

Manganese(II) complexes of some nitrogen-oxygen and nitrogen-sulphur donor ligands

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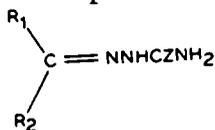
Abstract. Manganese(II) complexes of the general composition, $Mn(L)_2X_2$ ($X = Cl$ or $1/2 SO_4$, $L =$ semicarbazones and thiosemicarbazones of acetone, ethyl methyl ketone and 2-methyl cyclohexanone) have been prepared and characterised by elemental analysis, magnetic moments, conductance measurements, IR, electronic and ESR spectral studies. All the complexes are six-coordinate octahedral.

Keywords. Thiosemicarbazone complexes; manganese(II); six co-ordinate octahedral; donor ligands.

1. Introduction

Manganese(II) in its coordination compounds exhibits marked preference for hard donor atoms such as oxygen and nitrogen. Manganese(II) complexes containing soft donor atoms (*e.g.*, P, As and S) are scanty in number (Pradhan and Raman 1974; Rana *et al* 1975; Chandra *et al* 1980) as compared with those of other transition metals, presumably due to difficulties encountered in preparing and preserving such complexes.

In this paper synthesis and characterisation of manganese(II) complexes of acetone semicarbazone (I_a), acetone thiosemicarbazone (I_b), ethyl methyl ketone semicarbazone (I_c), ethyl methyl ketone thiosemicarbazone (I_d), 2-methyl cyclohexanone semicarbazone (I_e) and 2-methyl cyclohexanone thiosemicarbazone (I_f) have been reported.



(a) $R_1 = R_2 = CH_3$, $Z = O$; (b) $R_1 = R_2 = CH_3$, $Z = S$; (c) $R_1 = C_2H_5$, $R_2 = CH_3$, $Z = O$; (d) $R_1 = C_2H_5$, $R_2 = CH_3$, $Z = S$; (e) $R_1 = R_2 =$ , $Z = O$; (f) $R_1 = R_2 =$ , $Z = S$.

2. Experimental

All the chemicals used were of AnalaR Grade.

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2.1. Preparation of ligands

The semicarbazones were prepared by coupling (Orgal 1955) semicarbazide hydrochloride (1 mol) with the corresponding ketone (1 mol) in the presence of sodium acetate (1 mol). On stirring white semicarbazones crystallised in each case. The same were filtered, washed with 50% ethanol and dried in an electric oven at $\sim 60^\circ\text{C}$.

Thiosemicarbazones were prepared by refluxing thiosemicarbazide (1 mol) with the corresponding ketone (1 mol) in the presence of 2 ml acetic acid. On cooling white thiosemicarbazones crystallized in each case. Thiosemicarbazones were worked out.

2.2 Preparation of complexes

Hot aquo-ethanolic solution of the respective metal salts were mixed with hot ethanolic solution of the respective ligand in a 1 : 2 molar ratio. The contents were refluxed on water bath for 2 hr. On cooling, white to yellow complex separated in each case. The same was filtered, washed with alcohol and dried over P_4O_{10} (in vacuum desiccator).

2.3. Physical measurements

Magnetic moments were carried out on Gouy balance using $\text{Hg} [\text{Co}(\text{CNS})_4]$ as a calibrating agent. Electronic spectra were recorded on DMR-21 automatic recording spectrophotometer. IR spectra were recorded on Perkin-Elmer 621 automatic recording spectrophotometer in KBr medium. ESR spectra were recorded on varian E_4 EPR spectrometer operating at ~ 9.4 GHz, and 100 kHz field modulation and phase sensitive detection.

Carbon and hydrogen were microanalysed. The nitrogen contents were determined by Kjeldahl's method. For estimation of manganese, a known amount of the complex was decomposed by repeated treatment with concentrated HNO_3 . The residue was extracted with dil HCl and precipitated with diammonium hydrogen phosphate and weighed as $\text{Mn}_2\text{P}_2\text{O}_7$.

3. Results and discussion

Elemental analysis revealed that the complexes were of general composition, $\text{Mn}(\text{L})_2\text{X}_2$ ($\text{X} = \text{Cl}$ or $\frac{1}{2} \text{SO}_4$).

