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Large Zero-Field Splitting in $Cs_3VCl_6 \cdot 3H_2O$

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The new compound $Cs_3VCl_6 \cdot 3H_2O$ was recently prepared[1] by McCarthy, who is carrying out an extensive spectroscopic investigation of it. The crystal structure is as yet unknown, but reasoning by analogy with such compounds[2] as $VCl_3 \cdot 6H_2O$ and $Cs_2VCl_5 \cdot 4H_2O$, combined with the results of McCarthy,[1] suggests that it is likely that the chromophore consists of an ion such as $[VCl_4(OH_2)_2]^-$ or $[VCl_5(OH_2)]^{2-}$. Of more interest for the current investigation is the fact that the crystal belongs to an orthorhombic space group, which allows a ready orientation for the measurement of the principal crystal axis magnetic susceptibilities. Our interest in the compound lies with the determination of the electronic structure of its ground state and especially the sign and magnitude of the zero-field splitting. The endeavor follows our earlier investigations of $[C(NH_2)_3]V(SO_4)_2 \cdot 6H_2O$[3] and $V(urea)_6Br_3 \cdot 3H_2O$.[4]

Experimental Section

Strongly dichroic crystals of $Cs_3VCl_6 \cdot 3H_2O$ were provided to us by McCarthy; they were grown from an aqueous solution of CsCl, VCl_3, and HCl. The orthorhombic crystals, with two molecules in the unit cell, probably belong to the space group *Imm*2.[1] Orientation of the crystal was easily accomplished by microscopy. The rhombs appear green in one direction when observed with plane-polarized light perpendicular to the long axis of the crystal, and this defines our parallel orientation. The crystals appear brown in the other two orthogonal orientations, and this defines our perpendicular orientation.

Isothermal susceptibilities were measured between 1.5 and 20 K by procedures which have been described previously.[5] Susceptibilities were measured along all three crystallographic axes, with the two perpendicular measurements coincident within experimental error.

Results

Trivalent vanadium, with a $^3A_2$ ground state in an axial field, is described by the usual spin Hamiltonian for $S = 1$

$$\mathcal{H} = g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B[H_x S_x + H_y S_y] + D[S_z^2 - {}^1/_3 S(S+1)] \qquad (1)$$

The set of energy levels resulting from this Hamiltonian is, for positive D, a doublet above a singlet, as is illustrated in Figure 1. Expressions 2 and 3 are obtained for the susceptibilities from the Hamiltonian.

$$\chi_{\parallel} = \frac{2Ng_{\parallel}^2\mu_B^2}{kT}\exp(-D/kT)[1 + 2\exp(-D/kT)]^{-1} \qquad (2)$$

$$\chi_{\perp} = \frac{2Ng_{\perp}^2\mu_B^2}{D}[1 - \exp(-D/kT)][1 + 2\exp(-D/kT)]^{-1} \qquad (3)$$

The measured susceptibilities are reported in Figure 2, along with the best simultaneous fit to eq 2 and 3. The resulting fit was better than the experimental error, and the best fit parameters are $g_{\parallel} = 1.93 \pm 0.02$, $g_{\perp} = 1.74 \pm 0.02$, and $D/k = 11.6 \pm 0.1$ K ($8.05\ cm^{-1}$). This best fit also required the addition of a high-frequency or temperature-independent paramagnetism term (TIP) of 0.008 ± 0.002 (∥) and 0.012 ± 0.002 (⊥) emu/mol. The presence of a TIP term was suggested by the fact that $\chi_{\parallel}$ does not appear to be approaching zero as the temperature goes to zero, as required by eq 2.

It is of interest to point out that these results require that the molecular magnetic z axes in this compound have the same orientation with respect to the crystal axes.

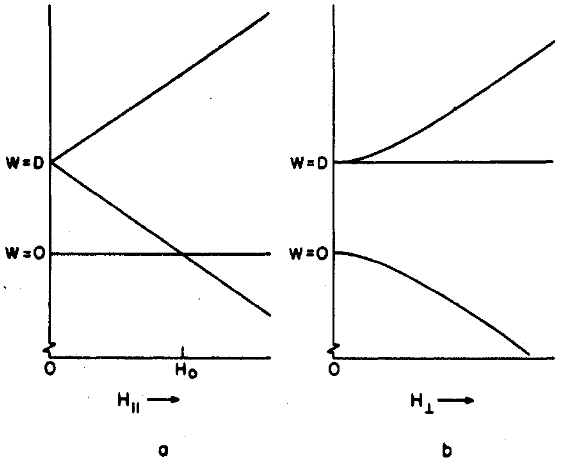

Figure 1. Lowest energy levels of V(III) and Ni(II) in axial crystalline fields as a function of external magnetic field parallel (a) and perpendicular (b) to the principal molecular magnetic axes.

