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Magnetic Susceptibilities below 1 K. Zero-Field Splitting in $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$

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The susceptibility of $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$ has been measured parallel to the trigonal axis over the temperature interval 40 mK–4.2 K and perpendicular to that axis between 1.2 and 4.2 K. The data are fitted by the set of parameters $g_\parallel = 1.985 \pm 0.01$, $g_\perp = 1.995 \pm 0.01$, $2D/k_B = 0.53 \pm 0.02$ K, and $zJ/k_B = -0.035 \pm 0.01$ K.

The advent of the ^3He–^4He dilution refrigerator[1] has recently made temperatures below 1 K readily accessible to the experimentalist. This equipment, which makes use of the fact that mixtures of ^3He and ^4He spontaneously undergo phase separation, thus allows the investigation of particularly weak interactions. Indeed, while previous susceptibility measurements from this laboratory went as low in temperature as 1.2–1.5 K,[2,3] we are now able to measure susceptibilities more-or-less routinely down to 40 mK, a decrease in thermal energy, k_BT, of a factor of 30!

This extension of our experimental capability has allowed us to measure precisely the zero-field splitting in the new compound $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$. An earlier investigation[4] of the related compound $[Cr(NH_3)_6](ClO_4)_2Cl{\cdot}KCl$ showed that the zero-field splitting took the relatively large value of 0.35 cm^{-1} (0.50 K) at 6 K. Our results allow the unambiguous evaluation of the sign and magnitude of the zero-field splitting as 0.53 ± 0.02 K in the cesium bromide analogue. Furthermore, although the crystal structures of these materials contain linear arrays of chromium(III) ions, they are well separated, and these results show that magnetic-exchange effects are very small.

The salt $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$ is uniaxial, belongs to space group $R\bar{3}m$, and has a D_{3d} site symmetry at the chromium ion.[4] The crystals form hexagonal plates with the face normal to the crystallographic c axis, thus making unambiguous the orientation of the crystals within the measuring field. The lattice contains linear arrays of $-Cs-Br-O_3ClO-(NH_3)_3Cr(NH_3)_3-OClO_3-Br-$ units, parallel to the c axis. In the isostructural salt $[Co(NH_3)_6](ClO_4)_2Cl{\cdot}KCl$ the cobalt atoms in the chain are separated by the c-axis dimension of 27.173 Å; the shortest distance between cobalt atoms in neighboring chains is 9.910 Å. One can safely anticipate that these distances are similar or even larger in the salt under study here.

Experimental Section

Well-formed single crystals were kindly supplied to us by Professor E. I. Solomon.

The complex differential susceptibility parallel to the threefold or c axis of $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$ has been measured between 0.040 and 4.2 K from the change in the mutual inductance between a primary and secondary coil induced by a change in the magnetization of the sample. Measurements perpendicular to the threefold axis were limited to the ^4He region. Sample weights ranged between 40 and 75 mg. Temperatures down to 40 mK were obtained by using a S.H.E. Model DRI-40/4000 ^3He–^4He dilution refrigerator. Details of the experiments performed in this apparatus are briefly described here, as well as in more detail elsewhere.[5] The apparatus used in the ^4He-temperature-region experiments has been described previously.[2,3]

The detection of changes in the mutual inductance between the primary and secondary coils (which is proportional to susceptibility changes in the sample) between 0.040 and 2 K is achieved through use of a low-impedance ac bridge in which a superconducting quantum interference device (SQUID) is used as a null detector. The measurements presented here were obtained by using an excitation voltage frequency of 16 Hz. The maximum excitation current through the primary coil is approximately 0.2 mA, which implies a maximum oscillating field of only 10 mOe. The coils are wound from superconducting wire, and a superconducting shield surrounds the coil system in order to exclude stray external fields. Temperature variation is achieved through electronic control of a resistance heater mounted on the dilution refrigerator mixing chamber to which the coil system is thermally anchored. The sample temperature is determined by means of a calibrated germanium thermometer, which is mounted on the outside of the mixing chamber. The data are converted from bridge readings to susceptibility values (in emu/mol) by matching of the data between 1 and 2 K with those obtained independently in the liquid-^4He apparatus. The accuracy of the absolute susceptibilities is estimated to ~1% above 1 K and gradually decreases to ~3% at 40 mK although the precision at the lower temperatures is substantially better.

