

## Magnetic and spectral characterization of new type of 4-methylpiperazine-1-carbodithioate complexes of manganese(II) and manganese(III)

Shashi B Kalia<sup>1</sup>, Geetanjali Kaushal<sup>2</sup>, Rajesh<sup>1</sup>, Monika Bharti<sup>1</sup>

<sup>1</sup>Department of Chemistry, Himachal Pradesh University, Shimla HP India

<sup>2</sup>Department of Chemistry, Lyallpur Khalsa College, Jalandhar Pb. India

**Abstract:** Two manganese(II) carbodithioates, i.e.  $[Mn(4-MPipzcdtH)_2](X)_2$  and two manganese(III) carbodithioates of the type  $[Mn_2(4-MPipzcdtH)_6(O_2)_2](X)_4$  (4-MPipzcdtH = 4-methylpiperazine-1-carbodithioic acid and X = ClO<sub>4</sub>, Cl) have been prepared. These have been characterized by elemental analyses, conductance, infrared and electronic absorption spectral and room temperature as well as variable temperature magnetic susceptibility measurements. Manganese(II) complexes exhibit antiferromagnetic behavior. Antiferromagnetic interactions through superoxo bridge have been proposed for temperature dependent magnetic behaviour of manganese(III) complexes.

**Keywords:** 4-methylpiperazine-1-carbodithioic acid; spectral; magnetic susceptibility measurements; manganese(II) and manganese(III).

### I. Introduction

Metal dithiocarbamates constitute a group of compounds with wide range of interesting and useful redox, magnetic, electrical and catalytic properties. Dithiocarbamates are known (1) to stabilize higher oxidation state of transition metals. It has been reported that in particular, when dithiocarbamate reacts with manganese(II), a light yellow bis(dithiocarbamate) manganese(II) complex is first formed. It is extremely air sensitive and is almost instantaneously oxidized (2) to dark violet tris(dithiocarbamate)manganese(III). The ongoing interest in coordination chemistry of 4-methylpiperazine-1-carbodithioic acid ligand is primarily because piperazine and its salts possess properties of potential antihelminthics, antirheumatic and antihistamine activity. (3) The present study reports the derivatisation of saturated heterocyclic secondary amine 1-methylpiperazine into its Zwitterionic carbodithioate ligand, i.e. 4-methylpiperazine-1-carbodithioic acid (4-MPipzcdtH). Manganese in its both +2 and +3 oxidation states has been stabilized under suitable conditions with 4-MPipzcdtH as ligand and perchlorate and chloride as counter anions. The acid ligand may become weak in strength due to its Zwitterionic nature and hence possesses a lower tendency of oxidizing the metal ion in the ordinary reaction conditions. However, to prevent oxidation even of trace amounts, the synthesis of manganese(II) complexes had to be done under rigorous oxygen-free conditions. In the absence of these conditions, the products undergo oxidation and mixed manganese(II) and (III) species are obtained.

### II. Experimental

All the chemicals used were of analytical reagent grade and used as such. The ligand 4-MPipzcdtH was prepared by the method as reported earlier. (4)

#### Preparation of the complexes

$[Mn(4-MPipzcdtH)_2]X_2$  (X = ClO<sub>4</sub>, Cl)

Slightly more than stoichiometric amount of solid 4-methylpiperazine-1-carbodithioic acid (0.100g; 0.568 mmol) was added with stirring in small portions (~10 mg) after successive intervals of 10 minutes in a total period of about one and a half hour to a degassed methanolic solution of 0.276 mmol of MnX<sub>2</sub>.xH<sub>2</sub>O (x = 6 when X = ClO<sub>4</sub> and x = 4 when X = Cl) kept at 35 °C. Dry nitrogen gas was passed continuously throughout the course of the reaction. Dark yellow coloured soluble complexes are obtained in the solution state as the solid carbodithioic acid dissolved. The solution of the complex was filtered quickly so as to remove any excess of the unreacted acid. Yellow crystalline samples of the complexes were obtained on evaporating the solvent by keeping the filtered solution under nitrogen in a P<sub>4</sub>O<sub>10</sub> desiccator. The whole reaction process and handling of samples for all physical measurements were carried out in a degassed dry bag kept dried overnight with P<sub>4</sub>O<sub>10</sub>.

