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Organometallic Halides: Structure and Magnetism of Tris[(η-pentamethylcyclopentadienyl)dichlorovanadium], $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$

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Summary: There are layers of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ parallel to the a,b plane in both crystalline forms of this antiferromagnetic cluster. In form I, each layer is rotated 60° with respect to neighboring layers, whereas in form II it is rotated by 30°.

Introduction

The preparation and some of the chemical and physical properties of tris[(η-pentamethylcyclopentadienyl)-dichlorovanadium], $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$, were reported recently by three separate groups.[1−3] As part of their work, Messerle and McElfresh and co-workers reported the crystal structure of $[(\eta\text{-C}_5\text{Me}_4\text{Et})\text{V}(\mu\text{-Cl})_2]_3$ and also that $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ exhibited antiferromagnetic exchange.[1] We determined the crystal structure of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$[2] and made a preliminary investigation of its magnetic behavior. Because there were some inexplicable features of the magnetic results of Messerle and McElfresh, we have further investigated both the crystal structure and magnetic behavior of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ and found that the cluster crystallized in two different forms. The crystal structure of the previously unreported form, the relationship between the two forms, and the magnetic behavior of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ are discussed here.

Results and Discussion

Structural Forms of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$. Earlier, we determined the molecular structure of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ by X-ray diffraction from a crystal of platelike habit with dimensions 0.60 × 0.60 × 0.25 mm.[2] We have now found that precipitation of the cluster from ether, as described earlier,[4] always produced a mixture of two crystalline forms, in addition to an amorphous material. The form which was investigated earlier is designated form I and had the cell dimensions given in Table 1. The second form, designated form II, had a more blocklike habit. Its cell dimensions are also given in Table 1, the only significant difference from form I being the β angle (71° in I, 87.8° in II). Preliminary examination of the crystals from several preparations showed that most of them were form II, but we were able to find only a single specimen of this form (irregularly shaped, dimensions 0.55 × 0.45 × 0.35 mm) that diffracted with sufficient intensity to determine the crystal structure. Because of the very low signal-to-noise ratio, the structure could be refined only to $R = 0.15$ (anisotropic V and Cl, isotropic C atoms). Full details are given in the Supporting Information.

Table 1. The Two Crystalline Forms of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$

form	I	II
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.8187(1)	11.780(4)
b (Å)	11.8395(1)	11.802(3)
c (Å)	16.0141(1)	15.957(6)
α (deg)	68.361(1)	68.31(2)
β (deg)	70.896(1)	87.84(3)
γ (deg)	60.160(1)	60.21(3)
V (Å^3)	1777.8(2)	1788(2)
Z	2	2

Although the data obtained from the crystal of form II was of low quality, it unambiguously defined the gross structure of the crystal and showed that there were no significant differences in the molecular dimensions of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ in form II compared to those discussed previously for form I.[2] Figure 1 shows the packing in forms I and II. In both forms, the molecules of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ are arranged in layers. The thickness of a layer is equal to the diameter of the C_5Me_5 ligand, and the central plane of a layer is defined by the plane of the vanadium atoms. In both forms, this central plane makes an angle of 4° (that is, almost parallel) to the *a*,*b* plane of the crystal. There are only repulsive H−H contacts (minimum distance 2.5 Å) between the $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ clusters within the layers. The (η-C_5Me_5) ligands, which are perpendicular to the planes of the vanadium atoms, form an interlocking zipper holding the layers and, therefore, the crystal together.

The difference between the two crystalline forms has its origin in the 30° rotation of the $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ molecule with respect to the center of symmetry of the

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(2) Abernethy, C. D.; Bottomley, F.; Decken, A.; Thompson, R. C. *Organometallics* **1997**, *16*, 1865.

(3) Aistars, A.; Newton, C.; Rübenstahl, T.; Doherty, N. M. *Organometallics* **1997**, *16*, 1994.

(4) The cluster $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ was prepared as described previously.[2]

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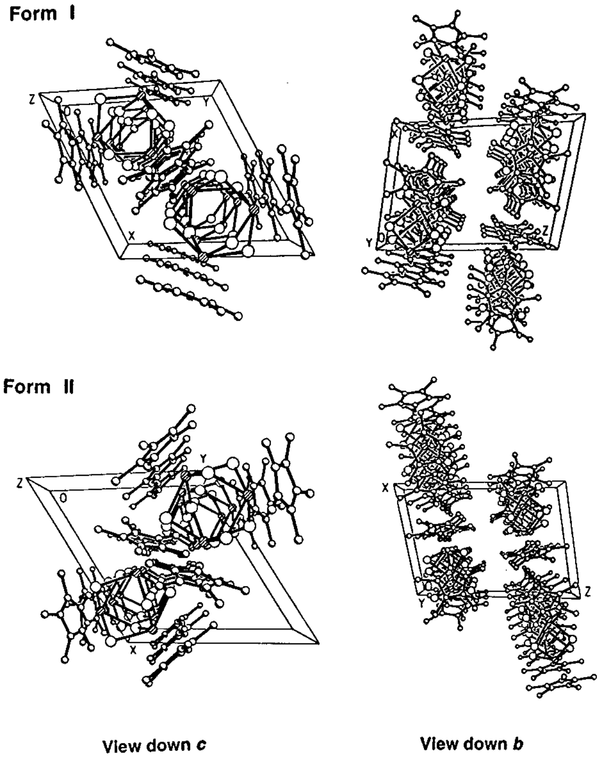

Figure 1. Packing diagrams for form I and form II of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$.

