MAGNETIC PROPERTIES OF SILVER PERMANGANATE*

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Magnetic susceptibility measurements at various temperatures and magnetic flux densities and diffuse reflectance spectra of carefully prepared and handled silver permanganate AgMnO₄ are reported. The key value for $\chi_{\rm M}$ (AgMnO₄) is $(2.75 \pm 0.1) \times 10^{-10}$ m mol⁻¹ at 300K and 1.3T. Our results confirm the model of a multicentre interaction suggested in the literature. In addition, our results clearly point at the importance of the preparation and storage of the sample under well - defined and reproducible conditions since the magnetic properties change significantly with higher temperatures tending to an increased paramagnetic behaviour.

Introduction

Almost all silver compounds with predominantly ionic bonding properties are light - sensitive and in many cases also thermally sensitive. Despite many investigations on silver permanganate looking at various properties, as, e.g. 3,4 thermal decomposition kinetics ', structural and resonance Raman' work it is doubtful whether the investigators were aware of the critical thermal sensitivity of this solid already operative at ambient temperatures. This study was prompted by recent structural investigations and own work on Ag - cluster compounds concerning their optical and magnetic behaviour'.

According to the literature the small energy separation between the limiting ionic forms Ag MnO_4 and $Ag^{2+}MnO_4^{2-}$ and the presence of a 2nd series transition metal ion with relatively good covalent bonding properties make some type of cation – anion interaction, in addition to the electrostatic one, likely.

Experimental

Silver permanganate was prepared in the dark. A cold solution (kept at ca. 5°C) of 8g $(4.7 \times 10^{-1} \text{ mol})$ AgNO₃ in 150ml H₂O was acidified with two drops of concentrated nitric acid and stirred vigorously. A cooled solution (kept near 0°C) of 5.5g $(3.5 \times 10^{-2} \text{ mol})$ KMNO₄ in 380ml H₂O, a-cidified in the same way, was added dropwise. It is necessary to work with an excess of silver ions to avoid a coprecipitation of AgMnO₄ and KMnO₄. The precipitating product was sufficiently pure (deduced from chemical analysis and IR spectra) and therefore not recrystallized, because a significant change in the magnetic properties of the compound prepared according to the usual procedures was observed. The obtained

AgMnO₄ is a nearly black, microcrystalline material for which unusual spectra in frozen solutions were observed '.'. Although we found that preirradiation with visible flashlight had no detectable influence on the magnetic and optical data the compound was stored in the dark at 2° C. The storage at moderate temperatures is necessary because the compound is thermally unstable at higher temperatures'. However, samples prepared and handled as described could be stored over a period of five months without significant change in their magnetic properties.

Bulk magnetic measurements were performed on the modified Faraday Balance SUS 10 (manufactured by A. Paar KG, Graz, Austria) between 77K and 350K. The magnetic flux densities ranged from 0.4T to 1.3T. The calibration followed common literature methods using KCl as standard for the diamagnetic region ¹¹ and Hg [Co(NCS) 4] as standard for the paramagnetic region ², respectively. Diffuse reflectance spectra were recorded down to liquid nitrogen temperatures on a Beckman DK-2A spectroreflectometer equipped with a modified Oxford Instruments Continuous Flow Cryostat CF100.

Results and Discussion

The magnetic data given in Table 1 and plotted partly as a guide to the eye in Fig.1 reveal both a strong, nonlinear temperature dependence and a dependence on the magnetic flux density of about 10% in the range between 0.4T and 1.3T. These results are in contrast to those published previously (1, 3). Our susceptibility value for AgMnO₄ at 300K and 1.3T is:

$$\chi_{\rm M} = (2.75 \pm 0.1) \times 10^{-10} \, {\rm m}^3 {\rm mol}^{-1}$$
.

For ${\rm KMnO}_4$ we find under the same experimental conditions a value of

$$\chi_{\rm M} = (2.51 \pm 0.1) \times 10^{-10} \, {\rm m^3 mol^{-1}}.$$

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Table 1. Magnetic susceptibility data (given in $10^{-10} \text{ m}^3 \text{mol}^{-1}$) for AgMnO₄ at various temperatures and magnetic flux densities.

