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Magnetic behavior of cobalt bromide hydrates including a deuterated form

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ABSTRACT

The magnetic properties of little examined $CoBr_2•2H_2O$ and new $CoBr_2•H_2O$ and $CoBr_2•D_2O$ are studied. Curie-Weiss fits, $\chi_M=C/(T-\theta)$, yield θ of −9.9, 9.4 and 10.0 K, respectively, over a 30–80 K linear range for each. Higher temperature data are fit assuming two moderately separated low lying Kramers doublets, with exchange accounted for in a mean-field approximation. Susceptibility maxima appear at 9.5, 15.4 and 15.5 K, with χ_{max} of 0.163, 0.375 and 0.435 emu/mol, respectively. Antiferromagnetic ordering is estimated to occur at 9.0, 13.7 and 13.8 K, in the same order. The ratio T_c/T_{max} is 0.95, 0.89 and 0.89, respectively, suggesting little low dimensional magnetic character in singly hydrated systems. Data at lower temperatures for the dihydrate are fit with an antiferromagnetic 3D-Ising model. For singly hydrated systems the large size of χ_{max} prevents this; weakened interchain antiferromagnetic interactions yield enhanced susceptibility maxima. Magnetization data exhibit field induced transitions near 13.5 kG for the dihydrate, and near 6.5 kG for singly hydrated systems with enhanced hysteresis. These transitions are interpreted as metamagnetic in nature.

1. Introduction

Standard references on the magnetism of transition metal compounds [1–3] contain many examples of 3d metal halide hydrates. Most common are di-, tetra- and hexahydrate forms. Dihydrates are the most thoroughly examined, and the most interesting regarding magnetic ordering properties at low temperatures. Among these bromides are less studied than chlorides, though often isostructural. They deserve more attention; fruitful comparisons of superexchange interactions via halide bridging ions of different size and polarizability could emerge.

We have been preparing and making magnetic measurements on bromide compounds which have been little studied or not at all relative to chloride counterparts. One recent report was concerned with several such Mn(II) compounds [4]. Two belonged to the relatively new monohydrate series, $MX_2•H_2O$, one containing D_2O in place of H_2O. The effect of deuteration on the magnetic behavior of transition metal compounds containing waters of hydration is not extensively examined. Our study of the magnetic behavior in the deuterated versions $MnCl_2•D_2O$ and $CoCl_2•D_2O$ of the earliest reported Mn(II) and Co(II) chloride monohydrates, presents important magnetic and structural comparisons as well as background for both the monohydrate series specifically and deuteration effects generally [5]. Most recently a similar series of nickel bromide hydrates was also examined [6]. In this report we present magnetic susceptibility and magnetization data for $CoBr_2•2H_2O$,$CoBr_2•H_2O$ and $CoBr_2•D_2O$.

The crystal structure of $CoBr_2•2H_2O$ is isomorphous with that of the Mn(II) bromide dihydrate [7]. Both are characterized by chemical and structural MBr_2MBr_2M... chains along the c axis of a monoclinic C2/m unit cell. The chains are not well isolated, neither structurally nor magnetically. The structure is the same as previously determined for the chloride dihydrates [8,9]. Magnetic properties of the bromide dihydrate are only modestly studied [10,11]; no susceptibility data have appeared, in contrast to the chloride dihydrate [12]. Our examination of $CoCl_2•H_2O$ [13–15] also reviews prior work on the dihydrate, while its properties are relevant for comparison with the new bromide monohydrate studied here. Powder susceptibility data on the bromide dihydrate are also worthwhile for comparison with similar data on the monohydrate.

2. Experimental

2.1. Materials and methods

In preparing $CoBr_2•2H_2O$ and $CoBr_2•H_2O$ high purity anhydrous cobalt dibromide was dissolved in deionized water and each solution placed in an oven for slow evaporation, with occasional grinding of the solid material forming in order to prevent occlusion of water. The temperature conditions for obtaining each hydrate were explored by trial and error. A temperature of 73 °C yielded the dihydrate, which is medium violet in color. To obtain the bromide monohydrate a higher temperature of 94 °C was needed; this substance is medium blue in

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color. These temperatures are comparable with those leading to the corresponding chloride hydrates. Fine grained polycrystalline material was obtained for each. Thermogravimetric analysis showed the hydration state in each case to be within 0.05 water unit of that intended (also applying to the D_2O system below). This is comparable precision to that for many other hydrated transition metal halide systems examined by us in the past.

Preparation and hydration state analysis of $CoBr_2•D_2O$ occurred in similar fashion, but with use of fully deuterated D_2O (99.8%, Acros Chemicals) as solvent in first a glove box, then a vacuum oven filled with Ar(g) for evaporation, in order to avoid contamination by atmospheric water. Trial and error determined 83 °C to be appropriate for obtaining this material; the color is a darker blue verging on purple. The temperature is virtually the same as that leading to $MnBr_2•D_2O$ [4]. As for Mn(II) compounds, somewhat lower temperatures are needed to obtain a given D_2O hydration state than for H_2O with some difference in color also apparent. Despite much effort $CoBr_2•2D_2O$ could not be reliably obtained. Data on samples with average $2D_2O$ content exhibited features implying the presence of components of different magnetic character.

2.2. Magnetic measurements

Magnetization and susceptibility measurements were made with a vibrating sample magnetometer and cryostat. Data shown are field cooled measurements except where otherwise indicated, and are corrected for the rather small effects of diamagnetism and demagnetization, and the minute contribution of the sample holder. Applied magnetic fields in susceptibility measurements range from 0.1 to 1.6 kG depending on the temperature. No field dependences of susceptibilities were seen, as expected for such modest field values. Polycrystalline samples of approximately 100 mg size were packed into nonmagnetic sample holders under dry conditions, weighed accurately, then screwed onto a nonmagnetic sample rod in immediate proximity to a calibrated Cernox resistance thermometer. Temperatures are accurate to ± 0.005–0.5 K depending on the range. Magnetic fields are accurate to ± max (2 G, 0.1%), and magnetization and susceptibility values to 1.5% absolute, with substantially better precision. In handling of the materials care was taken to minimize exposure to atmospheric water vapor.