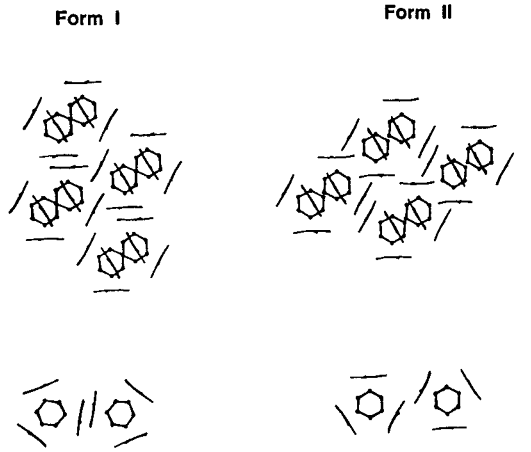

Figure 2. Relative orientations of the $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ clusters with respect to one another in crystalline form I and form II.

unit cell in form II compared to form I, as shown in Figure 2. Each of the two molecules in a unit cell belongs to a neighboring, not the same, layer. The arrangement of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ molecules within a layer is the same in both crystalline forms, but the different orientations with respect to the center of symmetry have the effect of rotating each layer in form I by 60° with respect to its neighboring layer, whereas the rotation in form II is 30°. Thus, the $(\eta\text{-C}_5\text{Me}_5)$ zipper, which is perpendicular to the V_3 plane, is linear in form I but has a zigzag arrangement in form II. This can be seen in Figure 1. Because the $(\eta\text{-C}_5\text{Me}_5)$ ligands abut directly in the perpendicular zipper, the distances between the central planes of the neighboring layers are larger in form I (7.67 and 8.29 Å) than in form II (6.40 and 6.68 Å).

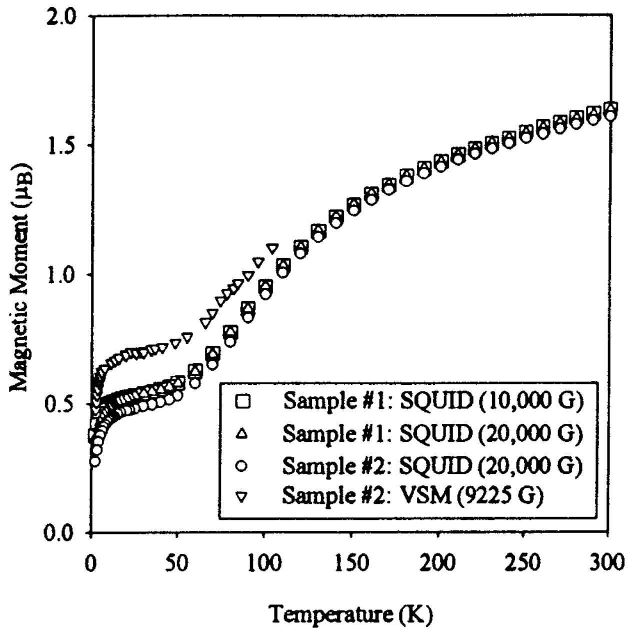

Figure 3. Magnetic moment (per mole of vanadium) of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ over the temperature range 2−300 K.

The structure of $[(\eta\text{-C}_5\text{Me}_4\text{Et})\text{V}(\mu\text{-Cl})_2]_3$, as determined by Messerle and co-workers,[1] is essentially identical to form I of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$.

Magnetic Behavior of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$. The magnetic moments (per mole of vanadium) of two different samples of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ are plotted as a function of temperature in Figure 3. The samples were taken from two different preparations and presumably, therefore, contained different proportions of forms I, II, and amorphous material. The moment of sample 1 was measured using a SQUID magnetometer[5] at applied fields of 10 and 20 kG, and there was no significant dependence of the moment on the applied field (see Figure 3). The moment of sample 2 was measured using both a SQUID and a VSM magnetometer.[5] There was good agreement between the moments of samples 1 and 2 measured with the SQUID instrument, which indicated that the magnetic properties of forms I and II were very similar. Note that the preliminary moments published previously were calculated per mole of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$,[2] whereas the present moments are reported per mole of $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2$.