т [к]	В=1.3т	в=1.от	В=0.7т	в=0.4т
300.0	2.73	2.77	2.84	3.00
281.9	2.81	2.83	2.89	3.06
271.4	2.86	2.86	2.98	3.11
261.3	2.99	2.92	3.01	3.16
251.6	2.94	2.97	3.04	3.16
242.1	2.98	3.00	3.09	3.27
232.7	3.03	3.04	3.13	3.27
223.7	3.08	3.10	3.20	3.37
214.9	3.12	3.15	3.23	3.39
206.3	3.18	3.21	3.31	3.48
197.8	3.24	3.26	3.34	3.53
190.0	3.29	3.32	3.41	3.58
180.9	3.36	3.39	3.49	3.64
172.6	3.44	3.46	3.56	
156.0 147.7	3.61 3.69	3.63 3.72	3.72 3.81	3.90 3.90 3.95
139.5	3.80	3.83	3.92	4.06
130.7	3.93	3.95	4.04	4.16
122.1	4.06 4.21	4.08	4.17 4.33	4.32
95.3 86.4	4.62 4.88	4.66 4.92	4.74	4.85
79.9	5.10	5.13	5.23	5.43

The error limits given refer to the averaged deviation within a single measurement series. The absolute values of the magnetic susceptibility of our samples vary under the described preparation and storage conditions by about 15%. It is important to note that samples kept at higher temperatures tend to become more paramagnetic and the dependence on the magnetic flux density increases, too.

The usual $1/\chi_{\rm M}$ vs. T - plot shows clearly both the dependence of the data on the magnetic flux density and their temperature dependence (Fig.1). The principal features do not change even if a correction for the temperature independent contributions is included. Due to the Van Vleck- or temperature independent paramagnetism (TIP) of the MnO₄ - species the corrected $\chi_{\rm M}$ value is still a positive number although the incremental contribution of the Ag ion is negative with a susceptibility value of about -3x10 m mol

Looking at the magnetic data from the viewpoint of a simple equilibrium picture between the limiting ionic forms as suggested in the literature', like

$$\operatorname{Ag}^{+}\operatorname{MnO}_{4}^{-}$$
 \longrightarrow $\operatorname{Ag}^{2+}\operatorname{MnO}_{4}^{2-}$

it turns out that the amount of ${\rm Ag}^{2+}{\rm MnO}_4^{2-}$ must be very small due to the weak overall paramagnetism as revealed in our data set. If the sample contains considerable amounts of Ag MnO₄ the paramagnetism resulting from the contributions of the two unpaired electrons should be at least two orders of magnitude larger than the one observed in our AgMnO₄ samples (Table 1). In addition, there must be some cooperative



Fig.1. $1/\chi_{\rm M}$ vs. T - plot of the molar susceptibility of AgMnO₄ for the two limiting magnetic flux densities.



Fig.2. Diffuse reflectance spectra of $\rm KMnO_4$ (a) and $\rm AgMnO_4$ (b) diluted in $\rm BaSO_4$ with $\rm BaSO_4$ as standard.

effect in the lattice which causes the dependence on the magnetic flux density and the deviation of the $1/\chi_{\rm M}$ vs. T - plot from the form of a straight line. In support to these arguments, we mention that the crystal structure of AgMnO₄ shows no indications for distinct_Ag-O₂-bonds as one would expect if defined Ag MnO₄ structural subunits were present in the lattice 1.4.

In addition, it is seen from diffuse reflectance spectra (Fig.2) that the visible permanganate absorption band of the silver compound is very broad, weakly structured, and shifted to longer wavelengths with respect to $KMnO_4$. Furthermore, no distinct vibronic structure appears in AgMnO₄. In passing it is worth mentioning that previously measured resonance Raman spectra of AgMnO₄ reveal unusual values for both the anharmonicity constant and the harmonic vibrational frequency. The IR - frequencies are shifted to longer wavelengths in comparison to other permanganate salts Vol. 65, No. 11

These anomalies were usually interpreted in terms of a higher covalency in AgMnO₄^{5,14}.

Based upon structural informations and approximate thermochemical calculations MEHNE et al.' suggested a multicentre interaction which causes cooperative effects over many MnO₄sites due to electron delocalisation. In fact, the results of the magnetic susceptibility measurements and the overall appearence of the diffuse reflectance spectra confirm such a model at this stage of our investigations.

In conclusion it must be emphasized again that many measurements reported in the litera-

ture probably contain artefacts due to preparing and/or handling $AgMnO_4$ at higher temperatures. This is especially critical in the valuation of any magnetic data.

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