Results

The measured susceptibilities are displayed in Figures 1 and 2 as data points. The parallel susceptibility displays, at high temperatures, Curie–Weiss behavior and, then, with lower temperatures, an unusual feature of an incipient broad maximum which begins to develop at about 300 mK. The susceptibility then increases and appears to be diverging at the lowest temperature of 40 mK. The perpendicular susceptibility obeys the Curie–Weiss law over the measured temperature interval.

The displayed curves were calculated according to the following procedures. The ground state of chromium(III) in an octahedral environment[6] is $^4A_2$. The degeneracy of this spin-$^3/_2$ system may be partially resolved into its $m_s = |\pm^1/_2\rangle$ and $|\pm^3/_2\rangle$ components by the presence of a small axial crystalline field. The separation is denoted by $2D/k_B$, where D has both sign and magnitude and k_B is Boltzmann's constant.

The spin-Hamiltonian appropriate to a system with axial symmetry is

$$\mathcal{H} = g_z\mu_B H_z S_z + g_\perp\mu_B H_\perp S_\perp + D[S_z^2 - \tfrac{1}{3}S(S+1)] \quad (1)$$

where μ_B denotes the Bohr magneton. The energy levels resulting are, for $H \| z$

$$E_{3/2,-1/2} = \tfrac{1}{2}g_z\mu_B H \pm (D + g_z\mu_B H) \quad (2)$$

$$E_{-3/2,1/2} = -\tfrac{1}{2}g_z\mu_B H \pm (D - g_z\mu_B H) \quad (3)$$

and for $H \perp z$

$$E_{3/2,-1/2} = \tfrac{1}{2}g_\perp\mu_B H \pm (g_\perp^2\mu_B^2H^2 + D^2 - g_\perp\mu_B HD)^{1/2} \quad (4)$$

$$E_{1/2,-3/2} = -\tfrac{1}{2}g_\perp\mu_B H \pm (g_\perp^2\mu_B^2H^2 + D^2 + g_\perp\mu_B HD)^{1/2} \quad (5)$$

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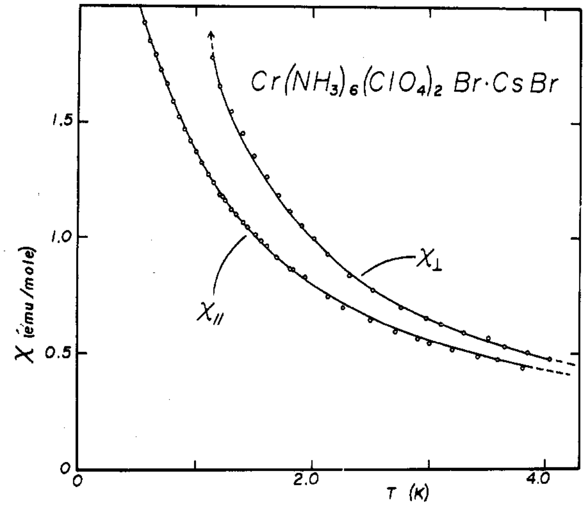

Figure 1. Single-crystal magnetic susceptibilities of $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$ above 1.2 K. The points are experimental, and the curves are fitted as described in the text.

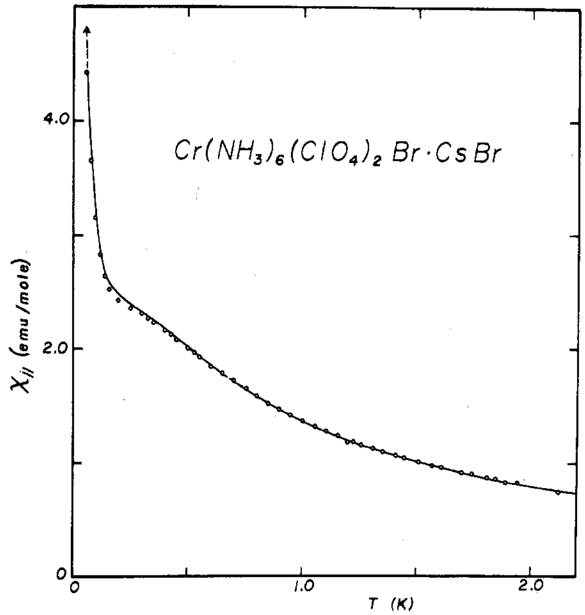

Figure 2. Parallel susceptibility of $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$ at low temperatures. The points are experimental, and the curves are fitted as described in the text.