Molecular-orbital calculations showed that the electrons which were responsible for the magnetic moment of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ were delocalized over the three vanadium atoms but localized within the $[\text{V}(\mu\text{-Cl})_2]_3$ units.[2,7] In both forms I and II, these units are isolated from one another within the layers of $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\mu\text{-Cl})_2]_3$ by the diamagnetic $(\eta\text{-C}_5\text{Me}_5)$ ligands. The interlayer spacing is different in the two forms but is so long (averaging 7.98 Å in form I and 6.54 Å in form II) that there will be no significant interaction between the [V(μ-

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(5) Magnetic moments were measured using a Princeton Applied Research vibrating sample magnetometer (VSM) operating at 9225 G[6] or a Quantum Design (MPMS) SQUID magnetometer operating at 10 or 20 kG.

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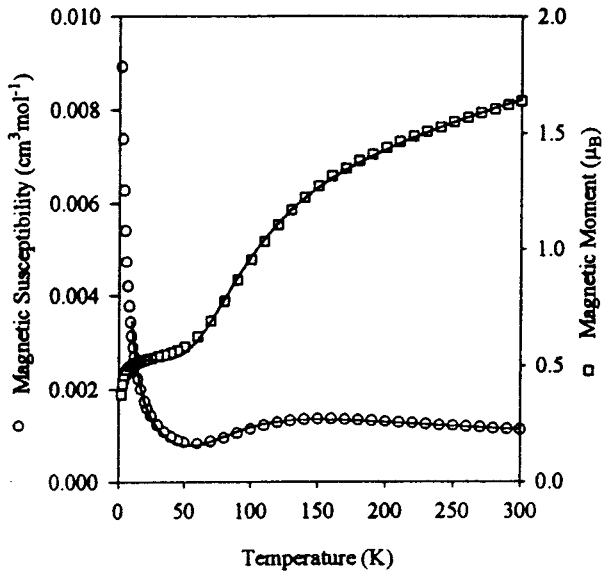

Figure 4. Magnetic susceptibility and magnetic moment of sample 1 over the temperature range 2–300 K, at a field strength of 10 kG. The lines were calculated as described in the text.

Cl)$_2$]$_3$ units in different layers. Thus, no significant difference in the magnetic behavior of forms I and II would be expected.

The difference between the data for sample 2 measured using the SQUID magnetometer and that measured using the VSM may arise from the layered arrangement of the [(η-C$_5$Me$_5$)V(μ-Cl)$_2$]$_3$ clusters of crystalline forms I and II. The layering would make the magnetic behavior of the crystals anisotropic. In packing powdered samples for measurement, a preferred, rather than random, orientation of microcrystals may occur. In measurements with the SQUID magnetometer, the orientation of the applied field is parallel to the sample, but in the VSM measurements the field is perpendicular.[8] Thus, an apparent difference in the magnetic behavior between SQUID and VSM data may be observed.

The magnetic susceptibility and magnetic moment for sample 1 at a field strength of 10 kG are plotted versus temperature in Figure 4. From a minimum at 60 K, the susceptibility passes through a maximum at 160 K. This behavior is typical for a system exhibiting intramolecular antiferromagnetic exchange. The increase in the susceptibility with decreasing temperature below 60 K is ascribed to a paramagnetic impurity.

Mackey and Martin used the Hamiltonian of eq 1 to calculate the magnetic susceptibility of a regular chain of three $S = 1$ centers, assuming isotropic Heisenberg exchange and equivalent g values.[9] The Hamiltonian

$$\boldsymbol{H} = -2J[(\boldsymbol{S}_1\cdot\boldsymbol{S}_2) + (\boldsymbol{S}_2\cdot\boldsymbol{S}_3)] - 2J_{31}(\boldsymbol{S}_3\cdot\boldsymbol{S}_1) \qquad (1)$$

of eq 1 was modified to an expression appropriate for an equilateral triangle of three $S = 1$ centers by equating the exchange integral between the central and terminal metal centers to that between the two terminal centers. The expression was further modified to take into account a fraction, P, of a paramagnetic impurity, as described previously.[8] A reasonable fit to the magnetic susceptibility versus temperature curve above 10 K was obtained by employing g, J, and P as variable parameters. The calculated curve shown in Figure 4 was obtained with the best fit values $g = 1.98$, $J = -113$ cm^{-1}, and $P = 0.035$; the goodness-of-fit parameter[8] was 0.0399. The J value is in good agreement with the value of -119 cm^{-1} obtained by Messerle and McElfresh and co-workers, but g is closer to the spin-only value than the 1.89 value obtained previously.[1]

Below 10 K, the magnetic moment decreased with decreasing temperature (see Figure 4) and the model used does not fit these data. The anomaly is ascribed to zero-field splitting in the paramagnetic ($S = 1$) impurity.[10]

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Supporting Information Available: Tables of magnetic data for [(η-C$_5$Me$_5$)V(μ-Cl)$_2$]$_3$ and crystal data, diffractometry conditions, refinement details, fractional coordinates, thermal parameters, interatomic distances, and angles for form II of [(η-C$_5$Me$_5$)V(μ-Cl)$_2$]$_3$ (14 pages). Ordering information is given on any current masthead page.

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