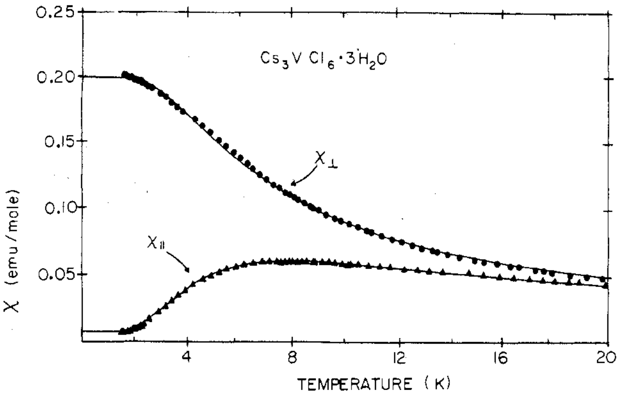

Figure 2. Parallel and perpendicular magnetic susceptibilities of $Cs_3VCl_6 \cdot 3H_2O$ at low temperatures. The points are experimental, and the curves are the best fits to the data, as described in the text.

Discussion

The above zero-field splitting is by far the largest yet measured for vanadium(III) in a pure compound. A value of $D/k = 8.5$ K was earlier observed[4] for $V(urea)_6Br_3 \cdot 3H_2O$, while 5.39 and 7.1 K were obtained, respectively, in the analyses of $[C(NH_2)_3]V(SO_4)_2 \cdot 6H_2O$[3] and $NH_4V(SO_4)_2 \cdot 12H_2O$.[6] The largest reported value for D is that for V^{3+} diluted by Al_2O_3,[7] with a value of $8.25 \pm 0.02\ cm^{-1}$ (11.88 K), although other workers[8] suggested that D is actually $8.06 \pm 0.15\ cm^{-1}$ (11.61 K) for this system. This short list in fact comprises all the zero-field splittings reported for vanadium(III) to date, and what may be significant but is certainly intriguing is that not only are they quite large values but also they are all positive with the spin doublet above the singlet. Both positive and negative values of D occur for divalent octahedral nickel,[9] which likewise has a $^3A_2$ ground state. The sign of D is important for this compound when further measurements are made at low temperatures in a magnetic field, as will be discussed below.

Antiferromagnetic interactions are expected to be weak in this compound. All of the spin degeneracy resides in the spin doublet which is nearly 12 K above the ground state. Comparison of this D with exchange terms for a variety of other hydrated halides of the transition metals[10] suggests that the exchange constant J should be smaller by at least an order of magnitude, and by the criterion of Moriya,[11] long-range antiferromagnetic ordering is therefore not possible. In other words, all of the magnetic entropy can be removed by depopulation of the $|\pm 1\rangle$ level as the temperature decreases, without the necessary intervention of other ordering processes. Nevertheless, the possibility persisted that subcritical antiferromagnetic interactions such as described by Moriya[11] and others[12] might be found in $Cs_3VCl_6{\cdot}3H_2O$. These interactions only appear in a measurement involving a magnetic field, such as the susceptibility but not the specific heat, and have been observed in a number of nickel compounds with large zero-field splittings, such as $NiSnCl_6{\cdot}6H_2O$[13] and $[Ni(C_5H_5NO)_6](ClO_4)_2$.[14] In fact, the fit did not improve significantly when eq 2 and 3 were corrected to allow for such a molecular field interaction, and the fit was judged inferior to that when the TIP term was added instead.

Calculations on trivalent vanadium have appeared[15] which lend credence to the presence of a TIP term. It arises from the mixing of the $^3E(^3T_1)$ level with the ground state; the excited level is expected to be of the order of 1000 cm^{-1} above the $^3A_2(^3T_1)$ state which is the main contributor to the magnetic susceptibility.

Another interesting aspect of this compound which remains to be explored experimentally, as mentioned above, concerns its behavior in an external magnetic field. As the present data show, the z principal axes of the two molecules in the unit cell have the same orientation with respect to the parallel or green axis, which then allows these molecular axes to be aligned parallel to an external field. As the field is turned on, the $m = \pm 1$ levels will diverge linearly in this orientation, Figure 1a, while the $m = 0$ level will remain essentially unchanged in energy. One can then calculate that the $|0\rangle$ and $|-1\rangle$ levels should cross at some $H_0 = 90$ kOe, which then provides a doubly degenerate ground state of effective spin $-\,^1/_2$ at $H_{\mathrm{eff}} = 0$. If the orientation were not so favorable, divergence of the levels, as in Figure 1b, would occur instead. Determination of the magnetization in high fields, such as recently carried out on $[C(NH_2)_3]V(SO_4)_2{\cdot}6H_2O$[16] and $FeSiF_6{\cdot}6H_2O$,[17] then allows a direct evaluation of the zero-field splitting. Furthermore, magnetic ordering may then take place at H_0 at some temperature of the order of the exchange interaction J/k between the metal ions, whereas magnetic ordering otherwise does not take place at $H_0 = 0$. Experiments of this type have been reported for $Cu(NO_3)_2{\cdot}2.5H_2O$[18] and are currently being carried out on $Cs_3VCl_6{\cdot}3H_2O$.