$[Mn_2(4-MPipzcdtH)_6(O_2)_2](X)_4$  (X = ClO<sub>4</sub>, Cl)

To a methanolic solution of 0.184 mmol of MnX<sub>2</sub>.xH<sub>2</sub>O (X = ClO<sub>4</sub> when x = 6 and X = Cl when x = 4) kept at 35 °C was added with stirring slightly more than stoichiometric amount of solid 4-methylpiperazine-1-

carbodithioic acid (0.100g; 0.568 mmol) in small portions (~10 mg) after successive intervals of 10 minutes in a total period of about one and a half hour. For oxidation of Mn(II) to Mn(III) air was continuously bubbled during the course of the reaction. The dark purple coloured soluble complexes are obtained in the solution state as the solid carbodithioic acid dissolved. The solution of the complex was filtered so as to remove any excess of unreacted acid. The solid complex was obtained on evaporating the solvent by keeping the filtered solution in a P<sub>4</sub>O<sub>10</sub> desiccator.

NOTE: Both in solid and solution state, the complexes are highly sensitive to moisture so all the reactions were carried out in the tightly stoppered conical flask. Otherwise, disproportionation or hydrolysis resulting in variable yellow coloured solutions of unknown stoichiometries are obtained. Also handling of the complexes for various physical measurements was done in a dry bag kept dried overnight with P<sub>4</sub>O<sub>10</sub>.

### Elemental analyses

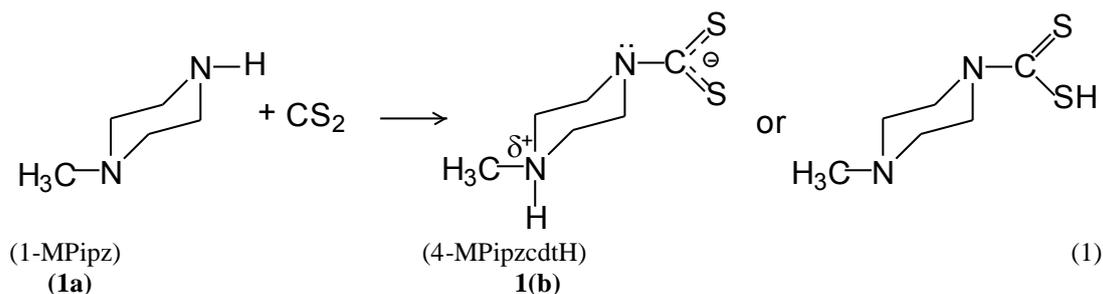
Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyzer, while nitrogen was determined by Kjeldahl's method. Manganese in the complexes was determined by EDTA titrations using Eriochrome Black T as an indicator. Chloride content was estimated volumetrically by mercuric nitrate titration using diphenylcarbazone indicator while sulfur was determined gravimetrically as barium sulfate.

### Physical measurements

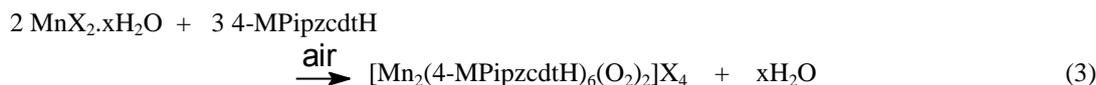
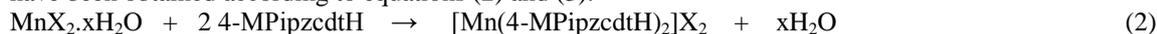
Infrared spectra of Zwitterionic complexes were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4000-600 cm<sup>-1</sup> region. Infrared spectra of all the complexes were recorded as nujol mull with cesium chloride plates as windows in the 600-200 cm<sup>-1</sup> region. DMSO solution electronic absorption spectra of the complexes, with the solvent as the reference, in quartz glass cells were recorded on Cary 100 Bio UV-Visible recording Spectrophotometer (range 200-900 nm) and Analytikjena Specord 200 UV-Visible recording Spectrophotometer (range 200-1100 nm). Molar conductances (10<sup>-3</sup> M solutions in methanol) were obtained at 25 ± 0.1 °C using a type Elico Conductivity Bridge CM-82T. The cell constant of the conductivity cell was 0.4530 cm<sup>-1</sup>. Room temperature magnetic susceptibility measurements for the complexes were made on finally powdered samples using Gouy method. These measurements were also made on a Vibrating Sample Magnetometer PAR-155 with variable temperature cryostat (model-152).

