

## The Magnetic Properties of Manganous Complexes

### Studies in Magnetochemistry 18\*

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The effective magnetic moments at room temperature of representative manganous complexes are reported. The temperature dependence of the susceptibility in the interval 85–295°K is studied for Mn(II)-bis-salicylaldehyde, Mn(II)-bis-salicylaldehyde-ethylenediimine and Mn(II)-bis-salicylaldehyde-*o*-phenylenediimine. Preparative details are given for these chelates. The magnetic moments found are compared with the predictions of the valence bond theory and the ligand field theory. A qualitative explanation of the apparent non-existence of planar manganous complexes with magnetic moment  $3.87 \mu_B$  is suggested. A slight discontinuity in the  $\chi^{-1}$ ,  $T$ -diagram of Mn(II)-bis-salicylaldehyde-ethylenediimine is reported. The reflection spectrum of the pink  $Mnpy_2Cl_2$  is interpreted as originating in a halogenbridged polymeric structure. Evidences for the non-existence of Reitzenstein's brown "isomer"  $Mnpy_2Cl_2$  are given.

The ground level of the  $3d^5$  electron system of the free  $Mn^{+2}$  ion is  $^6S$ . Assuming ideal Russell-Saunders coupling the magnetic moment of the free manganous ion is  $5.92 \mu_B$ . When the manganous ion is the central-ion in complexes more or less pronounced deviations from the ideal free ion value of the magnetic moment may be expected according to the type of bond and the spatial arrangement of the ligands. The valence bond theory thus predicts three different magnetic moments, *viz.*  $5.92 \mu_B$ ,  $3.87 \mu_B$ , and  $1.73 \mu_B$ . In the two last mentioned cases, with reduced spin multiplicity, the bonding electrons are supposed to utilize the planar  $dsp^2$ -hybrid and the octahedral  $d^3sp^3$ -hybrid, respectively.

The magnetic moments actually found in manganous complexes are almost invariably about  $5.9 \mu_B$  corresponding to the sextet ground level. A slightly higher value,  $6.2 \mu_B$  is reported by Wiley, Tyson, and Stellar<sup>1</sup> in the case of the manganous-kojate. However, only the manganous hexacyanides exemplify the case of the lowest spin multiplicity, while no certain instances of compounds with a quartet ground level are reported. As an illustration of the

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Table 1. Effective magnetic moments in Bohr magnetons of complex manganous compounds.

	Temp. °C	$\mu_{eff}/\mu_B$
MnSO <sub>4</sub>	19	5.85
[Mn(OH <sub>2</sub> ) <sub>4</sub> ]SO <sub>4</sub>	19	5.96
[Mn(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ](NH <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	17	5.84
Mnpy <sub>2</sub> Cl <sub>2</sub> I brown	17	5.67
Mnpy <sub>2</sub> Cl <sub>2</sub> II pink	18	5.89
Mnpy <sub>2</sub> Cl <sub>2</sub> III pink	18	5.96
Mnpy <sub>2</sub> Br <sub>2</sub>	18	5.96
Mnpy <sub>2</sub> Br <sub>2</sub>	18	6.00
[Mn(SCN) <sub>6</sub> ]K <sub>4</sub> · 3H <sub>2</sub> O	18	6.06
[Mn(CN) <sub>6</sub> ]K <sub>4</sub> · 3H <sub>2</sub> O	17	2.13

experimental results some manganous complexes earlier prepared and measured magnetically by one of us<sup>2</sup> are stated in Table 1.

The magnetic results mentioned in Table 1 are equally well described by the theory of crystalline field potential (v. Vleck and his school<sup>3</sup>). According to this theory the electric field from the ligands causes a sort of intramolecular Stark splitting of the energy levels of the central ion. In case of the manganous ion the Stark splitting leaves a sextet level lowest in octahedral and tetrahedral ligand fields of weak and intermediate strength, while at strong ligand fields a doublet becomes the ground level, and a reduction of the magnetic moment occurs as observed for K<sub>4</sub>Mn(CN)<sub>6</sub>.

