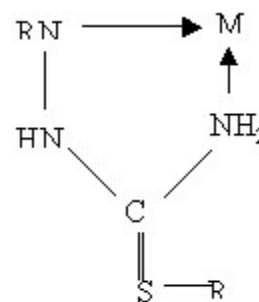


Fig. 1 (b)

Trans configuration of thiosemicarbazide showing monodentate nature (Figure 1a) Bonding through the sulphur atom only. (figure 1b) Bonding through the hydrazinic nitrogen and amide nitrogen.

for parameters B and C could be obtained using transitions ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (4G) and ${}^6A_{1g} \rightarrow {}^4E_g$ (4D). The value of Dq were taken from the work of Orgel³⁶. Slater Condon – Shortly parameters F_2 and F_4 are related to the Racah inter – electronic repulsion parameters B and C, as follows³⁷ $B = F_2 - 5F_4$ and $C = 35F_4$. By using values of the Reach parameter B and C, values for the parameter F_2 and F_4 have been calculated (Table 3).

The calculated values of β and Hx of complexes as in Table 3 shows appreciable ionic character. An estimate of β has been obtained from the nephelauxetic parameter, Hx, for the ligand and nephelauxetic parameter, Km, of the metal ion as $1.2(1 - b) = Hx Km$. The values of parameter (Hx) for the complexes have been calculated using covalency contribution of Manganese (II) ion (0.07). The numerical value 786 cm^{-1} for b of the three Mn^{2+} ion³⁸ has been used to calculate the value for β .

Table 1 : Magnetic moment (B.M.) and ESR data

Complexes	μ_{Effec} (B.M.)	g
Mn (SSC) ₂ Cl ₂	5.87	2.014
Mn (SSC) ₂ Br ₂	6.06	2.122
Mn (SSC) ₂ SO ₄	5.94	2.116
Mn (STSC) ₂ Cl ₂	5.97	2.076
Mn (STSC) ₂ Br ₂	6.04	2.052
Mn (STSC) ₂ SO ₄	5.99	2.021
Mn (STSC) ₂ (SCN) ₂	6.05	2.037

The ESR spectra of the complexes have been recorded as polycrystalline sample as shown in Fig 1.a – 1.b. Polycrystalline sample gives one broad isotropic signal centered around approximately free electron g – value as in Table I. ESR Signal is easily detected over a large range of temperatures in any crystal field symmetry since there is no nearby crystal field state. Further, a resonance is readily detected even for a large zero field splitting, because d^5 is an odd- electron system whose ground state is a Kramer's doublet and whose degeneracy is only completely removed by a magnetic field.

Table: 2 Electronic spectral bands (cm⁻¹) and their tentative assignment

Complexes	${}^6A_{1g \rightarrow 4p}$ ${}^4T_{1g}$	${}^6A_{1g \rightarrow (4D)}$ 4E_g	${}^6A_{1g \rightarrow (4G)}$ 4E_g	${}^6A_{1g(4G) \rightarrow}$ ${}^4A_{1g}$
Mn (SSC) ₂ Cl ₂	33350	25102	21060	19484
Mn (SSC) ₂ Br ₂	32266	29860	25100	20000
Mn (SSC) ₂ SO ₄	33202	28550	25100	18200
Mn (STSC) ₂ Cl ₂	31300	28450	23605	19335
Mn (STSC) ₂ Br ₂	32254	25475	24554	18632
Mn (STSC) ₂ SO ₄	31556	24870	23500	18620
Mn(STSC) ₂ (SCN) ₂	31804	29530	24502	20400

Table 3 : Ligand field parameters

Complex	$D_q(\text{cm}^{-1})$	B(cm ⁻¹)	Hx(cm ⁻¹)	b	F_4	F_2	C
Mn (SSC) ₂ Cl ₂	715	690	3270	0.86	95	1158	2.23
Mn(SSC) ₂ Br ₂	740	725	3150	0.89	96	1033	3.42
Mn (SSC) ₂ SO ₄	760	610	3168	0.79	93	1068	3.64
Mn (STSC) ₂ Cl ₂	687	650	3358	0.82	96	1136	3.06
Mn (STSC) ₂ Br ₂	665	648	3028	0.83	89	1080	3.27
Mn(STSC) ₂ SO ₄	658	629	3227	0.81	92	1089	3.60
Mn(STSC) ₂ (SCN) ₂	734	720	3415	0.92	97	1206	1.54

CONCLUSION

It is concluded that all the complexes were found to have composition $Mn(\text{ligand})_2X_2$ (where $X=Cl^-$, Br^- and $\frac{1}{2} SO_4^{2-}$). They show magnetic moments in the range of 5.93 – 6.03 BM at room temperature. Electronic spectra of the complexes display weak absorption bands in the range 18200 – 20400 cm^{-1} , 21060– 2500 cm^{-1} , 24870 – 29860 cm^{-1} , 31300 – 33350 cm^{-1} , assigning ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (4G)

(10B+5C), ${}^6A_{1g} \rightarrow {}^4E_g$ (4G) (10B+5C), ${}^6A_{1g} \rightarrow {}^4E_g$ (4D) (17B+5C) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4P) (7B+7C) transitions, respectively. A six coordinate octahedral geometry has been assigned for these complexes.

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