In each case, the plus sign before the parentheses refers to the first indicated energy level.

In the limit of small $g_\perp\mu_BH/D$, eq 4 and 5 may be written in more tractable form as

$$E_{3/2,-1/2} = \tfrac{1}{2}g_\perp\mu_BH \pm \left(D - \tfrac{1}{2}g_\perp\mu_BH + \frac{3g_\perp{}^2\mu_B{}^2H^2}{8D}\right) \tag{6}$$

$$E_{1/2,-3/2} = -\tfrac{1}{2}g_\perp\mu_BH \pm \left(D + \tfrac{1}{2}g_\perp\mu_BH + \frac{3g_\perp{}^2\mu_B{}^2H^2}{8D}\right) \tag{7}$$

With use of these energy levels to construct the partition functions Z_i ($i = \|, \perp$), the molar susceptibility χ_i may be calculated from the standard relationship

$$\chi_i = \frac{N_0k_BT}{H_i}\left(\frac{\partial \ln Z_i}{\partial H_i}\right) \tag{8}$$

where N_0 is Avogadro's number, T is the absolute temperature, and H_i refers to either the parallel or perpendicular orientation of the external measuring field. The derived susceptibilities for the two directions are

$$\chi_\| = \frac{N_0g_z{}^2\mu_B{}^2}{4k_BT}\left(\frac{1 + 9\exp(-2D/k_BT)}{1 + \exp(-2D/k_BT)}\right) \tag{9}$$

$$\chi_\perp = \frac{N_0g_\perp{}^2\mu_B{}^2}{k_BT}[1 + \exp(-2D/k_BT)]^{-1} + \frac{3N_0g_\perp{}^2\mu_B{}^2\tanh(D/k_BT)}{4D} \tag{10}$$

These equations have been applied[7] to a study of antiferromagnetism in the more complicated case of the chromium alums. However, to our knowledge, these equations have not previously been applied to experimental data on a chromium(III) compound with uniaxial symmetry.

Finally, although magnetic ordering has not been observed in this system, it was found to be necessary to correct the paramagnetic susceptibility for subcritical exchange effects. In a molecular field treatment[8] this results in the relationship for the corrected susceptibility χ_i' of

$$\chi_i' = \frac{\chi_i}{1 - (2zJ/N_0g_i{}^2\mu_B{}^2)\chi_i} \tag{11}$$

where $i = \|$ or $\perp$ and zJ measures the exchange interaction.

The resulting best fits, which are the curves drawn in the figures, yield the parameters $2D/k_B = 0.53 \pm 0.02$ K, $zJ/k_B = -0.035 \pm 0.01$ K, $g_z = 1.985 \pm 0.01$, and $g_\perp = 1.995 \pm 0.01$. The exchange correction is antiferromagnetic in sign. The perpendicular susceptibility above 1.1 K is not sensitive to small variations in the value of D/k_B, and thus the value reported results primarily from the fit to the parallel susceptibility. On the other hand, the relatively large absolute value of $\chi_\perp$ results in this data set being quite sensitive to the magnitude of the exchange correction. Indeed, the best fit to $\chi_\perp$ was obtained with zJ/k_B of 0.00 K, with a rather small uncertainty of ± 0.005 K.

Attempts were made to fit $\chi_\|$ with the exchange correction set equal to zero, and a good fit could thus be obtained above 250 mK, with $2D/k_B = 0.62$ K. However, this fit was quite poor below 250 mK, where $\chi_\|$ rises rapidly and therefore becomes quite sensitive to the exchange correction.

Discussion

The behavior of $\chi_\|$, which appears at first glance to be unusual, is readily explained within the context of the usual electronic structure of chromium(III) complexes. Although our measurements extend to quite low temperatures, it was not found necessary to include a contribution to the susceptibility from dipole–dipole interactions. This is in accord with the crystallographic results, for the shortest metal–metal distance is close to 10 Å.

The EPR spectrum of chromium(III) doped into $[Co(NH_3)_6](ClO_4)_2Cl{\cdot}KCl$ was observed by Wilson and Solomon[4] to yield a zero-field splitting of 0.43 K at 150 K. This value was found to increase with decreasing temperature and ultimately to approach the value of 0.50 K at low temperatures. The latter value was obtained from the spectral behavior of the pure chromium compound. The quantitative agreement of these independent estimates of $2D/k_B$ with that value derived from $\chi_\|$ lends important corroborative evidence favoring the inclusion of the antiferromagnetic-exchange correction.