Magnetic moments of these complexes were in the range 5.8 – 6 B.M., corresponding to five unpaired spins (Figgis and Lewis 1964) (table 1). Molar conductivity of the complexes in acetone showed that the complexes were non-electrolytes, suggesting that the anions coordinate to manganese. In aqueous solution the conductivity was in the range $150\text{--}160 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, indicating that the complexes were 1 : 2 electrolytes (Gerzy 1971). This may be due to the formation of $[\text{Mn}(\text{ligand})_2(\text{H}_2\text{O})]_2^{2+}$ species in water.

Table 1. Colour and composition of manganese(II) complexes.

Complex	Colour	% Mn	% C	% H	% N	g-value	μ_{eff} (B.M.)
Mn(acsc) ₂ .Cl ₂	White	15.58 (15.45)	26.82 (26.90)	2.41 (2.51)	23.68 (23.59)	2.003	5.87
Mn(acsc) ₂ .SO ₄	White	14.52 (14.43)	26.13 (26.12)	2.48 (2.36)	22.06 (21.92)	2.002	5.86
Mn(emsc) ₂ .Cl ₂	White	14.35 (14.32)	31.38 (31.25)	2.88 (2.86)	21.92 (21.85)	1.993	5.94
Mn(emsc) ₂ .SO ₄	White	13.48 (13.50)	29.38 (29.34)	2.62 (2.70)	20.58 (20.54)	1.996	5.98
Mn(mchsc) ₂ .Cl ₂	White	11.70 (11.85)	41.35 (41.36)	6.50 (6.46)	17.90 (18.10)	1.995	5.99
Mn(mchsc) ₂ .SO ₄	White	11.34 (11.25)	39.38 (39.26)	6.25 (6.13)	17.28 (17.18)	1.996	5.86
Mn(actsc) ₂ .Cl ₂	White	14.18 (14.17)	24.78 (24.74)	2.32 (2.32)	21.68 (21.65)	1.995	5.86
Mn(actsc) ₂ .SO ₄	White	13.34 (13.32)	23.28 (23.24)	2.20 (2.18)	20.34 (20.38)	2.004	5.95
Mn(emtsc) ₂ .Cl ₂	Light Yellow	13.25 (13.22)	28.04 (28.84)	2.68 (2.64)	20.29 (20.19)	1.993	5.98
Mn(emtsc) ₂ .SO ₄	Light Yellow	12.45 (12.47)	27.30 (27.21)	2.52 (2.49)	19.06 (19.05)	1.997	6.01
Mn(mchtsc) ₂ .Cl ₂	Light Yellow	11.92 (11.89)	41.40 (41.38)	6.48 (6.45)	18.15 (18.10)	2.018	6.01
Mn(mchtsc) ₂ .SO ₄	Light Yellow	11.09 (11.08)	38.78 (38.71)	6.03 (6.09)	16.95 (16.93)	1.998	6.03

acsc = Acetone semicarbazone ; actsc = Acetone thiosemicarbazone ; emsc = Ethyl methyl ketone semicarbazone ; emtsc = Ethyl methyl ketone thiosemicarbazone ; mchsc = 2-Methyl cyclohexanone semicarbazone ; mchtsc = 2-Methyl cyclohexanone thiosemicarbazone.

d-d transitions in octahedral manganese(II) complexes were of extremely low intensity because of their doubly forbidden nature.

The complexes exhibited four weak intensity absorption bands in the range 31100-32500, 29200-29500, 24300-24800 and 20300-20800 cm^{-1} . These bands may be assigned (Heidt 1958) as ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$ ($10B + 5C$), ${}^6A_{1g} \rightarrow {}^4A_g, {}^4A_{1g} ({}^4G)$ ($10B + 5C$), ${}^6A_{1g} \rightarrow {}^4E_g ({}^4D)$ ($17B + 5C$) and ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4P)$ transitions respectively. The values of *B* and *C* were calculated using the transitions, ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g} ({}^4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g ({}^4D)$, this is due to the fact that the energies of these two transitions are independent of crystal field splitting energy and depend (Prete and Tosi 1976) only on the parameters *B* and *C*.

