

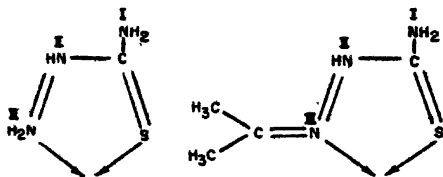
# Complexes of Zinc(II) and Manganese(II) with Thiosemicarbazide and Thiosemicarbazones

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A series of complexes of the type  $[MLX_2]$ ;  $[ML_2X_2]$  and  $[ML_2] \times n$ , ( $X = Cl^-$  or  $Br^-$ ,  $X' = ClO_4^-$ ) of Zinc(II) and Manganese(II) with thiosemicarbazide or thiosemicarbazones of acetone or benzaldehyde (L) were prepared. These compounds were characterised and possible stereochemistry was deduced on the basis of analytical data, infrared spectra, conductivity and room temperature magnetic susceptibility measurements. The compounds were found to exhibit coordination number four or six with tetrahedral or octahedral configurations, respectively.

THE thiosemicarbazide and thiosemicarbazones have attracted special attention due to their activity against viruses, protozoa small pox and certain kinds of tumour<sup>1-3</sup>, since Domagk's original discovery<sup>4</sup> of their antitubercular activity. It is known that some drugs have increased activity when administered as metal complexes<sup>5,6</sup> and a number of metal chelates inhibit tumour growth<sup>7</sup>. In cancer treatment it has been shown that the active species is not the thiosemicarbazone itself but a metal chelate of the thiosemicarbazone<sup>8,9</sup>. After Mashima's work<sup>10</sup> coordination chemists also took interest in thiosemicarbazide and thiosemicarbazone as potential ligands. The fact that coordination occurs through the terminal hydrazine nitrogen ( $N^{III}$ ) atom and sulphur of the thiocarbonyl group in these ligands has been established by infrared measurements and X-ray structure determinations<sup>11-15</sup>.



Thiosemicarbazide

Acetonethiosemicarbazone

Further, it is becoming increasingly clear that zinc plays a vital role in biological processes. Zinc deficiency can cause unusual disorder in the development of the body,

disorder in metabolic system and prostrate gland and can result in mental retardation. Hence, it is thought worthwhile to study the complexation with divalent zinc. In the present work, we now report the preparation and characterization of some Zinc(II) and Manganese(II) complexes with thiosemicarbazide (Tsc) and thiosemicarbazones of acetone (Actsc) and benzaldehyde (Bztsc).

## Experimental

The chemicals used were all of AR grade. The thiosemicarbazones were prepared as per known method<sup>16</sup>. Zinc and manganese were estimated by standard methods<sup>16</sup>. Halogens and sulphur were estimated gravimetrically as Silver halide and Barium sulphate respectively. Perchlorate was estimated after reduction as Silver Chloride. Infrared spectra in the range 4,000-650  $cm^{-1}$  were recorded on nujol mulls using unicam SP-200 double beam spectrophotometer. The magnetic susceptibilities were measured with a Guoy balance and calculations were made computing Pascal's constants for diamagnetic corrections<sup>17</sup>. The molar conductance measurements were made on nitromethane solutions ( $\sim 10^{-3}M$ ) using Toshniwal conductivity bridge. The analytical, molar conductance and magnetic susceptibility data of the complexes are given in Table 1. The principal infrared absorption bands of the ligands and the complexes are returned in Table 2. The assignments are based on earlier work on thiosemicarbazide<sup>10</sup> and some copper(II) complexes<sup>26</sup>.