## III. Results and discussion

Synthesis of the ligand (4-MPipzcdtH) follows the reaction (Equation 1)



Zwitterionic complexes of 4-MPipzcdtH with MnX<sub>2</sub>.xH<sub>2</sub>O (X = ClO<sub>4</sub>, Cl) reported in the present investigation have been obtained according to equations (2) and (3).



(X = ClO<sub>4</sub> when x = 6 and X = Cl when x = 4)

The manganese(II) complexes being highly air sensitive, required careful handling and their synthesis was carried out in a dry bag dried with P<sub>4</sub>O<sub>10</sub>.

These are stable in their solid state for long periods, though it is still advisable to store them under vacuum in a P<sub>4</sub>O<sub>10</sub> desiccator. They have, however, the tendency to be oxidized in the course of the reaction used for their synthesis, i.e. in solution state. The synthesis of two manganese(III) 4-methylpiperazine-1-carbodithioic acid complexes with chloride and perchlorate as counter anions was tried by the air oxidation method (Equation 3). But the resulting manganese(III) carbodithioates are found to have different chemical

formulae and quite different physical characteristics (Table 1). Manganese(II) complexes are soluble in methanol and DMSO. The complexes do not melt but decompose between 184-200 °C. The molar conductance values of methanolic solution of the complexes  $[\text{Mn}(4\text{-MPipzcdtH})_2](\text{X})_2$  ( $\text{X} = \text{ClO}_4, \text{Cl}$ ) having bivalent metal ions lie in the range  $162\text{-}132 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  corresponding to 1:2 electrolytic behaviour. (4)

### Infrared spectral studies

The ligand (4-MPipzcdtH) exists as a Zwitterion is evident from the fact that in the IR spectra of solid 4-MPipzcdtH and its metal complexes, new broad band as compared to the free heterocyclic amine, 1-MPipz, around  $3600\text{-}3200 \text{ cm}^{-1}$  for the acid and  $3650\text{-}3200 \text{ cm}^{-1}$  (Table 2) for the complexes assignable to  $\nu(\text{N-H})$  was observed (1b). The occurrence of this band at higher wave number than the usual values of  $3400\text{-}3200 \text{ cm}^{-1}$  indicates that in the present case the interaction of the lone electron pair on nitrogen with positively charged hydrogen probably is stronger than the normal nitrogen-hydrogen interaction as shown in structure 1(b).