The value of the magnetic moment of K<sub>4</sub>Mn(CN)<sub>6</sub> stated in Table 1 is somewhat higher than the "spin only" value 1.73  $\mu_B$  of one unpaired electron. It is rather difficult to prepare this substance of a sufficient purity as the presence of even minute amounts of other manganese compounds may increase the susceptibility considerably. The rather large range of moments quoted in the literature reflects this. However, it is interesting that the deviation from the value 1.73  $\mu_B$  may also be explained theoretically. A quantum mechanical calculation by Kotani<sup>4</sup>, taking into account the spin-orbit interaction, leads to an effective magnetic moment of about 2.5  $\mu_B$  at room temperature. According to Kotani's calculations the effective magnetic moment decreases slowly when the temperature is lowered and converges against the "spin only" value when the temperature approaches the absolute zero. A study of the temperature dependence of the susceptibility of this and a few other manganous-cyano-complexes is being carried out in this laboratory at present.

Particular interest is connected to the measurements of the three preparations Mnpy<sub>2</sub>Cl<sub>2</sub> I, II and III. Reitzenstein<sup>5</sup> prepared a pink compound of this composition and furthermore a brown substance of apparently the same composition, which have been considered as *cis-trans* isomers. The magnetic moment of the brown preparation I is lesser than the moment of the pink preparation III, which may be due to the presence of higher oxidation states of manganese. This assumption is supported by the fact that preparation I becomes darker brown when exposed to the air for some time. After recrystalli-

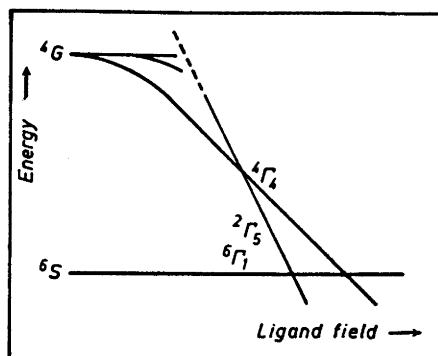


Fig. 1. Theoretical Orgel diagram for octahedral manganous complexes. (For explanation of terms see Ref. 7).

zation of I from ethanol the pink preparation II was obtained having nearly the theoretical value  $5.92 \mu_B$  for the magnetic moment (compare also the results of the Cl-determinations in the three cases). The brown "isomer" is probably not a chemically pure substance. Neither the directions given by Reitzenstein nor systematic variations of the experimental conditions yielded well defined products. In one of the more or less brownish powders now obtained, the presence of higher oxidation states of manganese could be demonstrated. X-Ray powder photograms (19 cm Bradley camera) supplied by P. F. Andersen M.sc. of this laboratory prove that all the lines in the powder-photogram of the pink compound appear in the powder photos of the brownish products with identical Bragg-angles and intensities. The powder photos of the brown products contain besides these lines a few foreign lines. In our opinion the only existing compound of the composition  $Mnpy_2Cl_2$  is the pink crystalline com-

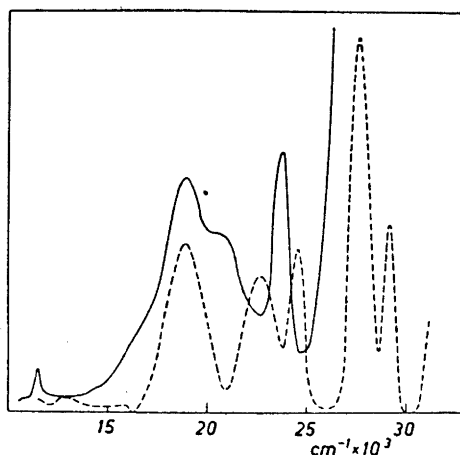


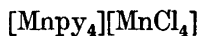
Fig. 2. Reflection spectra of  $MnCl_2 \cdot 4 H_2O$  (punctuated) and  $Mnpy_2Cl_2$  (full drawn) measured with a Beckman spectrophotometer model DU. Ordinate in arbitrary units. Abscissae frequencies in Kayser-units =  $cm^{-1}$ .

pound with the magnetic moment  $5.96 \mu_B$  which moment, according to the valence bond theory, excludes a planar configuration.