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Without that correction the derived $2D/k_B$ is too large. Nevertheless, the magnetic ions in this crystal are so far apart that it should come as no surprise that the superexchange interactions are so very weak.

The observed g values are typical of those found with chromium(III). It is not clear what significance, if any, should be attached to the lack of an exchange correction to the fit of the perpendicular-susceptibility data. It was judged not worthwhile to extend the measurement of $\chi_\perp$ to lower temperatures.

In conclusion, the analysis of low-temperature magnetic susceptibility measurements has been shown to be a powerful technique for the precise determination of ground-state zero-field splittings of the magnitude commonly observed in chromium(III) complexes.

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Metal–Hydrogen Stretching Frequencies from μ_3-Bridged Metal Hydride Cluster Complexes and Hydrogen Adsorbed on Metal Surfaces

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Metal–hydrogen stretching frequencies of μ_3-bridging hydrogen ligands have been determined from the infrared spectra of a number of metal hydride cluster complexes. A vibrational model is described which suggests that the ratio of the antisymmetric and symmetric M–H stretching frequencies is related simply to the angular disposition of the three M–H bonds. This model is equally applicable to the study of hydrogen atoms adsorbed on metal surfaces.

Introduction

In recent papers the vibrational frequencies associated with the metal–hydrogen stretching modes of μ_2-bridging[1,2] and interstitial[3] hydrogen ligands in metal cluster complexes have been described. Of the various types of hydrogen ligand environment encountered in metal clusters, that which is least satisfactorily characterized by vibrational spectroscopy, or indeed by any technique, is the μ_3-bridged site. Here we report the infrared absorption frequencies corresponding to the vibrations of μ_3-bridging hydride ligands in a number of metal hydride cluster complexes, and a vibrational model is developed which leads to a simple relationship between the M–H stretching frequencies and the M_3H geometry.

Few hydrogen ligands in μ_3-bridged sites have been directly located by diffraction techniques. Of the complexes considered here only for $H_4Co_4(\pi\text{-}C_5H_5)_4$ have hydrogen positions been determined; the hydride ligands have been located by X-ray diffraction ca. 0.8 Å above the centers of the four Co_3 faces.[4] Although some early controversy surrounded their structures, it now seems likely that a similar hydrogen environment exists in the mixed-metal clusters $HMCo_3(CO)_{12}$ (M = Fe, Ru, and Os), by analogy with the structure of the phosphite derivative $HFeCo_3(CO)_9(P(OCH_3)_3)_3$, where the hydrogen ligand has been shown by the more accurate neutron diffraction study to be situated ca. 0.98 Å above the center of the Co_3 triangle.[5-8] Evidence for μ_3-bridged environments in the other complexes is less direct and derives from observations of enlarged M_3 faces and "swept-back" carbonyl ligands.[9,10]

Theory of the Vibrational Model

The three vibrational modes of a μ_3-bridging hydrogen ligand in a pyramidal C_{3v} environment comprise a nondegenerate symmetric M–H stretching mode, $\nu_{MH}{}^{sym}$, and a doubly degenerate antisymmetric M–H stretching mode, $\nu_{MH}{}^{asym}$. In the extreme case of the hydrogen atom lying in the plane of the three metal atoms, D_{3h} symmetry, the vibrations would become a nondegenerate out-of-plane deformation and a doubly degenerate M–H stretching mode. The observed vibrational frequencies are thus expected to be somewhat sensitive to the separation of the hydrogen ligand from the plane of the metal atoms. If we take the standard vibration equations for a pyramidal M_3H molecule (see, for example, ref 11a) using a central force field, and introduce the approximation that the M–M stretching frequencies are very much lower than the M–H stretching frequencies, we obtain expressions 1 and 2 for the two M–H stretching fre-

$$\nu_{MH}{}^{sym} = [(1 + 3m_M \cos^2 \beta/m_H)(k_r/m_M)]^{1/2}/2\pi c \qquad (1)$$

$$\nu_{MH}{}^{asym} = [(1 + 3m_M \sin^2 \beta/2m_H)(k_r/m_M)]^{1/2}/2\pi c \qquad (2)$$

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