

MAGNETISM AND MOLECULAR CONSTITUTION OF SOME MANGANESE COMPOUNDS

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THE magnetic method has recently afforded useful information on the valency of particularly the paramagnetic ions since changes in principal valency bring about changes in magnetic moments which can be correlated with atomic structure.

In general, atoms in which the sub-groups are incompletely filled exhibit paramagnetism. Sommerfeld,¹ Bose,² Stoner³ and Van Vleck⁴ have obtained the following derivation for the paramagnetic susceptibility of ions of the transition elements:—

$$\chi_M = \frac{N \beta^2 \{4S(S+1)\}}{3k(T)}$$

Manganese exists in different valency states, but comparatively little use has been made of this method in defining the structure of compounds of this element.

Manchot and Gall⁵ claim to have obtained complex salts of univalent manganese. On account of their extreme instability, Szego and Ostinelli⁶ found magnetic determination of the complexes impossible.

The paramagnetic susceptibility of bivalent manganese salts has been extensively studied.⁷ The number of Bohr magnetons was found to be in agreement with the value resulting from spin only, *viz.*,

$$\sqrt{4S(S+1)} = 5.92.$$

Johnson,⁸ and Jackson⁹ determined the susceptibility of the compounds of trivalent manganese and found the value of magnetons to be very nearly the theoretical value for trivalent manganese, namely,

$$\sqrt{4S(S+1)} = 4.90.$$

The permanganates exhibit feeble paramagnetism independent of temperature as is theoretically predicted for the element in the septavalent states.

It is obvious from the instances quoted that the co-relationship between paramagnetism and valency can be utilized in determining the valency of this element and the present investigation was, therefore, undertaken in order to elucidate the constitution of some of its compounds of indefinite structure recorded in literature.

Experimental

The various products to be investigated were prepared as follows:—

Mangano-halides of Pyridine.

Compounds of pyridinium halides with manganese halides have been described by several authors. They include compounds of the type (i) $\text{MnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ (Pincussohn¹⁰) and (ii) $\text{MnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ (Reitzenstein¹¹).

Reitzenstein described the latter compound as light green and assigned to it the above formula containing quadrivalent manganese, mainly on the ground that the more probable formula which fitted his analysis equally well had already been assigned by Pincussohn to his yellow compound (i).

Meyer and Best¹² prepared a corresponding bromo-compound which was of white colour, resembling that of Pincussohn's and they gave $\text{MnBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{HBr}$ formula to their compound which supported Pincussohn's work and criticised Reitzenstein's formulation of his compound (ii).

Taylor¹³ investigated the anomaly presented by the three different colours assigned to salts of similar composition and he suggested that the light green salt (ii) is $(\text{C}_5\text{H}_5\text{NH})_2 \cdot \text{MnCl}_4$ and Pincussohn's yellow compound is an impure specimen of salt (ii) associated with small amounts of a pink compound $\text{MnCl}_2 \cdot \text{C}_5\text{H}_5\text{NHCl} \cdot \text{H}_2\text{O}$ which had not been described previously.

In the present investigation the two compounds were prepared by the following method:—

1. The hydrated manganous chloride (62.5 gm.) was dissolved in pure conc. hydrochloric acid (750 c.c.) and 50 gm. of pyridine were added. The liquid was evaporated to 100 c.c. and on cooling, pink needle-like crystals were obtained. The crystals were washed with alcohol and dried under vacuum. (Found: Mn = 21.2%; Calc. = 21.2%.)

2. The green compound was obtained in a pure form by repeated crystallisation of the compound from the filtrate. The crystals were washed with absolute alcohol and dried in vacuum (Taylor¹³). (Found: Mn = 15.4%. Calc. = 15.4%.)

3. *Potassium Mangani-Chloride*. K_2MnCl_6 .—The compound was prepared in the following manner¹⁴: 5 gm. of potassium permanganate were warmed with 150 c.c. of glacial acetic acid until energetic reaction commenced. The flask was immediately immersed in a low temperature bath of ice and salt, and the solution saturated with dry hydrogen chloride. The undissolved dioxide of manganese was filtered off, the solution again cooled and re-saturated with hydrogen chloride. The dark shining crystals that separated out were filtered, washed with cold hydrochloric acid saturated with hydrogen chloride gas and dried over soda-lime under reduced pressure. (Found: Mn = 16.3% ; Calc. = 16.2%.)