Concerning the non-existence of planar manganous complexes with magnetic moment  $3.87 \mu_B$  Dr. Klixbüll Jørgensen has kindly pointed out to us that referring to the energy level diagram in Fig. 1 the following arguments might be given, (for further details and explanation of the terms used compare for instance Ref.<sup>7</sup>).

In octahedral complexes the  ${}^2\Gamma_5$ -level crosses the  ${}^6\Gamma_1$ -level at a smaller ligand field strength than is the case with  ${}^4\Gamma_4$ . When the octahedron of 6 ligands are tetragonally deformed the quartet and the doublet levels are further split, but in view of the relative slopes of the  ${}^2\Gamma_5$  and  ${}^4\Gamma_4$ -lines it seems rather improbable that this splitting should cause an interchange of the sequence of the crossing points with the  ${}^6\Gamma_1$ -level. Thus one may conclude that provided the intramolecular Stark-pattern caused by four co-planar ligands is comparable with that caused by a tetragonally deformed octahedral arrangement of 6 ligands, the existence of planar manganous-complexes with the magnetic moment  $3.87 \mu_B$  seems energetically less probable.

In the particular case of  $\text{Mnpy}_2\text{Cl}_2$  the results of the magnetic measurements are in conformity with the formula



and with a halogenbridged chain-like structure as well. In view of the reflection spectrum discussed below we prefer the latter possibility.

The reflection spectra of  $\text{Mnpy}_2\text{Cl}_2$  and of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  are shown in Fig. 2. Following the arguments of Orgel<sup>6</sup> the bands of the latter are identified as follows (frequencies in Kayser units =  $\text{cm}^{-1}$ ).

$$\begin{array}{lll} 18\ 800\ {}^4\Gamma_4\ (\text{G}) & 22\ 700\ {}^4\Gamma_5\ (\text{G}) & 24\ 600\ {}^4\Gamma_1\ (\text{G})\ \text{and}\ {}^4\Gamma_3\ (\text{G}) \\ 27\ 600\ {}^4\Gamma_5\ (\text{D}) & 29\ 200\ {}^4\Gamma_3\ (\text{D}) & \end{array}$$

By analogy the spectrum of  $\text{Mnpy}_2\text{Cl}_2$  is interpreted in the following way: The narrow band at 23 800 K is due to the transition  ${}^6\Gamma_1\ (\text{S}) \rightarrow {}^4\Gamma_1\ (\text{G})$  and  ${}^4\Gamma_3\ (\text{G})$ . The red shift of this band gives evidence for an increased anionic character of the complex<sup>7</sup>. The broad band in the region 15 000 K to 23 000 K shows two maxima and a shoulder towards the red. The maximum with the highest wavenumber, being due to the transition  ${}^6\Gamma_1\ (\text{S}) \rightarrow {}^4\Gamma_5\ (\text{G})$ , is also shifted towards the red. This red shift is at least partly a consequence of the former, but an increased ligand field strength probably also contributes. The last maximum together with the shoulder is believed to originate in a tetragonal splitting of the  ${}^4\Gamma_4\ (\text{G})$  level. This interpretation suggests that  $\text{Mnpy}_2\text{Cl}_2$  has a halogen-bridged polymeric structure *i.e.* octahedra sharing 2 Cl<sup>-</sup> and with 2 pyridine molecules in *trans* position analogous to that found by X-ray analysis of the violet  $\text{Copy}_2\text{Cl}_2$ <sup>8</sup>.

