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Magnetism of $CuCl_2{\cdot}2D_2O$ and $CuCl_2{\cdot}2H_2O$, and of $CuBr_2{\cdot}6H_2O$

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ABSTRACT

The magnetic properties of little examined $CuCl_2{\cdot}2D_2O$ are studied and compared with those of $CuCl_2{\cdot}2H_2O$. New $CuBr_2{\cdot}6H_2O$ is also examined. Susceptibility maxima appear for chlorides at 5.35 and 5.50 K, in the above order, with estimated antiferromagnetic ordering at 4.15 and 4.25 K. Curie-Weiss fits yield g of 2.210 and 2.205, and Weiss θ of −6.0 and −4.7 K, respectively, in $\chi_M = C/(T - \theta)$. One-dimensional Heisenberg model fits to susceptibilities, including interchain exchange in a mean-field approximation, are performed. Interchain exchange is significant but much weaker than intrachain. The bromide hexahydrate strongly differs magnetically from any chloride hydrate, but exhibits notable similarities and differences compared to previously studied $CuBr_2$. A broad susceptibility maximum occurs near 218 K, only 4% lower than for $CuBr_2$, but with almost twice the magnitude. Powder X-ray diffraction data for $CuBr_2{\cdot}6H_2O$ may be best accounted for by a monoclinic unit cell that is metrically orthorhombic. The volume per formula unit is consistent with trends in metal ionic radii. However, an alternative monoclinic cell with 5% smaller volume more readily rationalizes the magnetism.

1. Introduction

While a vast array of Cu(II) compounds has been prepared and examined magnetically and crystallographically [1,2], some quite simple ones have been little studied or not at all. We have been examining various halide hydrates of the 3d transition metal ions Mn(II), Ni(II) and Co(II). Of interest have been chloride and bromide dihydrates (often isostructural, though bromides are less thoroughly studied) and monohydrates. The latter are only recently examined compared to dihydrates. Substitution of D_2O for H_2O has also been pursued. Deuteration effects on the magnetic behavior of transition metal compounds are not extensively examined, but range from very small to substantial. The hydrogen bonding which tends to occur in water containing systems, its potential sensitivity to D for H substitution, and the consequences for magnetic properties where waters coordinated to metal ions provide superexchange pathways, is of interest. Reports on the magnetic and structural characteristics of Mn(II) and Co(II) chloride monohydrates including deuterated forms [3], and more recently examined Mn(II) [4], Ni(II) [5] and Co(II) [6] bromide di- and monohydrates, revealed intriguing variations in the effect of deuteration on magnetic and structural properties.

An effort to prepare Cu(II) systems of similar type was made, but with much more limited success. The only slightly examined deuterated system $CuCl_2{\cdot}2D_2O$ is prepared and studied. More familiar $CuCl_2{\cdot}2H_2O$ is examined for comparison purposes. Small but nontrivial differences between them are observed. A previously unreported bromide hydrate, $CuBr_2{\cdot}6H_2O$, is prepared and studied. Notable similarities and differences are found relative to previously examined anhydrous $CuBr_2$ [7,8]. Powder X-ray diffraction suggests two possibilities for the crystallographic unit cell of the hexahydrate.

2. Experimental

2.1. Materials and methods

Little or no literature guidance exists concerning preparation of two of the present materials. Very crystalline reagent grade $CuCl_2{\cdot}2H_2O$ was employed for magnetic measurements; thermogravimetric analysis (TGA) confirmed the hydration state very well. Although studied before at low temperatures, it was examined in order to check the moderate to high temperature magnetic behavior compared with the deuterated system, as well as the low temperature behavior, measured on the same apparatus.

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An early aim was to prepare and study both $CuCl_2{\cdot}H_2O$ and $CuCl_2{\cdot}D_2O$. For the first an aqueous solution of the dihydrate was evaporated to dryness, with occasional grinding to avoid occlusion of water, for a wide range of oven temperatures. For the latter high purity anhydrous copper chloride was dissolved in fully deuterated D_2O (99.8%, Acros Chemicals) and the solution placed in a vacuum oven filled with Ar(g) to exclude atmospheric water vapor. Prior work had shown that the temperature for obtaining a specific hydration state of a D_2O system could differ significantly from that for the H_2O system. Despite many attempts with a wide range of oven temperatures, neither singly solvated form was obtained. However, $CuCl_2{\cdot}2D_2O$ was successfully prepared. A temperature of 63 C was suitable, with care to avoid extra oven time. The crystalline medium green solid was very similar in appearance to $CuCl_2{\cdot}2H_2O$. The solvation state was confirmed to within 0.05 D_2O per formula unit by TGA.

Another initial aim was to prepare variously hydrated, and deuterated, bromide compounds, starting with high purity anhydrous copper bromide. Much success had been met in preparing Mn(II), Ni(II) and Co(II) chlorides and bromides, monohydrate and dihydrate forms, including D_2O substituted materials. Despite much effort similar approaches largely failed for Cu(II). The only hydrate which could be obtained, after many attempts, was $CuBr_2{\cdot}6H_2O$, from evaporation of an aqueous solution near 71 C. The reflective black crystalline material analyzed very well, within 0.05 water per formula unit, as hexahydrate by TGA. Its magnetic properties have not been reported before. Instrumental limitations precluded any attempt to prepare the deuterated counterpart.