TABLE 1—ANALYSES, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF ZINC (II) AND MANGANESE (II) COMPLEXES

Complex	Colour	M. P. (°C)	% Metal Found/Calc.	% Halogen Found/Calc.	% sulphur Found/Calc.	$\Lambda_m$ (mhos)	$\mu_{eff}$ (B. M)
1. $[Zn(Tsc)_2](ClO_4)_2$	White	192	11.04/11.13	11.98/12.07	16.50/16.39	204	diamag
2. $[Mn(Tsc)_2](ClO_4)_2$	White	140	9.60/9.51	12.13/12.28	16.81/16.66	224	5.90
3. $[Zn(Tsc)_2Cl_2]$	White	145	20.82/20.52	22.60/22.26	20.10/20.14	4.4	diamag
4. $[Zn(Tsc)_2Br_2]$	Pale yellow	148	16.14/16.04	39.00/39.22	15.90/15.74	4.1	diamag
5. $[Mn(Tsc)_2Cl_2]$	Light pink	178	17.83/17.83	22.96/23.01	20.60/20.82	3.8	6.20
6. $[Mn(Tsc)_2Br_2]$	Pale yellow	180	13.90/13.84	40.40/40.25	16.00/16.15	4.4	6.02
7. $[Zn(Actsc)Cl_2]$	White	242	24.30/24.44	26.60/26.50	12.00/11.99	4.0	diamag
8. $[Zn(Bztsc)_2Cl_2]$	White	182	13.35/13.21	14.00/14.33	13.00/12.96	4.4	diamag
9. $[Mn(Actsc)_2Cl_2]$	White	155	14.00/14.16	18.00/18.26	16.20/16.52	6.4	5.90
10. $[Mn(Bztsc)Cl_2]$	White	165	11.33/11.34	14.60/14.63	13.20/13.23	3.8	6.07

TABLE 2—INFRARED SPECTRA (CM<sup>-1</sup>) OF ZINC(II) AND MANGANESE(II) COMPLEXES.

Compound	$\delta(\text{NH}_2)$ and Amide band		$\nu(\text{CN})$ and $\delta(\text{NH}_2)$	$\nu(\text{C}=\text{S})$
Tsc	1643 (VS)	1617 (VS)	1532 (S)	805 (S)
Actsc	1640 (VW)	1592 (VS)	1515 (VS)	792 (S)
Bztsc	1640 (VW)	1586 (VS)	1520 (S)	760 (S)
[Zn (Tsc) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1640 (VS)	1588 (S)	1575 (S)	720 (S)
[Mn (Tsc) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1635 (B)	1590 (S)	1560 (S)	705 (S)
[Zn (Tsc) <sub>2</sub> Cl <sub>2</sub> ]	1628 (VS)	1603 (VS)	1560 (S)	720 (S)
[Zn (Tsc) <sub>2</sub> Br <sub>2</sub> ]	1633 (VW)	1613 (VS)	1540 (S)	725 (S)
[Mn (Tsc) <sub>2</sub> Cl <sub>2</sub> ]	1633 (VW)	1613 (VS)	1555 (S)	705 (S)
[Mn (Tsc) <sub>2</sub> Br <sub>2</sub> ]	1640 (S)	1608 (VS)	1555 (S)	715 (S)
[Zn (Actsc)Cl <sub>2</sub> ]	—	1603 (VS)	1550 (S)	720 (S)
[Zn (Bztsc) <sub>2</sub> Cl <sub>2</sub> ]	—	1588 (VS)	1555 (S)	720 (S)
[Mn (Actsc) <sub>2</sub> Cl <sub>2</sub> ]	—	1588 (VS)	1550 (S)	725 (S)
[Mn (Bztsc) <sub>2</sub> Cl <sub>2</sub> ]	—	1588 (VS)	1545 (S)	715 (S)

S = Sharp, VS = Very sharp, B = Broad, VW = very weak.

### Preparation of complexes :

1.  $[\text{ML}_2] X'_2$  complexes : The complexes were prepared by reacting alcoholic solutions of metal perchlorate and thiosemicarbazide ( in presence of a few drops of acetic acid) in 1 : 3 molar ratio and refluxing for two hours. On cooling, white crystalline compounds were obtained in both the cases of Zinc and Manganese. The compounds were filtered, washed with absolute alcohol followed by ether and dried *in vacuo*.

### 2. $[\text{ML}_2\text{X}_2]$ and $[\text{MLX}_2]$ complexes :

**Thiosemicarbazide complexes :** Alcoholic solutions of metal halides and thiosemicarbazide solution in hot absolute alcohol (in presence of a few drops of acetic acid) in : 2 molar ratios were refluxed for two hours and cooled. In some cases, the compounds were obtained only after keeping overnight. The compounds were filtered, washed with alcohol followed by ether and dried *in vacuo*. The same compounds were obtained even when the metal halides and thiosemicarbazide were reacted in 1 : 3 molar ratio.

**Thiosemicarbazone complexes :** Alcoholic solution of metal chloride was refluxed with alcoholic solution of thiosemicarbazone (acetone or benzaldehyde) in 1 : 2 molar ratio for two hours. No compound was obtained even on keeping overnight. The volume was reduced to half by suction and cooled, when solid compounds having the composition  $[\text{ML}_2\text{Cl}_2]$  separated out. They were filtered, washed with alcohol followed by ether and dried *in vacuo*.