From the magnetochemistry of nickel(II)-complexes several planar, diamagnetic chelates with tetradentate Schiff-base ligands of the type salicylaldehyde-ethylenediimine are well known. In the light of the above discussion it was therefore considered worth while to study the magnetic behaviour of similar manganous compounds. We have prepared and studied the magnetic properties of manganous-bis-salicylaldehyde-ethylenediimine and manganous-

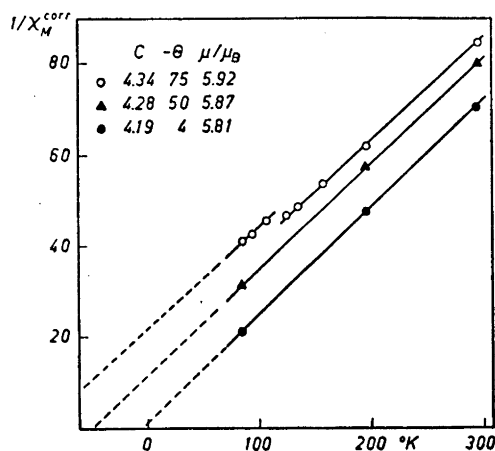


Fig. 3. Reciprocal corr. molar susceptibility of manganous-bis-salicylaldehyde ▲, manganous-bis-salicylaldehyde-ethylenediimine ○, and manganous-bis-salicylaldehyde-o-phenylenediimine ● plotted against the abs. temperature.

bis-salicylaldehyde-*o*-phenylene-diimine and for comparison also manganous-bis-salicylaldehyde, although this latter compound could not be obtained in a quite satisfactory purity.

Fig. 3 illustrates the results of the magnetic measurements over a range of temperatures. The reciprocal molar susceptibility corrected for the diamagnetism of the ligands and the diamagnetism of the electron system of the manganous ion is plotted against the absolute temperature. The straight lines, representing the Curie-Weiss relation, are fixed by means of a least square analysis of the data. In the figure is also stated the values of the Curie constant  $C$ , the Weiss-correction  $\Theta$  and the mean magnetic moment calculated from the formula  $\mu = 2.84 \sqrt{\chi_M^{\text{cor}}(T - \Theta)} \mu_B$ . The magnetic moments are only a little smaller than the "spin only" value of five unpaired electrons, thus indicating a sextet ground level clearly.

It is noteworthy that while the Weiss correction for the salicylaldehyde-*o*-phenylenediimine-compound is only  $-4^\circ$ , this constant has a considerably higher value for the salicylaldehyde- and the salicylaldehyde-ethylenediimine-compounds *viz.*  $-50^\circ$  and  $-75^\circ$ , respectively. Since a residual orbital contribution and anisotropy effects are not expected for manganous compounds the  $\Theta$ -values may be ascribed to exchange interactions. It is in accordance with this point of view that the presumably most diluted *o*-phenylene-diimine-compound has the smallest  $\Theta$ -value.

In the temperature range 85—107°K the susceptibilities of the salicylaldehyde-ethylenediimine-complex are from 8 to 10 % lower than calculated from the Curie-Weiss line based upon the susceptibilities measured between 125 and 295°K. A rough estimate of the values gives the relation  $\chi_M^{\text{cor}} = \frac{4.48}{T + 99}$

for  $85 < T < 107^\circ\text{K}$ . In this temperature interval obviously a change in the crystals occurs, which increases the exchange forces ( $\Theta$ ). A decrease in the atomic distances explains this effect; however, since no X-ray information is available this question cannot be settled for the present.

## EXPERIMENTAL

### Preparation and analysis of the compounds

The materials used for the preparation of the compounds were the tetrahydrates of manganous chloride and manganous sulphate, anhydrous manganous bromide prepared from the oxide and hydrogen bromide, potassium cyanide, potassium thiocyanate and furthermore pyridine, salicylaldehyde, ethylenediamine and *o*-phenylenediamine. The potassium cyanide was the purest product available. The other substances were c.p. chemicals. The Schiff-bases prepared from salicylaldehyde and the amines were re-crystallized from 96 % ethanol.

Manganese was determined as manganous sulphate or potentiometrically according to *Lingane and Karplus*<sup>9</sup> after destruction of the complexes and chelates with concentrated sulphuric acid to which was added a small amount of concentrated nitric acid. Chloride was determined argentometrically after Volhard.

*Anhydrous manganous sulphate* was obtained by dehydration of the tetrahydrate (constant weight).

*Manganous sulphate tetrahydrate*. Some of the most well developed and apparently not dehydrated crystals were selected for the magnetic measurement. The evidence for the composition of this salt is of course not entirely satisfactory. A slight deviation in the water content has, however, no significant influence upon the value of  $\mu_{\text{eff}}$ .