The carbon-nitrogen bond of  $>\text{NCS}_2$  group in the Zwitterionic manganese(II) and manganese(III) carbodithioates has been found to absorb in the range  $1474\text{-}1461 \text{ cm}^{-1}$  as compared to that for free ligand ( $1442 \text{ cm}^{-1}$ ). (4) This range is intermediate between a  $\nu(\text{C=N})$  band ( $1690\text{-}1640 \text{ cm}^{-1}$ ) and  $\nu(\text{C-N})$  band ( $1360\text{-}1250 \text{ cm}^{-1}$ ), indicating a partial double bond character between carbon and nitrogen. (4) Observation of the two bands in the region  $998\text{-}972 \text{ cm}^{-1}$  (separated by less than  $20 \text{ cm}^{-1}$ ) for  $\nu_a(\text{SCS})$  vibration and one band for the  $\nu_s(\text{SCS})$  stretch in the region  $687\text{-}642 \text{ cm}^{-1}$  in the complexes suggest the unsymmetrical chelating bidentate mode of coordination to the metal ion. (5) A shift in the  $\text{C}=\text{N}$  stretching frequency to higher energy in going from the free 4-MPipzcdtH ligand to its manganese complexes also supports the typical bidentate character of the 4-methylpiperazine-1-carbodithioic acid. In the manganese-4-MPipzcdtH complexes with perchlorate as the counter anion, the band around  $1126\text{-}1080 \text{ cm}^{-1}$  is assigned to the  $\nu_3$  vibration of the ionic perchlorate of  $T_d$  symmetry. Also, the observation of another band around  $624 \text{ cm}^{-1}$  due to the  $\nu_4$  vibration of the perchlorate group reveals the ionic nature of this group. The absence of the  $\nu(\text{ClO}_4)$  band at  $920 \text{ cm}^{-1}$  further supports the ionic nature. (4) In the far IR spectra of the complexes, additional bands in the  $360\text{-}354 \text{ cm}^{-1}$  region, as compared to the free 4-MPipzcdtH ligand, ascribable to the M-S stretching mode have been observed (Table 2). (6-13)

### Magnetic susceptibility studies

The complexes  $[\text{Mn}(4\text{-MPipzcdtH})_2](\text{ClO}_4)_2$  and  $[\text{Mn}(4\text{-MPipzcdtH})_2]\text{Cl}_2$  display measured room temperature magnetic moment values 5.81 B.M. and 5.72 B.M. respectively (Table 3). These values are indicative of five unpaired electrons in a manganese(II),  $d^5$  case. The high-spin  $d^5$  configuration gives an essentially spin-only temperature independent magnetic moment value of  $\sim 5.9$  B.M. because for the  ${}^6A_{1g}$  ground term there is no T.I.P. and no reduction of the moment below the spin-only value by spin-orbit coupling with higher ligand field term is expected. Like the octahedral  ${}^6A_{1g}$  ground term for the high-spin system the tetrahedral  ${}^6A_1$  ground term shows magnetic moments very close to the spin-only value, 5.92 B.M. and which are also independent of temperature. (14) Since the room-temperature  $\mu_{\text{eff}}$  values for the two bis(4-methylpiperazine-1-carbodithioic acid) manganous complexes with perchlorate and chloride as the counter anions were found to be less than spin-only value expected for five unpaired electrons, the magnetic susceptibility measurements were taken up at different temperatures between 80 and 296.5 K. The  $\mu_{\text{eff}}$  values for the two complexes decrease from 5.81 or 5.72 at 296.5 K to 4.20 or 4.08 at 80 K respectively. This decrease in  $\mu_{\text{eff}}$  values with temperature can be correlated with an interchain antiferromagnetic exchange interaction termed super-exchange which has been reported by Reiff and Eisman (15) to be responsible for this type of magnetic behaviour in  $\text{Mn}(\text{Et}_2\text{dtc})_2$ . Super-exchange pathway involving the bridging sulfur atoms of the dithiocarbamate ligand rather than direct exchange mechanism has been suggested for these antiferromagnetic interactions in  $\text{Mn}(\text{Et}_2\text{dtc})_2$ ; the direct metal-metal interactions have been excluded because of the large metal-metal distance ( $\sim 3.6 \text{ \AA}$ ). It is assumed that superexchange mechanism is operating in  $[\text{Mn}(4\text{-MPipzcdtH})_2](\text{ClO}_4)_2$  and  $[\text{Mn}(4\text{-MPipzcdtH})_2]\text{Cl}_2$  complexes; and the complexes may be assigned linear polymeric structure with one sulfur atom of each carbodithioic acid shared by two adjacent manganous ions. (16) An exchange pathway  $M_1(d_{yz}) \parallel L(p_z) \parallel M_2(d_{yz})$  or  $M_1(d_{xy}) \parallel L(p_x) \parallel M_2(d_{xy})$  ( $180^\circ d^5 - d^5$  exchange) may result in an antiparallel coupling of spins. (15,16)

