(NH₄)₃CrO₈: A new S = 1/2 system exhibiting no magnetic transition down to 0.3 K

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Received 5 October 2004; accepted 23 March 2005
Available online 5 July 2005

Abstract

Recent studies related to quantum computation suggest a need for developing a well-characterized low-spin, e.g., S = 1/2, metal complex with limited or no significant hyperfine interactions. To this end, we here report the synthesis, crystal structure and magnetic and thermodynamic characterization of ammonium peroxychromate, (NH₄)₃CrO₈, a new compound of Cr(5+), with a 3d⁴/C0₂y₂, S = 1/2 ground state, with about 92% molecules devoid of any metal hyperfine interaction. It is the first Cr(5+) compound exhibiting a structural phase transition (at 137.5 K) tentatively assigned to the order–disorder motion of the NH₄⁺ ions, but it remains paramagnetic down to 0.3 K. The compound is stable for years if stored in a refrigerator, but it could explode if crushed or subjected to high pressure, or heated to well above room temperature.

Keywords: EPR; Order–disorder; S = 1/2; Peroxychromate

1. Introduction

Recently, there has been a surge in the search for simple paramagnetic systems that could serve as models for understanding the magnetization dynamics and control of the states of an ensemble of electronic spins in relationship to quantum computation and information storage at the molecular dimensions [1,2]. The molecular complex K₆[V₁₅As₆O₄₂(H₂O)]·8H₂O, commonly abbreviated as V₁₅, with its ground state spin S = 1/2 is a case in point [3–5]. V₁₅ consists of 15 V(4+) ions, coupled antiferromagnetically so as to result in this lowest spin ground state. However, the essentially 100% abundant nucleus of Vanadium, ⁵¹V, has a large nuclear spin, I = 7/2, and hence a sizable and complex hyperfine interaction in general. It thus seemed worthwhile that another S = 1/2 system be developed in which the dominant isotope of the paramagnetic ion possesses no nuclear spin. The present work was undertaken with this point in view, and we here report on the synthesis, structural and magnetic characterization of ammonium peroxychromate, (NH₄)₃CrO₈, a new compound based on Cr(5+), a 3d⁴ system. Magnetic susceptibility and heat capacity measurements demonstrate that it has a ground state spin of 1/2, with no magnetic ordering down to sub-helium temperatures. The dominant nucleus of the Cr ion, ⁵²Cr, with natural abundance at about 92%, has no nuclear spin, and thus it satisfies the criterion of a lack of hyperfine interaction. Below we describe our measurements that support this claim.

2. Experimental

2.1. Synthesis

Crystals of (NH₄)₃CrO₈ were synthesized via modification of the method of Riesenfeld [6]. Specifically,
(NH₄)₃CrO₈ was synthesized by dissolving (NH₄)₂CrO₄ or CrO₃ in NH₄OH at room temperature. This solution was then cooled to −5 °C at which point H₂O₂ is added drop wise [6–10]. This process yields mm-size crystals. Crystals can be kept for more than a year at freezing temperatures. Decomposition occurs quickly if allowed to warm up and the compound can be explosive if pressure or heat is applied.

2.2. X-ray

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was resolved by the Direct Methods in SHELXTL5, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms located from a Difference Fourier map. N1 is located on a 4 symmetry center thus only one H atom exists in the asymmetric unit, and it was refined freely. N2 is located on a 42 m center thus the four tetrahedrally oriented H atoms are heavily disordered. Two H atoms were found and were refined riding on their N2 atom. Because of symmetry, the H atoms around N2 are octahedrally oriented which is theoretically not correct for an ammonium cation but is close to two disordered sets that are related by 2-fold rotation or mirror symmetry. The asymmetric unit consists of 1/8 CrO₈³⁻ (located on a 42 m center), 1/8 NH₄⁺ (located on a 42 m center), and another NH₄⁺ ion located on a 4 symmetry element (1.4 in the asymmetric unit). Thus, the stoichiometry is CrO₈(NH₄)₃. The structure was also solved and refined in sub space groups of I42 m but these refinements did not provide any better results and did not remove the disorder of the H atoms around N2. A total of 26 parameters were refined in the final cycle of refinement using 254 reflections with I > 2σ(I) to yield R₁ and wR₂ of 1.70% and 5.00%, respectively. Refinement was done using F².