4. *Silver Permanganate*.—Saturated solutions of potassium permanganate and silver nitrate were mixed in stoichiometric proportions, the temperature being kept in the neighbourhood of 0° C. The dark violet crystals that separated out were drained from the mother-liquor under suction. The salt is fairly soluble in warm water. It was repeatedly crystallised from it, and the crystals were dried under vacuum at a low temperature.

The compound was analysed for silver by Volhards method:—A known weight of the compound was treated with a little nitric acid, the precipitated manganese dioxide filtered off and the solution titrated against standard sulpho-cyanide solution. The permanganate MnO_4' was determined directly by titration. (Found: Ag = 47.60% ; Calc. = 47.58%.) (Found: MnO_4' = 52.17% ; Calc. = 52.42%.)

5. *Potassium Mangani-Cyanide*. $K_5Mn(CN)_6$.—Manchot and Gall⁵ reported the complex cyanide compounds of sodium and potassium in which manganese exhibits univalency. The compound was prepared by the reduction of $Na_4Mn(CN)_6$. 10 gm. of sodium mangano-cyanide prepared from manganous acetate and sodium cyanide¹⁵ were dissolved in 2% sodium hydroxide and 8 gm. of aluminium powder added in small amounts at a time. After 5 minutes when the solution had acquired golden yellow colour it was rapidly filtered into a solution of 30 gm. KOH and 60 gm. KCN, saturated with potassium chloride. A white finely divided precipitate was formed. This was removed by centrifuging. It was washed with 200 c.c. of 10% KOH and then with 10% KCN and finally given a wash with 700 c.c. of ice-cold water. The salt is extremely unstable and in order to avoid decomposition, it was kept under potassium cyanide solution.

Magnetic Data.—The susceptibility determinations were carried out on a modified form of Gouy's balance, and χ was calculated according to

the equation :

$$\chi_{p_2} = \frac{1}{m_{p_2}} \left\{ (\chi_{p_1} m_{p_1} - \chi_a m_{ap_1}) \frac{\omega_{p_2}}{\omega_{p_1}} + \chi_a m_{ap_2} \right\}$$

where χ_{p_1} and χ_{p_2} are respectively the specific susceptibility of the standard substance and of the specimen, ω_{p_1} and ω_{p_2} are the respective pulls, m_{p_1} and m_{p_2} are the respective masses and m_{ap_1} and m_{ap_2} are the masses of air displaced respectively by the standard substance and by the specimen.

The specific susceptibilities of the compounds were determined in the solid state. In the case of the complex cyanide, the substance was moist and some decomposition could not be avoided. The susceptibility tube was packed by centrifuging, the access of air being avoided, as far as possible, by means of a protective layer of 10% KCN solution over the complex cyanide packing. The susceptibility value for the moist complex cyanide was calculated after deducting for the contribution of the cyanide layer.

In the following table, the value of χ in each case represents the mean of at least three observations.

TABLE I

Name	Formula	Specific Susceptibility $\times 10^6$	Temp. $^{\circ}\text{C}$.
1. Pink Pyridinium Compd.	.. $\text{C}_5\text{H}_5\text{NH} \cdot \text{MnCl}_2 \cdot \text{H}_2\text{O}$	55.80	21.0
2. Green Pyridinium Compd.	.. $2\text{C}_5\text{H}_5\text{NH} \cdot \text{MnCl}_4$	41.29	21.0
3. Pot. Mangani-Chloride	.. $2\text{KCl} \cdot \text{MnCl}_4$	18.05	20.0
4. Silver Permanganate	.. $\text{Ag} \cdot \text{MnO}_4$	- 0.28	27.0
5. Pot. Mangani-Cyanide	.. $\text{K}_5 [\text{Mn}(\text{CN})_5]$	4.0 ± 1.0	20.0

Discussion of Results

Manganohalides of Pyridine :

1. *Pink Compound*.—Taylor¹³ has suggested $\text{MnCl}_2 \cdot \text{C}_5\text{H}_5\text{NHCl} \cdot \text{H}_2\text{O}$ as the formula to his compound. The experimental value of χ , 55.8×10^{-6} , compares very well with the theoretical value 56.4×10^{-6} , calculated on Bose-Stoner formula for bivalent manganese, after the necessary corrections have been made for the presence of other groups.