2.2. Magnetic measurements

Magnetization and susceptibility measurements were made with a variable temperature vibrating sample magnetometer system. The data shown are field cooled measurements and are corrected for the rather small effects of demagnetization and diamagnetism, including the extremely small contribution of the sample holder. Very finely ground polycrystalline samples were packed into nonmagnetic sample holders under dry conditions, accurately weighed (masses ranged from 150 to 370 mg, the last for high MWT bromide hexahydrate), screwed onto a nonmagnetic sample rod in immediate proximity to a calibrated Cernox resistance thermometer, and introduced into a cryostat helium atmosphere. Temperatures are accurate to 0.005–0.5 K depending on the range. Magnetic field values are accurate to max(2 G, 0.1%) and magnetization and susceptibility data to 1.5% absolute, with substantially better precision. By virtue of signal size, magnetic susceptibility measurements typically occurred with an applied field of 800 G for temperatures below and moderately above (to 25 K) 4.2 K, and higher fields as necessary as the temperature increased. Close proportionality of the measured moment to applied field was checked and confirmed throughout warming. The maximum field used was 6.5 kG near 300 K. For the bromide hexahydrate, with very small moment, a 6.5 kG field was employed over the whole temperature range in order to obtain a sufficiently large signal. In all handling of materials care was taken to minimize exposure to atmospheric water vapor.

2.3. Powder X-ray diffraction

In preparing an X-ray diffraction sample all handling was in a nitrogen filled glove bag. The bag was purged twice and a small dewar of liquid nitrogen was allowed to evaporate in the bag in order to minimize humidity. A few milligrams of sample were ground with an agate mortar and pestle with a drop of Paratone™ oil and the mix was spread onto a zero-diffraction quartz plate for powder XRD. The sample and plate were transferred using an air free container to a Rigaku Miniflex + powder X-ray diffractometer (Cu K-alpha) housed inside a nitrogen filled glove box (Mbraun UNIlab™). Scans were acquired at 10 data points per degree from 10 to 90 degrees 2-theta at a rate of 1 degree per minute.

Jade 6.1™ was used to perform background correction, K-alpha 2 removal, and peak finding. Peaks with a height of 2% or greater relative to the maximum peak height in the diffraction pattern were used for cell indexing. Cell indexing was completed using McMaille (version 4) software [9].

3. Results

3.1. Magnetic susceptibilities

3.1.1. $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$

Published magnetic susceptibility data for the dihydrate [10,11] are mainly at low temperatures. So high temperature data were obtained for comparison with the deuterated system. Inverse molar susceptibilities for these two compounds appear in Fig. 1. In addition to correction for diamagnetism, estimated as -84×10^{-6} emu/mol for both, correction has been made for a plausible Van Vleck temperature independent contribution of 60×10^{-6} emu/mol [2]. Correction for the very small sample holder contribution was also made. Deviations from linearity above 200 K can appear unpredictably absent perfect data taking, from the instrumental difficulty of ensuring good thermal equilibrium at higher temperatures. Such data are not included in the data fitting; the linear fit ranges are broad and high enough to yield reliable parameters. A Curie-Weiss fit line in the 30–200 K range for $CuCl_2{\cdot}2H_2O$ appears, with $C = 0.456$ emu-K/mol and $\theta = -4.7$ K, and statistical uncertainties of about 0.003 and 0.3 (same dimensions) respectively. The corresponding g is 2.205, rather characteristic of Cu(II) compounds. For $CuCl_2{\cdot}2D_2O$ the 40–200 K range is linear and the fit line shown has C and Θ values of 0.458 emu-K/mol and -6.0 K, with similar uncertainties. The corresponding g of 2.210 is again normal for Cu(II), and θ is slightly more negative than for the $2H_2O$ compound.

In Fig. 2 appear the molar susceptibilities at low temperature, along with model fit curves to be described. While very similar the two sets are not indistinguishable. The χ_{max} of 0.0328 ± 0.0004 emu/mol are virtually identical and agree very well with published data for the dihydrate [11]. However, the T_{max} are slightly but nontrivially different, 5.50 and 5.35 K, for $2H_2O$ and $2D_2O$ respectively, each ±0.05 K uncertain. For the $2H_2O$ compound our T_{max} is somewhat higher than the not very well defined value of 5.35 K inferred from less numerous data [11] which also do not

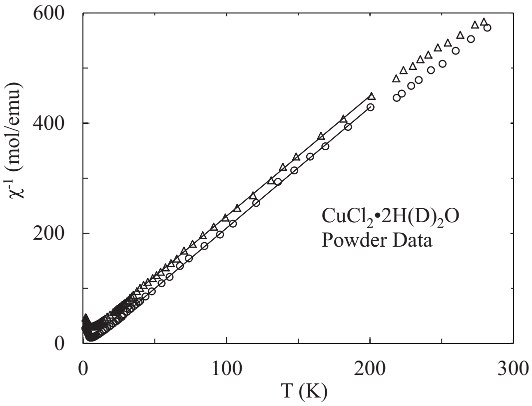

Fig. 1. Inverse molar magnetic susceptibilities vs temperature for $CuCl_2{\cdot}2H_2O$ (circles) and $CuCl_2{\cdot}2D_2O$ (triangles), with former shifted down 20 mol/emu for clarity. Curie-Weiss fits, described in text, are the straight lines.