The corresponding molybdenum and chromium compounds fail to emit. One important difference in these compounds is their lack of prominent shoulders on the 400-nm absorption band (Figure 1). Assuming effective C_{4v} symmetry and a relatively weak axial ligand field, the intense absorption at ~400 nm is assigned as the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1)$ transition.[12] The heavy-metal effect[13] leads us to assign the low-energy shoulder in the tungsten compounds as the corresponding singlet → triplet absorption. The metal effect as well as the overlap of the emission and absorption are consistent with assigning the emission as the $^3E(e^3b_2^2a_1) \rightarrow {}^1A_1(e^4b_2^2)$ transition. An emission lifetime has not been measured, but emission could not be seen when using a chopper.[14] Triplet lifetimes of d^6 systems are often short,[15] and with the large spin-orbit coupling in tungsten we expect fast radiative decay.

The fact that the emitting state is of the same energy for the $W(CO)_5(L)$ complexes strongly suggests that the axial ligand field is dominated by the CO trans to L. Such dominance by strongly π-bonding axial ligands in tetragonal complexes has been noted previously[16] in reference to electronic absorption spectra. In the present case the effect is particularly striking because of the similarity of free $W(CO)_5$ and $W(CO)_5(L)$. However, the emission intensity data given in Table II demonstrate that the ligand L does play an important role in relative rates of nonradiative and radiative decay. The role of the ligand here is twofold: (1) the ligand apparently can stabilize the C_{4v} $W(CO)_5$ group, *cf.* $W(CO)_5$ *vs.* $W(CO)_5(NEt_3)$; and (2) the ligand can provide facile nonradiative decay pathways such as high-energy vibrational modes or chemical reaction, *cf.* $W(CO)_5(NH_3)$ *vs.* $W(CO)_5(NEt_3)$ and $W(CO)_5$(pyridine) *vs.* $W(CO)_5$(*trans*-2-styrylpyridine).[17]

Table II. Emission Intensities for Some $W(CO)_5(L)$ Complexes

Complex	Intensity[a]
$W(CO)_5$	Weak
$W(CO)_5(NH_3)$	Weak
$W(CO)_5(NEt_3)$	Strong
$W(CO)_5$(pyridine)	Strong
$W(CO)_5$(*trans*-2-styrylpyridine)	*b*

[a] Under similar, but not, identical conditions. [b] No emission detectable.

Acknowledgment. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF OSR-71-1958), and the Army Research Office—Durham.

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[14] Samples with lifetimes $\geq 10^{-3}$ sec could have been easily observed.

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Received June 21, 1971

Zero-Field Splitting in Hexaureavanadium(III) Bromide Trihydrate

Sir:

The measurement of specific heats at low temperatures offers an important and unambiguous method for the determination of relatively large zero-field splittings in paramagnetic systems, for the sign as well as the magnitude of the splitting may be determined. The present report, the first attempt to determine the zero-field splitting in $V(urea)_6Br_3 \cdot 3H_2O$ (I), presents an example of this procedure. This molecule, with a $^3A_2$ ground state,[1] suffers a trigonal distortion which may be described by the zero-field spin Hamiltonian ($S = 1$)

$$\mathcal{H} = D[S_z^2 - (1/3)S(S + 1)] + E(S_x^2 - S_y^2)$$

The resulting set of energy levels may be used, following standard procedures,[2] to calculate the magnetic contribution to the specific heat.