2. *Green Compound*.—Reitzenstein¹¹ has suggested for the compound the formula $\text{MnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ in which manganese is quadrivalent. Taylor,¹³ however, represented it as $\text{MnCl}_4 \cdot (\text{C}_5\text{H}_5\text{NH})_2$. Reitzenstein's formula

predicts for the compound, a χ -value of 17.20×10^{-6} on the Bose-Stoner relationship whereas Taylor's formula gives it a χ -value of 40.84×10^{-6} which agrees well with the experimental value.

According to Hund¹⁶ the effective Bohr magneton number can be calculated from the equation

$$\mu_B = 2.839 \sqrt{\chi_M T}.$$

This gives a value for μ_B of 5.95 Bohr magnetons in close agreement with the theoretical deductions of Sommerfeld¹ who calculated the magnetic moment from the relationship

$$\mu_B = \sqrt{4S(S+1)}$$

and found a value of 5.92 for bivalent manganese.

The corrections applied for the presence of other groups are : $C_3H_5N = -49.2 \times 10^{-6}$, $H_2O = -12.90 \times 10^{-6}$ (*International Critical Tables*), $Cl = -22.2 \times 10^{-6}$ (Leiterer¹⁷).

3. *Potassium Mangani-Chloride*. K_2MnCl_6 .—Meyer and Best¹⁴ have suggested that manganese in the double chloride is quadrivalent. The theoretical value of χ , calculated on the above formula, after correcting for the presence of K^+ and Cl^- is 17.8×10^{-6} . This is in fair agreement with the experimental value of 18.05×10^{-6} and hence the magnetic data supports the quadrivalency of manganese in the compound. In this case $\chi_{Mn\ ion}$, the ionic susceptibility, has a value 6416×10^{-6} and the Bohr magneton number as experimentally found on the Hund formula works out to 3.89 which is in agreement with the calculated value 3.873 for quadrivalent manganese.

(Corrections for $K^+ = -18.5 \times 10^{-6}$ and $Cl^- = -22.2 \times 10^{-6}$.)

4. *Silver Permanganate*.—Septa-valent manganese predicts for the compound diamagnetism or feeble paramagnetism, independent of temperature. The experimental χ -value of -0.28×10^{-6} for the permanganate is in accord with this theoretical expectation.

5. *Potassium Mangani-Cyanide* (K_5MnCN_6).—According to Bose,¹⁸ the effective atomic number Z' of the co-ordinating atom in any complex compound equals $Z' = N - E + P \times 2$ where N is the atomic number of the co-ordinating atom, E is its primary valency in the given compound and P is 4, 6, etc., according as the compound is fourfold, sixfold, etc. On Manchot's formula $K_5[Mn(CN)_6]$, univalent Mn-ion should have zero-moment for six electron-pair-bond and consequently the molecule should exhibit diamagnetism or feeble paramagnetism. The same conclusion is reached on Welo and Baudisch¹⁹ and Sidgwick's interpretation of the

structure of the complex. Pauling²⁰ has given a quantum mechanical treatment of the electron-pair-bond and his interpretation leads to similar conclusions.

The complex, however, gives a minimum χ_M -value of $1,200 \times 10^{-6}$. It, therefore, appears that the product obtained by Manchot's method is an impure specimen of $K_5Mn(CN)_6$, contaminated possibly with $K_3[Mn(CN)_4]$, since the latter is known to be mainly formed (Manchot and Gall)⁵ even by slight variation of conditions. If formed, $K_3[Mn(CN)_4]$ can readily account for the paramagnetic behaviour of the product, since theory predicts strong paramagnetism for this complex.

It must, however, be borne in mind that the magnetic results for this compound are only tentative and of a qualitative nature, because of the complications arising from the extreme instability of the product and the difficulty of obtaining it pure. Furthermore, although the general manner in which the magnetic properties of complex ions are to be interpreted is fairly clear, yet many details are still obscure.

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