3. Results

3.1. Magnetic susceptibilities

3.1.1. Moderate to high temperature data

The inverse molar magnetic susceptibilities of $CoBr_2•2H_2O$, $CoBr_2•H_2O$ and $CoBr_2•D_2O$ appear in Fig. 1. The data are corrected for diamagnetism (−113, −99 and -99×10^{-6} emu/mol, respectively) and demagnetization, both quite small effects. Reliably linear ranges for moderate to high temperatures are not evident, as for $CoCl_2•H_2O$ previously [14]. Instrumental effects are responsible for the highest temperature upturn in dihydrate data; such can appear absent perfect data collection, and are excluded from analysis. The range 30–80 K is the best common linear regime for all three, and Curie-Weiss form fits, $\chi_M = C/(T-\theta)$, are represented by the lines in the figure. Data below 30 K are more densely spaced and influenced by short range order effects, hence not included in the fits. Parameter values appear in Table 1. The negative θ for dihydrate contrasts markedly with the positive values for the other two systems. Via the standard relation $C = N_o g^2 \mu_B{}^2 S(S+1)/3k$, and $S = 3/2$, the corresponding g are 2.54, 2.50 and 2.51 respectively. These are plausible average g for Co(II) compounds, well above 2.0 because of orbital contributions. Assuming an effective S′= ½ (see below) the corresponding g are 5.67, 5.59 and 5.61 respectively. These are plausible average values for a highly anisotropic ground doublet [1].

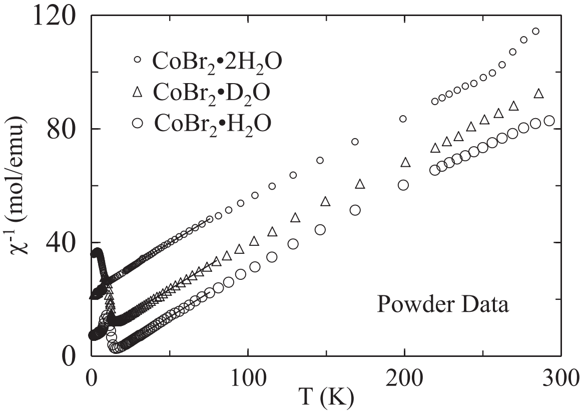

Fig. 1. Inverse molar magnetic susceptibilities vs. temperature for $CoBr_2•2H_2O$ (small circles), $CoBr_2•H_2O$ (large circles) and $CoBr_2•D_2O$ (triangles). Lines are Curie-Weiss fits described in text. For clarity triangle data are shifted up 10 mol/emu, and small circle data 20 mol/emu.

In weak octahedral coordination the crystal field ground term of Co(II) is a $^4T_{1\,g}$ level. Crystal field distortions and spin-orbit coupling split this into six Kramers doublets. Curie(-Weiss) behavior will result if only the ground doublet is significantly populated over the temperature range employed (e.g., 30–80 K here), or if temperatures are so high that any thermally accessible doublets are virtually equally populated. At sufficiently low temperature departures from such behavior occur because of short-range order resulting from exchange interactions. Spectroscopic information on doublet separations is rarely available, but values of a few hundred equivalent K are typical. We adopt here the approach applied previously [5,14] to chloride compound data, and assume that the first excited doublet is a moderate ΔE above the ground doublet, but that more excited doublets are far higher in energy and make negligible contribution to the susceptibility. Allowance is made for different g values, g_1 and g_2, characterizing the ground and excited doublets. The Van Vleck equation [2] applied to this situation, treating each of the two doublets as an effective S′= ½, yields

$$\chi \;=\; 0.0938\,\frac{g_1^2+g_2^2 e^{-\Delta E/kT}}{T(1+e^{-\Delta E/kT})} \tag{1}$$

where the numerical prefactor has dimensions emu K/mol. Exchange interactions, obviously present, are accounted for in a mean-field approximation, employing the expression [16]

$$\chi_{ex} = \chi/[1-(2zJ/N_0 g^2 \mu_B^2)\chi], \tag{2}$$

where J is a mean interaction over z neighbors, and the exchange convention $H_{ex} = -2\,J\sum_{i>j} S_i\cdot S_j$.

Susceptibility data were fit from 30 K to 300 K (250 K for dihydrate) employing Eqs. (1) and (2). The fitted curve appears in each of Figs. 2, 3 and 4, displayed in both chi and inverse chi vs T representations. Parameter values appear in Table 1. The rms fit deviations are 0.33%, 0.74% and 0.65% in the order the compounds appear in the table, and are similar to those obtained previously for chloride compounds [5,14]. The g values are plausible for such anisotropic doublets, with that for the excited doublet somewhat larger. The energy separation increases in the order $2H_2O$, D_2O, H_2O, though the variation is not large. This is also the order in which curvature in the inverse chi vs T representations increases. The zJ/k values are the same sign as the θ values. Moreover, substitution into the mean field relation [1,2]

$$\theta = 2S(S+1)zJ/3k \tag{3}$$

yields −7.5, 9.2 and 12.6 K respectively, similar to observation.

Insufficient information is available to apply any multiparameter ligand field model, also involving idealized assumptions such as tetragonal distortion. Individual Kramers doublets are variably aniso-