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SYNTHESIS AND MAGNETIC PROPERTIES OF A NEW 2D IONIC FERROMAGNET: THE BIS(BENZYLAMMONIUM) TETRABROMOCHROMATE(II), $(C_6H_5CH_2NH_3)_2CrBr_4$

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The bis(benzylammonium) tetrabromochromate(II), $(C_6H_5CH_2NH_3)_2CrBr_4$, has been synthesized and characterized. The compound is a new example of a 2D ionic ferromagnet, with the ordering temperature $T_c = 58$ K. The analysis of the static powder magnetic susceptibility versus temperature plot gives a value of the near-neighbour exchange constant, $J/k = 13.1$ K.

1. Introduction

$(RNH_3)_2MX_4$ (R = alkyl or aryl group, M = divalent metal ion and X = halide) is a family of layer perovskite compounds, which has received considerable attention mainly because the materials show two-dimensional physical properties [1]. In this respect the corresponding Cr(II) derivatives were not studied until recently [2] and we reported that the series of organic-intercalated salts $(RNH_3)_2CrCl_4$, where $R = C_nH_{2n+1}$, $n = 1$–12, is ferromagnetic and characterized by only two groups of sharp absorption bands, arising from quintet–triplet transitions in the visible region [3]. With the aim of synthesizing new 2D ionic ferromagnets we have carried out the synthesis of the corresponding bromide derivatives. In this paper the synthesis and the low temperature magnetic behavior of the title compound is presented.

2. Results and discussion

Since the Cr(II) compound is very sensitive to air and moisture, the synthesis and all the manipulations were carried out by Schlenk techniques under O_2-free nitrogen. To a hot solution of Cr(II) in glacial acetic acid, prepared by passing HBr gas through a suspension of finely divided Cr metal, was slowly added a stoichiometric quantity of benzylammonium bromide. On cooling, yellow-green plates of bis(benzylammonium) tetrabromochromate(II) were obtained. Calculated for $C_{14}H_{20}N_2CrBr_4$: C = 28.61%, H = 3.40%, N = 4.76%; Cr = 8.85%, Br = 54.38%. Found: C = 28.32%, H = 3.42%, N = 4.68%, Cr = 8.65%, Br = 54.08%. Preliminary X-ray powder photographs indicate that the compound is isomorphous with the corresponding chloro analogue [4] and therefore probably has a layer structure. Magnetic susceptibility measurements in the temperature range 4.2–297 K were determined by using a Faraday apparatus. The polycrystalline sample was placed inside a quartz sphere, sealed under nitrogen, with a drop of glue and suspended by a fine silica wire from a Sartorius electronic vacuum microbalance. The magnetic field and the gradient were supplied by two superconducting solenoids. The magnetization measurements were made at field strengths up to 4 T. The diffuse electronic reflectance spectra of the title compound is characterized by two sharp spin-forbidden bands similar to those observed in the corresponding chloro derivative [3]. The inverse magnetic powder susceptibility vs temperature plot of the compound is reported in fig. 1. A Curie–Weiss law $\chi = C/(T-\theta)$ is followed in the high temperature range, with Curie and Weiss constants of 3.67 and 77 K, respectively, indicating the predominant ferromagnetic character. The compound has an effective magnetic moment $\mu_{\text{eff}} = 5.4BM$, well above the spin-only value. The magnetization measurements up to 4 T, at 249 K, confirm that all the spins are in the paramagnetic state. The experimental values fit the theoretical magnetization:

$$M_{\text{at}} = \frac{Ng^2\mu_B^2S(S+1)}{3k_B(T-\theta)}H,$$

for $S = 2$, $g = 2.1$ and $\theta = 77$ K. The observed susceptibility was corrected for the diamagnetism of the constituent atoms and for temperature-independent paramagnetism. To analyse the temperature dependence

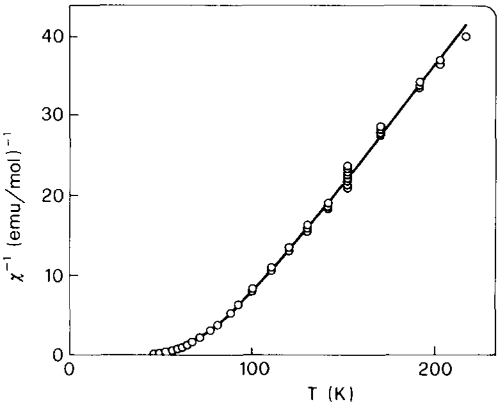

Fig. 1. Inverse molar magnetic suceptibility, χ^{-1}, of $(C_6H_5CH_2NH_3)_2CrBr_4$, as a function of temperature in the range 50–250 K. The solid line is a fit of the data to the Rushbrooke–Wood equation.