The room temperature magnetic moment values of the manganese(III) complexes under study, viz.  $[\text{Mn}_2(4\text{-MPipzcdtH})_6(\text{O}_2)_2](\text{ClO}_4)_4$  and  $[\text{Mn}_2(4\text{-MPipzcdtH})_6(\text{O}_2)_2]\text{Cl}_4$  are found to be 5.48 and 5.30 B.M. respectively (Table 3). These values neither correspond to the spin-free nor to the spin-paired, octahedral manganic complexes but the values are much above than those expected for high-spin and low-spin manganese(III) complexes. For the weak octahedral crystal field (high-spin) manganese(III)  $d^4$  ion, with electronic configuration  $t_{2g}^3 e_g$  the electronic ground state is the  ${}^5E_g$  which emerges from the  ${}^5D$  Russell-Saunders' term of the  $d^4$  free ion. For such a ground state the TIP contribution which is given by  $4N\beta^2/10Dq$ , ignoring electron delocalization, is so small (about  $50 \times 10^{-6} \text{ c.g.s. mole}^{-1}$ ) that it may be neglected as compared to the first order Zeeman effect susceptibility  $\chi^1$  which is  $\simeq 10,000 \times 10^{-6} \text{ c.g.s. mole}^{-1}$  at 300 K. For

the  ${}^5E_g$  ground state the magnetic moment is expected to lie below the spin-only value (17) for four unpaired electrons by the factor  $(1-2\lambda/10Dq)$  and is given by  $\mu_{\text{eff}} = 4.90 (1-2\lambda/10Dq)$ . Having a value of  $10Dq \approx 15,000 - 12,500 \text{ cm}^{-1}$  with free ion value of  $\lambda = 88 \text{ cm}^{-1}$  for manganese(III) ion ( $\lambda$  is the spin-orbit coupling parameter for the free ion term and here it is positive because of the d shell being less than half filled) the magnetic moment for an octahedral complex is expected to be about 4.83 B.M. (14) In a strong crystal field of octahedral symmetry (low-spin) around manganese(III)  $d^4$  ion, the  ${}^3T_{1g}$  is the ground electronic state and is dominantly determined by the  $t_{2g}^4$  electronic configuration. The magnetic moment of the spin-paired trivalent manganese compound, e.g.  $K_3[Mn(CN)_6]$ , ranges from 3.50 B.M. at 300 K to 3.31 B.M. at 80 K. (17) The calculated room-temperature magnetic moment, employing the spin-orbit coupling constant of the free ion  $\lambda = -177 \text{ cm}^{-1}$  ( $\lambda$  is negative because of the  $t_{2g}$  sub-shell being more than half-filled) and ignoring electron delocalization and low symmetry ligand field components for  ${}^3T_{1g}$  ( $d^4$ ) ground state, is 3.6 B.M. But the position of the maximum in the magnetic moment and the rate of change of moment with temperature are not exactly in agreement with the reported values which indicate that electron delocalization and a low symmetry ligand field component must be taken into account in an exact treatment.

The abnormal values of room-temperature magnetic moment of the complexes, viz.  $[Mn_2(4-MPipzcdtH)_6(O_2)_2](X)_4$  ( $X = ClO_4, Cl$ ) persuaded us to measure the susceptibilities at low temperatures. Magnetic behaviour of the complexes has been depicted in Figure 1. The magnetic and electronic properties of the complexes have been explained by assuming eight coordination around manganese(III) ion. However these properties are not so easy to be explained for eight coordinate complexes.