The values of B and C were in the range of 643-743 cm^{-1} and 4394-4518 cm^{-1} respectively. The value for the parameter D_q (623-801 cm^{-1}) could be evaluated with the help of curve transition energies $\nu_s D_q$ given by Orgal using energy level due to transition, ${}^6A_{1g} \rightarrow {}^4T_{1g}$. The value of the D_q parameter could not be obtained using transitions ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}({}^4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$, because these transitions are independent of D_q with almost zero slope. The values of D_q were in the range of 623-801 cm^{-1} .

The electron-electron repulsion in complexes is less than in the free ion, resulting in an increased distance between electrons and thus an effective increase in size of the orbitals. On increasing delocalisation β value decreases and is less than one in complexes. The β value has been calculated using B complexes/ B free ion (where the B value for free ion is 786 cm^{-1}).

ESR spectra of the complexes have been recorded as polycrystalline samples and in aqueous solution ESR spectra are isotropic and show one broad signal in each case. g -values have been calculated and presented in table 1. In polycrystalline samples manganese(II) complexes usually give broad signals (McGarvey 1966; Reed and Cohn 1970) attributed to forbidden transitions where $\Delta m_s = 1$ and $\Delta m_l \neq 0$.

In aqueous solutions all the complexes exhibit ESR spectra containing six lines due to hyperfine interaction between the unpaired electron with ${}^{55}\text{Mn}(I = 5/2)$. The nuclear magnetic quantum number, m_l , corresponding to these lines are $-5/2, -3/2, -1/2, +1/2, +3/2$ and $+5/2$ from low to high field.

All the complexes exhibit similar ESR spectra in aqueous solution. It is likely that in aqueous solution the complex exists as a common complex ion, $[\text{Mn}(\text{ligand})_2 \text{aq}]^{2+}$. This is confirmed by conductometric measurements in aqueous solution. The line width attributed to transition $+1/2 \leftrightarrow -1/2$ is only slightly higher (~ 115 G) than that of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (93 G).

3.1 Infrared spectra

The important IR bands and their tentative assignments are given in tables 2 and 3. Only the bands due to the $\nu_{(\text{C}=\text{O})}$, $\nu_{(\text{C}=\text{S})}$ and $\nu_{(\text{C}=\text{N})}$ have been discussed.

3.2 Semicarbazones and $\text{Mn}(\text{semicarbazones})_2\text{X}_2$

As expected, the $\delta_{(\text{NH}_2)}$ of the hydrazinic nitrogen of semicarbazide (1622 cm^{-1}) is absent in the IR spectra of semicarbazones (Levanon 1968). It has also been observed that the amide-II band is shifted towards the lower side than that of semicarbazide. The effect is due to the electron density drift from hydrazinic nitrogen (Campbell and Grazeskowiak 1968).

The characteristic absorption of the carbonyl group in semicarbazones is observed (Dyer 1974) at 1690-1700 cm^{-1} . In the complexes this band is shifted towards the lower side by ~ 45 cm^{-1} . This amide II band in semicarbazones has been observed at 1556-1588 cm^{-1} . In the complexes this band is also shifted towards lower wave number by ~ 30 cm^{-1} . These observations sug-

Table 2. Selected IR bands (cm^{-1}) of semicarbazones and its complexes.

Compound	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{C}=\text{O}}$		
		I	II	III
acsc	1650(s)	1690(s)	1556(m)	1350(m)
Mn(acsc) ₂ Cl ₂	1675(s)	1650(s)	1525(m)	1230(m)
Mn(acsc) ₂ SO ₄	1670(s)	1640(s)	1530(m)	1340(m)
emsc	1667(s)	1695(s)	1588(m)	1355(m)
Mn(emsc) ₂ Cl ₂	1680(s)	1660(s)	1550(m)	1245(m)
Mn(emsc) ₂ SO ₄	1685(s)	1655(s)	1550(m)	1390
mchsc	1680(s)	1700(s)	1584(m)	1352(m)
Mn(mchsc) ₂ Cl ₂	1695(s)	1660(s)	1550(m)	1245(m)
Mn(mchsc) ₂ SO ₄	1695(s)	1665(s)	1560(m)	1350(m)

Table 3. Selected Infrared bands (cm^{-1}) of thiosemicarbazones and complexes.