*Ammonium manganous dioxalate dihydrate*. This compound was prepared after the method of Sonchay and Lenssen<sup>10</sup>. No higher hydrates were isolated. (Found: Mn 18.30, Calc.: Mn 18.13).

*Potassium manganous thiocyanate trihydrate*. The method used to prepare the complex is essentially that of Walden<sup>11</sup>. Only red crystals were used for the analysis and the magnetic measurement. Brownish crystals were discarded. (Found: Mn 9.04. Calc. Mn 8.95).

*Potassium manganous hexa-cyanide trihydrate*. The procedure given by Christensen<sup>12</sup> was followed. (Found: Mn 13.14. Calc.: Mn 13.04).

*Dipyridinomanganous chloride*. Preparation No. I, brown powder, was obtained as described in the paper of Reitzenstein<sup>5</sup>. (No. I. Found: Cl 24.65. Calc. Cl 24.98). The preparation of this brown substance was carried out with success only once.

A portion of No. I was recrystallized from ethanol. The pink crystals were washed with ether and dried in vacuum; thus we obtained prepare No. II, the composition of which also is  $\text{Mnpy}_2\text{Cl}_2$ . (No. II. Found: Cl 24.61. Calc. Cl 24.98).

The third specimen, preparation No. III, was produced by addition of pyridine to a solution of manganous chloride in ethanol. Further treatment as in the case of No. II. (No. III. Found: Cl 24.88. Calc. Cl 24.98).

It seems to be a mere accident if Reitzenstein's "kaffeebraune" compound is precipitated. If the aqueous solution of manganous chloride is saturated with oxygen, one obtains a substance of a light brown colour. In other experiments oxygen was continuously passed through the solution during the preparation. In these cases deeper brown solids were precipitated. Specimens selected for analysis gave 24.26 % Cl and 24.87 % Cl. However, the substance was not homogeneous. The total yield was ground in a mortar and the content of Cl was now 26.85 % and 26.95 %. In another series of experiments the ratio of the concentration of manganous chloride to pyridine was varied from 1 : 4 to 1:20. The colour of the precipitates became deeper brown when decreasing this ratio. One of the deepest brown products gave evolution of chlorine when boiled with hydrochloric acid (potassium iodide paper).

These evidences, the X-ray results above mentioned, and the magnetic measurements on preparations I, II, and III discussed above indicate that the existence of a well defined brown or darkbrown compound of the composition  $\text{Mnpy}_2\text{Cl}_2$  is doubtful. The reason for

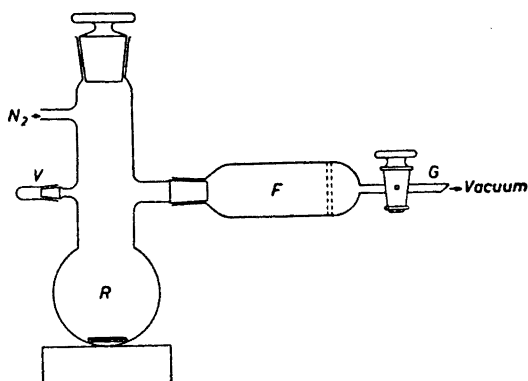


Fig. 4. Apparatus for preparation of manganous-bis-salicylaldehyde.

the brown colour may be that the pink compound is contaminated with a manganese compound in which the oxidation state of manganese is higher than 2. In our opinion the pink, crystalline substance above described as II or III is the only existing defined compound of the composition  $Mnpy_2Cl_2$ .

*Dipyridinomanganous bromide.* This complex was prepared following the method of Grossmann<sup>13</sup>. (Found: Mn 14.89. Calc. Mn 14.73).

*Hexapyridinomanganous bromide.* Crystals of this compound were obtained by cooling a boiling solution of anhydrous manganous bromide in pyridine (Grossmann<sup>13</sup>). The substance gives off pyridine easily at room temperature. (Found: Mn 7.87. Calc. Mn 7.97).