Trigonal dodecahedral arrangement of eight coordination is found in several complexes containing bidentate ligands in which the two coordinated atoms are very close together (ligands having small bite), e.g.  $NO_3^-$ ,  $O_2^{2-}$  in  $Cr(O_2)_4^{3-}$  and  $Co(NO_3)_4^{2-}$  ions and the  $Ti(NO_3)_4$  molecule; when the ligand bite increases square antiprismatic geometry becomes favourable. Since in the complexes  $[Mn_2(4-MPipzcdtH)_6(O_2)_2](X)_4$  ( $X = ClO_4, Cl$ ) both the 4-methylpiperazine-1-carbodithioic acid and  $O_2^-$  ligands have small bite,  $D_{2d}$  geometry should be preferred. It is expected that the  $D_{2d}$  low symmetry should lead to magnetic moments near the spin-only values. The room-temperature magnetic moment of the complexes  $[Mn_2(4-MPipzcdtH)_6(O_2)_2](ClO_4)_4$  and  $[Mn_2(4-MPipzcdtH)_6(O_2)_2]Cl_4$  are 5.48 B.M. and 5.30 B.M. respectively at 296.5 K. The expected  $\mu_{\text{eff}}^{S.O.}$  value for the complexes for a total number of five unpaired electrons- four of manganese(III) ( $d^4$ ) and one of  $O_2^-$  ion- is 5.92. A value below the spin-only value for five unpaired electrons is difficult to be accounted for, but at least approximately the expected value is obtained. The magnetic moment of the complexes have been found to decrease with decrease of temperature and approaches 5.12 and 5.08 respectively at 80 K (Figure 1). The decrease in the magnetic moment suggests some antiferromagnetic exchange interactions which can be present in the complexes due to the bridging nature of the carbodithioate ligand and hence the indirect mechanism of superexchange interaction for antiparallel coupling may be suggested. The products of several preparations at varying room temperatures (27-35 °C) exhibited the same properties. Despite this consistency and the seemingly valid interpretation of the magnetic and forthcoming electronic spectral properties by assuming trigonal dodecahedral geometry for these compounds, the presence of the superoxo ion, and its mode of coordination- either as a bridge between two manganese(III) ions or having an end-on linkage-can be confirmed only by X-ray crystallographic techniques.

### Electronic absorption spectral studies

The colour of DMSO solution of two complexes containing manganous ions is pale yellow. The room temperature magnetic moment value  $\sim 5.8$  B.M. of the complexes indicates  ${}^6A_1$  ground state irrespective of the octahedral geometry (which may be assumed to have been achieved through bridging carbodithioato ligands between two metal ions) or tetrahedral geometry for the complex.

For the complexes  $[Mn(4-MPipzcdtH)_2](ClO_4)_2$  and  $[Mn(4-MPipzcdtH)_2]Cl_2$ , a well defined weak band occurring at 753-766 nm is assigned to  ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$  transition. A relatively narrow and middle band around 615-620 nm and third broad and weak transition around 533-565 nm are assigned to the transitions  ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$  and  ${}^4E_g(G), {}^4A_{1g}(G) \leftarrow {}^6A_{1g}$  respectively (Table 3). (14) The observed bands are not too intense to be attributed to the tetrahedral stereochemistry of the complexes around manganese(II) ion. The third band at 565 nm shows a sign of structure around 473 nm thus indicating that this band has been appropriately assigned to the transitions to the terms which are almost degenerate:  ${}^4E_g(G)$  and  ${}^4A_{1g}(G)$ .

The electronic spectra of trigonal dodecahedral complexes seem to consist almost entirely of charge transfer bands. In the electronic absorption spectra of the two complexes  $[Mn_2(4-MPipzcdtH)_6(O_2)_2](ClO_4)_4$  and  $[Mn_2(4-MPipzcdtH)_6(O_2)_2]Cl_4$  under study a strong and very broad band in the ultraviolet region extending between 250-348 nm has been observed and can be assigned to a charge transfer transition. Another strong and broad band which lies between 470-637 nm seems to be a mixed 'd-d' and charge transfer band because of its spread and intensity (Table 3).