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Concerted Base Hydrolysis Bailar Inversion of Λ-Dichlorobis(ethylenediamine)cobalt(III). A Circular Dichroism Study[1]

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Several years ago Dittmar and Archer[2] reported that the inversion reaction

$$\Lambda\text{-}Co(en)_2Cl_2^+ \xrightarrow{2OH^-} (\Delta > \Lambda)\text{-}Co(en)_2(OH)_2^+ + 2Cl^- \tag{1}$$

is concerted because the reactions

$$\Lambda\text{-}Co(en)_2(OH)Cl^+ \xrightarrow{OH^-} (\Lambda > \Delta)\text{-}Co(en)_2(OH)_2^+ + Cl^- \tag{2}$$

and

$$\Lambda\text{-}Co(en)_2Cl_2^+ \xrightarrow{OH^-} (\Lambda > \Delta)\text{-}Co(en)_2(OH)Cl^+ + Cl^- \tag{3}$$

both go with a predominance of retention (for the cis ion formed—actually (3) gives trans > cis). Whereas analysis of reactions 1 and 2 was clear-cut with or without multicomponent spectral analysis, the stereochemical analysis of reaction 3 relied upon concurrent polarimetric and multicomponent spectral results. The results were internally consistent, but in the analogous base hydrolysis of the corresponding *trans*-$Co(en)_2(OH)Cl^+$ ion, the multicomponent analysis proved to be fallible.[3] Slight errors in extinction coefficients or a minor impurity caused an error of up to 7% in the product analysis of the trans reaction. Therefore, with the availability of high-precision circular dichroism instrumentation in our laboratory[4] we decided to investigate the chirality of this system, the silver-free base hydrolysis analogue of the classic Bailar inversion reaction.[5] Actually all base hydrolysis products are studied as the aqua species obtained through acid quenching of the reactions.

Experimental Section

Syntheses. The complexes were prepared and resolved according to reported procedures: Λ-*cis*-$[Co(en)_2Cl_2]Cl{\cdot}H_2O$,[6] Λ-*cis*-$[Co(en)_2(H_2O)Cl]Br_2{\cdot}H_2O$,[7,8] and Λ-$[Co(en)_2CO_3]ClO_4$.[7] The last was converted to Λ-*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ in cold 0.5 M $HClO_4$, a reaction known to be completely stereoretentive.[9]

Anal. Calcd for $Co(C_2H_8N_2)_2Cl_3{\cdot}H_2O$: C, 15.8; H, 6.0; N, 18.5. Found:[10] C, 16.1; H, 6.2; N, 18.2. Calcd for $Co(C_2H_8N_2)_2Cl(H_2O)Br_2{\cdot}H_2O$: C, 11.7; H, 4.9; N, 13.6. Found: C, 11.8; H, 4.8; N, 13.3. Calcd for $Co(C_2H_8N_2)_2CO_3ClO_4$: C, 17.7; H, 4.6; N, 16.5. Found: C, 17.2; H, 4.6; N, 16.4.

All reaction vessels, deionized deaerated water, chemicals, solutions, and transfer syringes and pipets were maintained at 0 °C for 2 h prior to use. The dissolution of samples, the quenching of reactions, and chromatographic separations were all conducted in a 0 °C bath surrounded by air at <5 °C. Replicate experiments were performed under all relevant conditions. A typical base hydrolysis experiment follows. Λ-$[Co(en)_2Cl_2]Cl{\cdot}H_2O$ (30 mg, 10^{-4} mol) dissolved in 4 ml of water was rapidly mixed with 1 ml of 1 M NaOH. After 15 s of vigorous shaking, the reaction was quenched with 10 ml of 0.5 M $HClO_4$ solution. The final volume was adjusted to 25 ml with water. A circular dichroism spectrum of the total solution was measured and ion-exchange separation of $Co(en)_2Cl_2^+$ and $Co(en)_2(H_2O)Cl^{2+}$ from $Co(en)_2(H_2O)_2^{3+}$ was accomplished on Dowex 50W-X8, 20–50 mesh, pretreated with 2 M $NaClO_4$ at pH 1.0 (adjusted with $HClO_4$). Ten milliliters of the solution was passed through the column and eluted with 10 ml of 2 M $NaClO_4$ acidified (pH 1.0) solution. A circular dichroism spectrum of the eluent was obtained. (Further elution with more acidified $NaClO_4$ produced no further spectral changes.)

Analogous reactions were studied with Λ-$Co(en)_2Cl(OH)^+$, i.e., Λ-$Co(en)_2(H_2O)Cl^{2+}$ in strongly basic solutions.

Circular Dichroism Spectra. The circular dichroism (CD) spectra of the optically active complexes were measured on a Cary 60