*Manganous-bis-salicylaldehyde.* Emmert, Gsottschneider and Stanger<sup>14</sup> prepared a hydrate containing  $1\frac{1}{2}$   $H_2O$  from manganous chloride and salicylaldehyde in aqueous ammonia (Found for C and H respectively, 51.84 % and 4.01 % calc 51.83 % and 3.81 %, respectively). Ray and Mukherjee<sup>15</sup> in a similar way prepared a dihydrate (Found: Mn 16.68. Calc. Mn 16.51). Our preparation was carried out as follows: The apparatus shown in Fig. 4 was evacuated and a current of nitrogen passed through. This operation was repeated several times. The following reagents were introduced into the reaction bulb *R* while a continuous stream of nitrogen was passed through: 1.0 g  $MnCl_2 \cdot 4H_2O$  was dissolved in 40 ml 50 % aqueous acetone (oxygen-free), 1.5 ml salicylaldehyde was added and furthermore drop by drop 10 ml water-acetone mixture + 5 ml conc. ammonia while stirring the mixture.

The apparatus was closed and the reaction mixture vigorously stirred for half an hour (magnetic stirrer). The liquid and the strawcoloured crystals were transferred to the filterbulb *F*. The crystals were filtered off by suction through *G* and washed with aqueous acetone and next with acetone, which was introduced through *V* by means of a long funnel. The washing operation was carried out in an atmosphere of nitrogen.

The apparatus was again closed and the precipitate was dried by pumping through *G* for some hours. The substance was finally dried in a high vacuum over  $P_2O_5$  at 110–120°C until the weight was constant. The dry compound does not become darker when exposed to the atmosphere. Seven different preparates were produced. (No. 1: Mn 19.42. No. 2: Mn 19.47; No. 3: Mn 19.15. Calc. Mn 18.49).

These particular 3 compounds were applied for the magnetic measurement in spite of their manganese content being too high. The magnetic moments of these substances are practically identical and equal to  $5.87 \mu_B$  and the Curie-Weiss line is nearly *parallel* to that of manganous-bis-salicylaldehyde-*o*-phenylenediimine. The surplus of manganese does not increase the magnetic moment more than 1 % of the theoretical value for ionic- or  $sp^3$ -bonds ( $5.92 \mu_B$ ). The main point is that the presence of the impurity does not make our statement concerning the non-planar configuration doubtful.

*Manganous-bis-salicylaldehyde-ethylenediimine.* 750 ml redistilled ethanol was placed in a 1 000 ml round-bottomed flask fitted with a mechanical stirrer and a fractionating column with condenser. A current of nitrogen was passed through the system and 100 ml ethanol was distilled over. Together with 3.0 g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  this distillate was returned to the remanens. 100 ml ethanol were again distilled off and returned to the flask together with 4.0 g salicylaldehyde-ethylenediimine. 100 ml ethanol was distilled over and 0.9 g solid NaOH was added to the reaction mixture. The column was adjusted so that the distillation was now very slow. Red crystals separated after 45 min, and after 4–5 h 2–3 g of red crystals were formed, which were filtered off (glassfilter-crucible) and washed with ethanol, acetone, and ether. These operations were all carried out in an atmosphere of nitrogen. Sometimes the red crystals were contaminated with a yellow precipitate, which was easily eliminated by washing with 0.04 M acetic acid.

Three independent specimens were prepared for the magnetic measurement. (No. 1: Mn 17.14; No. 2: Mn 17.19; No. 3: Mn 17.03. Calc. Mn 17.10).

*Manganous-bis-salicylaldehyde-o-phenylenediimine.* This substance was obtained by a method similar to the preceding. The reaction-mixture turned strongly red after half an hour. After one hour the precipitate was so dense that the preparation had to be interrupted. A dark yellow spongy mass of 1 cm long crystals was obtained.

Two independent preparates were produced for the magnetic measurement. (No. 1: Mn 14.80; No. 2: Mn 15.02. Calc. Mn 14.88).