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**Table 1.** Elemental analytical data and physical data of carbodithioic acid ligand and its manganese complexes

Sr. No.	Compound (Composition) Formula Weight	Elemental Analysis Found (Calculated) (%)					Yield (%)	Decomp. Temp. (°C)	Colour	
		C	H	N	S	M				Cl
1.	4-MPipzcdtH (C <sub>2</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub> ) 176	41.03 (40.90)	6.02 (6.81)	16.15 (15.90)	35.90 (36.36)	–	–	90	200	Creamish yellow
2.	[Mn(4-MPipzcdtH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (C <sub>22</sub> H <sub>24</sub> N <sub>4</sub> S <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> Mn) 605.9	23.64 (23.76)	4.01 (3.96)	8.89 (9.24)	20.87 (21.12)	8.85 (9.06)	–	90		Yellow
3.	[Mn(4-MPipzcdtH) <sub>2</sub> ]Cl <sub>2</sub> (C <sub>22</sub> H <sub>24</sub> N <sub>4</sub> S <sub>4</sub> Cl <sub>2</sub> Mn) 477.9	29.77 (30.12)	4.87 (5.02)	11.82 (11.71)	26.85 (26.71)	11.89 (11.49)	14.94 (14.85)	91	184	Yellow
4.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub> (C <sub>44</sub> H <sub>48</sub> N <sub>8</sub> S <sub>8</sub> O <sub>2</sub> Cl <sub>4</sub> Mn <sub>2</sub> ) 1627.8	26.74 (26.53)	4.87 (4.42)	10.77 (10.32)	23.74 (23.59)	6.34 (6.74)	–	90		Purple
5.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ]Cl <sub>4</sub> (C <sub>44</sub> H <sub>48</sub> N <sub>8</sub> S <sub>8</sub> O <sub>2</sub> Cl <sub>4</sub> Mn <sub>2</sub> ) 1371.8	31.01 (31.49)	4.98 (5.24)	12.23 (12.24)	27.64 (27.99)	7.63 (8.00)	10.84 (10.35)	92	190	Purple

**Table 2.** Some coordinatively diagnostic features of infrared spectra (cm<sup>-1</sup>) and molar conductance values,  $\Lambda_M$  (ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) of Manganese 4-methylpiperazine-1-carbodithioic acid complexes

Sr. No.	Compound	$\nu(\text{N-H})/\nu(\text{O-H})$	$\nu(\text{C-H})/\text{H}_2\text{C}=\text{N}$	$\nu(\text{C}=\text{N})$	$\nu_s(\text{SCS})$	$\nu_a(\text{SCS})$	$\nu(\text{Cl-O})$	$\nu(\text{M-S})$	$\Lambda_M$
1.	4-MPipzcdtH	3600 b - 3200 s	2850 s	1442 s	975 s	675 w	–	–	–
2.	[Mn(4-MPipzcdtH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	3510 b - 3205 s	2934 s	1461 s	987 s, 974 m	687 w	1126 vs, 624 s	358 m	162.64
3.	[Mn(4-MPipzcdtH) <sub>2</sub> ]Cl <sub>2</sub>	3320 b - 3230 s	2994 s	1474 s	989 s, 972 m	642 w	–	360 m	132.54
4.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	3650 b - 3200 s	2922 s	1463 s	998 s, 932 m	685 w	1080 vs, 624 s	354 m	–
5.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ]Cl <sub>4</sub>	3521 b - 3232 s	2978 s	1472 s	989 s, 973 m	642 w	–	355 m	–

**Table 3.** Electronic absorption spectra (nm) and  $\mu_{\text{eff}}$  values of Manganese 4-methylpiperazine-1-carbodithioic Acid Complexes

Sr. No	Compound	Band Assignments	$\mu_{\text{eff}}$ (B.M.)
1.	[Mn(4-MPipzcdtH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	<sup>4</sup> T <sub>1g</sub> (G) ← <sup>6</sup> A <sub>1g</sub>	5.81
2.	[Mn(4-MPipzcdtH) <sub>2</sub> ]Cl <sub>2</sub>	<sup>4</sup> T <sub>2g</sub> (G) ← <sup>6</sup> A <sub>1g</sub>	5.72
		<sup>4</sup> E <sub>g</sub> (G), <sup>4</sup> A <sub>1g</sub> (G) ← <sup>6</sup> A <sub>1g</sub>	
3.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	Charge transfer transitions	5.48
4.	[Mn <sub>2</sub> (4-MPipzcdtH) <sub>6</sub> (O <sub>2</sub> ) <sub>2</sub> ]Cl <sub>4</sub>	Mixed d-d and charge transfer bands	5.30