of the susceptibility at temperatures well above T_C, the Rushbrooke–Wood series expansion method has been used [5]. Writing the exchange Hamiltonian as follow:

$$H = \sum_{n,m} J\mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where the summation n,m covers all pairs of nearest-neighbour ions i, j, the susceptibility is given by a power series:

$$\frac{Ng^2\mu_B^2}{\chi J} = 3\theta + \sum_{n-1}^{\infty} \frac{C_n}{\Theta^{n-1}}. \tag{2}$$

$\Theta = k_B T/JS(S+1)$ and the coefficients C_n depend on the value of the spin S. When the exchange is ferromagnetic the C_n are multiplied by $(-1)^n$, so for $S = 2$ eq. (2) becomes:

$$\begin{aligned} Ng^2\mu_B^2/\chi = {} & \tfrac{1}{2} k_B T \\ & + J(-4 + 9x - 9.072x^2 + 55.728x^3 \\ & - 160.704x^4 + 116.640x^5), \end{aligned} \tag{3}$$

where $x = J/k_B T$.

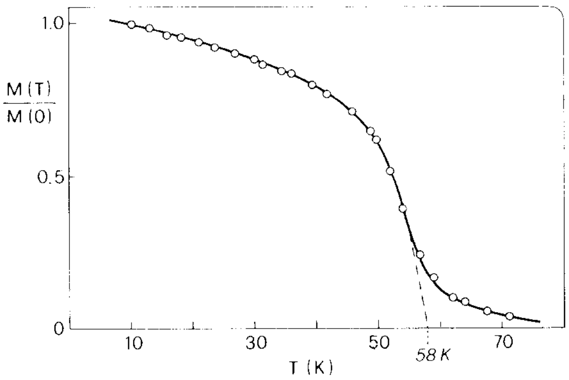

Fig. 2. Reduced magnetization versus temperature plot for $(C_6H_5CH_2NH_3)_2CrBr_4$.

Fig. 1 shows the susceptibility plotted as $1/\chi$ against temperature, together with the best fit curve calculated according to the eq. (3). The best values of J/k and g found are 13.1 K and 2.00. The reduced magnetization versus temperature plot for the title compound is shown in fig. 2.

The curve shows appreciable rounding above the spontaneous ordering temperature T_c, which is characteristic of low-dimensional magnets. It is therefore difficult to identify precisely T_c, although a reasonable estimate would be 58 K. The external applied magnetic field, i.e. 920 Oe, introduces an uncertainty in the location of the ordering temperature T_c. Previously, in the case of tetrachloroderivatives we observed that the true T_c, measured with a SQUID magnetometer and a.c. mutual inductance bridge technique, was ≈ 10 K less than that found with the Faraday method. If we compare the values, found with the same technique, we observe that there is a definite increase in the ordering temperature, passing from bis(benzylammonium) tetrachlorochromate(II) [4] to the corresponding bromide. Finally, the magnetization vs field plot, at temperatures well below T_c, shows that the compound does not saturate completely, suggesting that we are probably in presence of a canted ferromagnet.

Single-crystal X-ray studies and zero-field magnetic susceptibility measurements are in progress to elucidate these points.

[1] L.J. DeJongh and A.R. Miedema, Advan. Phys. 23 (1974) 1.

[2] C. Bellitto and P. Day, J. Chem. Soc. Chem. Commun. (1976) 870, J. Chem. Soc., Dalton Trans. (1978) 1207.

[3] C. Bellitto, T.E. Wood and P. Day, Inorg. Chem. 24 (1985) 558.

[4] C. Bellitto, T.E. Wood and P. Day, Proc. XV Italian Congress of Inorganic Chemistry, Bari (1982) 313.

[5] G.S. Rushbrooke and P.J. Wood, Molec. Phys. 1 (1958) 257, M.E. Lines, J. Phys. Chem. Solids 31 (1970) 101.