In a previous publication by Asmussen<sup>2</sup> it was pointed out that it is very difficult to prepare manganous chelates by means of Schiff-bases as chelating agents in so well defined composition that a magnetic measurement has any sense. The preparation methods here described seem to give compounds for which the magnetic susceptibilities are sufficiently reproducible. However, it must be admitted that we have not succeeded in preparing the analogous chelates with bis-salicylaldehyde-putrescine and bis-salicylaldehyde-cadaverine. Manganous-bis-salicylaldehyde could not be prepared following the method described above for manganous-bis-salicylaldehyde-ethylenediimine.

### Magnetic measurements

The determination of the magnetic susceptibilities were carried out by the Gouy-method as described by Asmussen and Soling<sup>16</sup>. The susceptibilities were measured at room temperature, then at 195°K and at 85°K and finally for control again at room temperature. Manganous-bis-salicylaldehyde-ethylenediimine No. 3 was measured at 5 temperatures between 85°K and 195°K. These temperatures were realized by means of a brass block which fitted in the Dewar vessel. The amounts of liquid air were so adjusted that the different temperatures were fixed within 5° intervals. At all temperatures except room temperature the measurements were performed 20–30 min after the specimen tube had been suspended in the cooling system. The measurement was repeated after 20–30 min. In some cases a third measurement was performed after another 20–30 min interval. The agreement between the results was in general excellent. The temperature dependence of the susceptibility for the preparate mentioned is illustrated by the data given in Table 2.

Table 2. Temperature dependence of  $\chi_M$  (corr) and  $\mu_{\text{eff}}$  for manganous-bis-salicylaldehyde-ethylenediimine No. 3.

°K	$\chi_M^{\text{cor}} \times 10^6$	$\mu_{\text{eff}}/\mu_B$	°K	$\chi_M^{\text{cor}} \times 10^6$	$\mu_{\text{eff}}/\mu_B$
290	11 965	5.29	125	21 374	4.64
195	16 157	5.04	107	21 949	4.35
157	18 634	4.88	94	23 488	4.22
135	20 529	4.73	85	24 416	4.09



Table 3. Susceptibilities and  $\mu_{\text{eff}}$  values for the 3 different manganous-bis-salicylaldehyde-ethylenediimine preparates.

Preparation number	°K	$\chi_g \times 10^6$	$\chi_M \times 10^6$	$\chi_M^{\text{cor}} \times 10^6$	$1:\chi_M^{\text{cor}}$	$\mu_{\text{eff}}/\mu_B$
1	291	36.11	11 600	11 760	85.03	5.25
2	294	36.10	11 596	11 756	85.06	5.28
3	294	36.20	11 629	11 789	84.82	5.29
1	195	49.58	15 927	16 087	62.15	5.03
2	195	49.63	15 943	16 103	62.11	5.03
3	195	49.96	16 047	16 207	61.69	5.05

The values for  $\chi_M^{\text{cor}}$  are calculated from  $\chi_M$  by means of the corrections for the diamagnetism of the ligands and the diamagnetism of the electron system of the  $\text{Mn}^{+2}$  ion. The values used for these corrections are  $-122 \times 10^{-6}$  and  $-160 \times 10^{-6}$  and  $-175 \times 10^{-6}$  for the bis-salicylaldehyde, the bis-salicylaldehyde-ethylenediimine and the bis-salicylaldehyde-*o*-phenylenediimine chelates, respectively. These corrections were calculated from Pascal's constants and the experimental value  $\chi_M = -64.4 \times 10^{-6}$  for salicylaldehyde measured by Rumpf and Leguin<sup>17</sup>. The diamagnetism of the  $\text{Mn}^{+2}$  ion was calculated<sup>2</sup> to  $-21 \cdot 10^{-6}$ .

The results of the measurements are shown in Fig. 3. We point out that the "points" in the diagram at each temperature are mean values of all measurements on different preparations of the compound in question. The data in Table 3 give an impression of the reproducibility of the measurements of the 3 different preparates of manganous-bis-salicylaldehyde-ethylenediimine.

The field strength dependence was investigated at room temperature. The susceptibilities of all compounds were field strength independent in the interval 700 to 8 000 Ørsted.

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