The specific heat of a 5.819-g single-crystal sample[3] of I is displayed in Figure 1. Measurements were made by the method of discontinuous heating, and temperatures were measured with a calibrated germanium resistance thermometer. The specific heat of the isomorphous[1,4] $Fe(urea)_6Cl_3 \cdot 3H_2O$ (II),[5] which was measured from 4.5 to 30°K, offered no indication of a magnetic contribution to the specific heat; this was anticipated, as the small zero-field splitting of the ^6S ion should not contribute a Schottky term in this temperature region, and cooperative magnetic effects should be important only at lower temperatures. Thus,

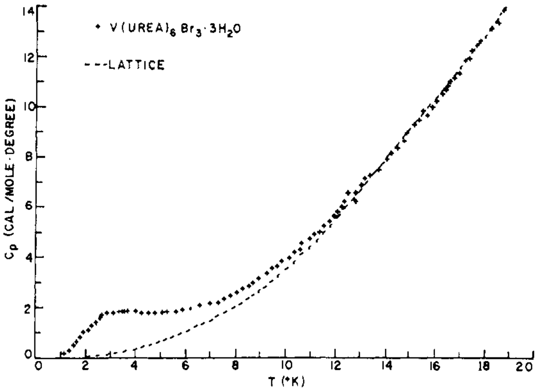

Figure 1. The measured specific heat of $V(urea)_6Br_3 \cdot 3H_2O$. Fewer than 10% of the experimental points below 6° are illustrated here. The dashed curve indicates the lattice contribution as estimated by the corresponding-states procedure.

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[1] R. Dingle, P. J. McCarthy, and C. J. Ballhausen, *J. Chem. Phys.* **50**, 1957 (1969). These authors investigated "$V(urea)_6Br_3$," but an elemental analysis was not provided for this material. Conversations with Dr. Dingle and Professor Ballhausen suggest that in all probability the substance discussed in this reference is the same as the compound reported here.

[2] E. S. R. Gopal, "Specific Heats at Low Temperatures," Plenum Press, New York, N. Y., 1966.

[3] *Anal.* Calcd: V, 7.22; Br, 34.02; C, 10.21; H, 4.25; N, 23.84. Found: V, 7.04; Br, 35.43; C, 10.05; H, 4.19; N, 23.80.

[4] Y. Okaya, R. Pepinsky, Y. Takeuchi, H. Kuroya, A. Shimada, P. Gallitelli, N. Stemple, and A. Beevers, *Acta Crystallogr.*, **10,** 798 (1957).

[5] A 4.621-g single crystal. *Anal.* Calcd: Fe, 9.69; Cl, 18.45; C, 12.49; H, 5.24; N, 29.15. Found: Fe, 9.63; Cl, 18.9; C, 12.59; H, 4.56; N, 29.30.

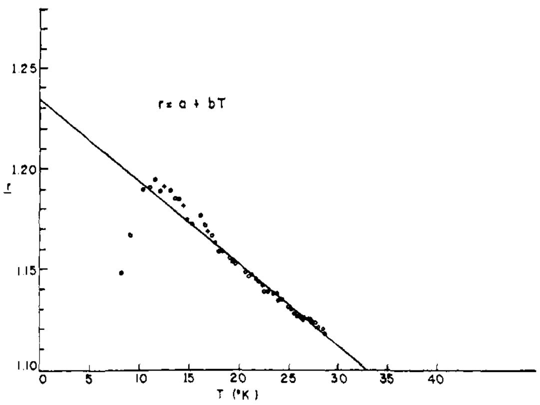

Figure 2. The plot of experimentally determined values of r *vs.* the temperature of the lattice of the vanadium compound.

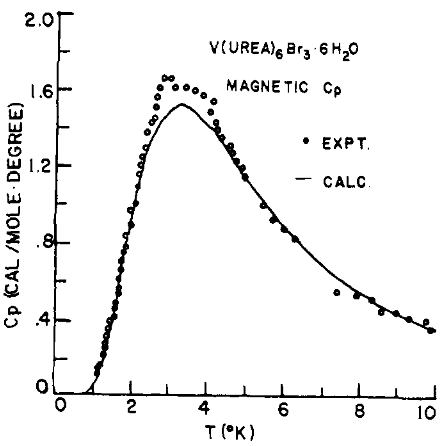

Figure 3. The derived magnetic specific heat of I, along with the fit to the spin Hamiltonian.

it was assumed that the vibrational contributions to the entropy and heat capacity of the vanadium and iron compounds are similar, and obey a law of corresponding states.