The compound  $[\text{Zn}(\text{Actsc})\text{Cl}_2]$  was obtained when  $[\text{ZnCl}_2]$  and acetone thiosemicarbazone solutions in absolute alcohol in 1 : 1 molar ratio were refluxed for half an hour. The composition of the separated compounds remains the same even though the metal chloride and ligand are taken in 1 : 2 molar ratio. The white microcrystalline compounds separated even while refluxing.

### Results and Discussion

Earlier, Jensen<sup>1,8-20</sup> reported some complexes of thiosemicarbazide with transition metal ions. Ablov and

Gerbeleu<sup>21</sup> have reported complexes of acetone, cyclohexanone and benzaldehyde thiosemicarbazones of Zinc(II). In these early works, metal complexes were prepared and analysed, but no information regarding their structures was obtained due to lack of spectroscopic and magnetic measurements. Wiles and Suprunchuk's work on infrared spectra of thiosemicarbazide<sup>22</sup> attracted the attention of many to use thiosemicarbazide and thiosemicarbazones as bidentate heteroligands. Few of them have already been tried for medical use and found that there is a significant correlation between antitumour activity of a group of heterocyclic aldehyde thiosemicarbazones in animal system and their metal chelating properties<sup>23-25</sup>.

The compounds now reported belong to three types, viz ;  $\text{MLX}_2$ ,  $\text{ML}_2\text{X}_2$  and  $\text{ML}_2\text{X}'_2$  where M = Zinc (II) or Manganese (II), L = thiosemicarbazide or acetone/benzaldehyde thiosemicarbazone, X = chloride or bromide and X' = perchlorate. The low values of molar conductance in nitromethane for  $\text{MLX}_2$  and  $\text{ML}_2\text{X}_2$  indicate that they are nonionic.  $\Delta m$  values for  $\text{Zn}(\text{Tsc})_2(\text{ClO}_4)_2$  and  $\text{Mn}(\text{Tsc})_2(\text{ClO}_4)_2$  are 204 and 224, respectively, indicating that they are 1 : 2 electrolytes. The ionic nature of the perchlorate group has also been established by infrared spectra. The magnetic moment values of manganese complexes at room temperature are found to be in the range 5.9-6.2 B.M. (Table-1) revealing the presence of 5 unpaired electrons. This shows that they are spinfree Manganese (II) complexes.

**Infrared Spectra :** In view of the work of Campbell and Grzeskowiak<sup>26</sup>, only the bands due to the C=S and C-N stretching frequencies are now considered. The sharp band at 805 cm<sup>-1</sup> in free Tsc is mainly due to the C=S stretching frequency with some contribution from either  $\delta(\text{NH}_2)$  or NCN stretching<sup>27,28</sup>. This band is shifted by as much as 80-100 cm<sup>-1</sup> (see table-2) on complex formation, indicating thereby the sulphur coordination to the metal atom.

In thiosemicarbazide, bands at 1643 cm<sup>-1</sup> and 1617 cm<sup>-1</sup> are assigned, respectively<sup>26,29</sup>, as the deformation bands of NH<sub>2</sub> group in hydrazine residue and the

amide II band of the primary amine. These bands were found to move to lower frequencies in all the Tsc complexes. In thiosemicarbazones, the former band disappears and the shift to lower frequency of the latter one is claimed<sup>22</sup> to be due to the electron withdrawing nature of the group resulting from carbonyl addition and is observed by C=N and other absorption bands. On complex formation, this band is observed in the range 1586-1603  $\text{cm}^{-1}$  as observed by earlier workers.

The 1532  $\text{cm}^{-1}$  band assigned as mainly  $\nu(\text{C-N}) + \delta(\text{NH}_2)$  in thiosemicarbazide is shifted to lower frequencies in thiosemicarbazones, probably due to the loss of some  $\delta(\text{NH}_2)$  contribution. On complex formation, this band was found to be shifted to higher frequencies in all the cases. This observation is similar to that of Beecroft and others<sup>15</sup>.

A broad band was observed in case of all perchlorate complexes at 1090  $\text{cm}^{-1}$  (not shown in the table) indicating that the perchlorate groups are ionic<sup>27</sup>.

The observations thus indicate that all the complexes now reported are octahedral formed by utilising  $4s 4p^3 4d^3$  bonding orbitals excepting the compound  $[\text{Zn}(\text{Actsc})\text{Cl}_2]$  which is obviously a tetrahedral complex involving the use of  $4s 4p^3$  hybrid orbitals.

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