Compound	δ_{NH_2} and Amide II band	mainly $\nu_{\text{C}=\text{N}}$	mainly $\nu_{\text{C}=\text{S}}$ N-C-N	mainly $\nu_{\text{C}=\text{S}}$
Mn(actsc) ₂ Cl ₂	1635(vs)	1560(s)	1150(m)	760
Mn(actsc) ₂ SO ₄	1630(vs)	1565(s)	1140(m)	765
emtsc	1604(vs)	1515(s)	1095(m)	795(s)
Mn(emtsc) ₂ Cl ₂	1635(vs)	1565(s)	1150(m)	760(s)
Mn(emtsc) ₂ SO ₄	1640(vs)	1565(s)	1160(m)	755(s)
mchsc	1600(vs)	1510(s)	1090(m)	830(m)
Mn(mchtsc) ₂ Cl ₂	1630(vs)	1565(s)	1160(m)	790(s)
Mn(mchtsc) ₂ SO ₄	1630(vs)	1565(s)	1155(m)	795(s)

vs = very sharp; s = sharp; m = medium

gest coordination through the $\nu_{\text{C}=\text{O}}$ oxygen. The strong band at 1650-1600 cm^{-1} in semicarbazones apparently has large contribution from $\nu_{(\text{C}=\text{N})}$ (Sterk and Ziegler 1966). Coordination through 'O' increases double bond character of the $\nu_{(\text{C}=\text{N})}$ band. This has been observed as a blue shift in the position of $\nu_{(\text{C}=\text{N})}$ band in all complexes as compared to the ligand.

3.3 Thiosemicarbazones and Mn(thiosemicarbazones)₂X₂

Formation of thiosemicarbazones from thiosemicarbazide involves substitution (Wiles and Suprunchuk 1969) of the electron withdrawing group (ketone) in place of two hydrogen atoms of the hydrazinic nitrogen. In addition, the amide II band (1617 cm^{-1}) is red shifted to 1600 cm^{-1} due to the shift in the electron density. However, on complex formation the position of this

band is shifted towards higher wave numbers. Such a shift to higher wave numbers is probably due to increase in the multiplicity of the C – N bond with the resulting stronger N – H in the amide group.

A band in the range 830-790 cm^{-1} in thiosemicarbazones is mainly due to the $\nu_{\text{C}=\text{S}}$ stretching frequency (Wiles *et al* 1967; Mashima 1964; Yamagushi *et al* 1958). This band is shifted towards the lower side $\sim 30 \text{ cm}^{-1}$ in the spectra of the complexes. A strong band at 1090 cm^{-1} has been observed in the IR spectra of thiosemicarbazones. This band has a contribution from the N – C – N stretching vibration (Burns 1968) or N – N stretching and N – C – N deformation vibrations. The band has also shifted to higher positions in the complexes, as also observed in the spectra of $\text{Ni}(\text{actsc})_2\text{X}_2$. The strong $\nu_{\text{C}-\text{N}}$ band in thiosemicarbazones has been observed at 1510-1520 cm^{-1} , which is shifted towards higher wave number of about 50 – 60 cm^{-1} as observed in $\text{Ni}(\text{actsc})_2\text{X}_2$ (Campbell *et al* 1976) complexes.

The above discussion suggests that semicarbazones and thiosemicarbazones behave as bidentate ligands, coordinating through O/S and hydrazinic nitrogen.

3.4 Bands due to anion

IR spectra of sulphate complexes show bands at 1195 (ν_3), 1110 (ν_3), 1030 (ν_3) and 960 (cm^{-1}) (ν_1) indicating that sulphate group acts as bridging bidentate ligand (Eskenzari *et al* 1966).

4. Conclusion

It has been observed that all the three ligands act as bidentate coordinating to the central metal ion through nitrogen of $\nu_{\text{C}=\text{N}}$ and O/S. All the complexes are paramagnetic and six-coordinate octahedral.

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