Following the procedures of Stout and Catalano,[6] a graphical method is used to relate the entropy of II, which is taken to furnish only a nonmagnetic lattice, to that of I. The quantity C_p/T *vs.* T was plotted for both compounds, smooth curves were drawn through the data, and the entropy was evaluated by graphical integration. The entropy of II was then plotted directly *vs.* T, but a magnetic contribution of $R \ln 3$ was subtracted from the data on I before these data were plotted on the same chart. One finds the temperature T', where $S(\text{II}, T')$ is equal to the corrected $S(\text{I}, T)$. The ratio T'/T is denoted by r. When r fits a prescribed function over a large temperature interval, the lattice entropy alone is changing in that region. It was assumed that, at high enough temperatures, r would take the linear form $a + bT$. The ratio T'/T was evaluated every 0.25 cal/(mol deg) on the entropy axis and plotted *vs.* T. The best straight line through all points above 15°K was found with $a = 1.234$, $b = -4.08 \times 10^{-3}$; the fact that a is large compared to 1 may be because a chloride compound is being compared to a compound containing the much heavier bromide ion, and the value of b illustrates the very small temperature dependence of r. Points below 15° were ignored because there is still a significant amount of magnetic entropy left in the vanadium sample, as shown by the curvature in r in this temperature region. A plot of r determined as described above is shown in Figure 2.

The lattice specific heat of I is then

$$C_p(\text{lat, I}, T) = C_p(\text{II}, rT)\left[1 + \frac{\mathrm{d} \ln r}{\mathrm{d} \ln T}\right] = C_p(\text{II}, rT)[1 + bT/(a + bT)]$$

Above 4.5°, the data from II are used directly in the above relationship to obtain the lattice contribution for I. Below this temperature the function $C_p = \alpha T^n$, with $\alpha = 2.72 \times 10^{-3}$ and $n = 3.08$, and where C_p has units of calories per mole per degree is used to represent the iron data; these parameters were found from a log–log plot of the iron data between 4.5 and 9°K.

The calculated lattice is subtracted from the measured data on I to yield the derived magnetic heat capacity of the vanadium compound, which is illustrated in Figure 3. The data can be fit quite well within the experimental error of 0.1 cal/(mol deg), with $D/k = 8.5 \pm 0.5$°K (5.9 ± 0.4 cm^{-1}) and with $E/k \sim 0$.

The data below 10° on the vanadium compound were also least squares fit on a computer directly to the sum of a Schottky term and a lattice term with D, E, α, and n all allowed to vary. The fit, again within experimental error, yielded $D/k = 8.4$°K, $E/k \sim 0$, $\alpha = 2.7 \times 10^{-3}$, and $n = 2.9$. The agreement between the two independent methods of analysis is gratifying.

This value of D may be compared with that (6.0 ± 0.5 cm^{-1}) reported[1] for $V(urea)_6(ClO_4)_3$. The close agreement in the value of the parameter between the two compounds confirms the similarity in the electronic and molecular structure which was suggested earlier.[1] Other values of the zero-field splitting of the $^3A_2$ ground state of trivalent vanadium which have been determined include 8.25 ± 0.02 cm^{-1} for V^{3+} diluted by Al_2O_3,[7] 3.74 cm^{-1} for $[C(NH_2)_3]V(SO_4)_2 \cdot 12H_2O$,[8] and 4.9 cm^{-1} for $NH_4V(SO_4)_2 \cdot 12H_2O$.[9] It is interesting to note that the sign of D for vanadium(III) is positive in all of these systems. Further experiments are underway to explore the likelihood of finding a system where the zero-field splitting is of opposite sign, for theory[10] does not seem to exclude such a possibility.

Acknowledgment. This research was supported by the National Science Foundation.

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Received April 19, 1971

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