2.3. Heat capacity and magnetization measurements

In order to detect a possible solid–solid or magnetic phase transition, we carried out heat capacity measurements over the range of 300 K down to 300 mK. These measurements were made with a Quantum Design Physical Properties Measurement System (QD PPMS) facility available at the National High Magnetic Field Laboratory in Tallahassee, Florida. dc magnetic susceptibility measurements were made using a Quantum Design SQUID magnetometer over a temperature range of 1.8–300 K.

2.4. Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR) spectroscopic measurements were carried out over a range of 2.8–295 K at X-band (~9.5 GHz), Q-band (35 GHz) and W-band (~93.5 GHz) using the Bruker (X- and Q-band) spectrometers; and a locally designed W-band system available as described earlier [11–14]. Both single crystals and powder samples were studied. Angular studies where done using a goniometer and the Q-band setup. The measured Zeeman splitting constants, g-values, clearly identified the compound as containing the Cr(5+) ion, based on our earlier reports [7,8,11–14].

3. Results and discussion

Fig. 1 shows a schematics of the CrO₈³⁻ moiety [11], which is the central part of our compound. Fig. 2 depicts the unit cell of (NH₄)₃CrO₈, based on our X-ray diffraction data as discussed above. The structure consists of essentially isolated Cr(5+), 3d¹ ions and one thus expects little or no magnetic exchange interaction between the Cr(5+) ions, as we had envisaged. Indeed, magnetic susceptibility measurements, shown in Figs. 3 and 4, fully supported this behavior: the saturated magnetic moment corresponded to an S = 1/2 system (Fig. 3), while the magnetic susceptibility data followed the
expected Curie-Weiss behavior (a straight line for the inverse susceptibility, $1/\chi$ versus $T$ plot), as seen in Fig. 4. The Curie constant was $C = 0.320$ mol K/emu and $\theta = -0.8$ K showing a weak antiferromagnetic coupling, if any, similar to the other peroxychromates [7–13]. From the effective moment ($\mu_{\text{eff}}/\mu_B = 1.596$) we calculate, assuming $S = 1/2$, that $g_{\text{iso}} = 1.8429$, which was essentially in agreement with the variable temperature, variable frequency EPR data (Figs. 6 and 7, vide infra).

Heat capacity data (Fig. 5), on the other hand, exhibited a small but sharp peak at 137.5 K, which indicated the presence of some form of an order–disorder phase transition. $\Delta S = 4.70$ J/mol K was calculated over the peak by graphing $C_p * T$ versus $T$ and then integrating; $\Delta S = \int C_p dT$. For a two state mixed system, the theoretically expected value is $\Delta S = R * \ln(2) = 5.76$ J/mol K, which indicates that the phase transition can be ascribed to an order–disorder mechanism. The order–disorder process must involve the reorientational motion of the $\text{NH}_4^+$ groups. We rule out the order–disorder change in the $\text{CrO}_8^{3-}$ units because other isostructural peroxychromates do not exhibit any such transition above 4 K. This postulate could be checked through X-ray structural studies around 137 K. The absence of any such anomaly in the magnetic susceptibility data (Fig. 4), clearly shows that the transition must be of a non-magnetic origin. This was supported by the absence of any noticeable anomalous change around 137.5 K in our detailed EPR measurements at the Q-band frequency (Fig. 7). The X, Q, and W-band EPR experiments yielded a $g_1 = 1.983 \pm 0.0005$ and $g_\perp = 1.950 \pm 0.0005$. These data yield $g_{\text{iso}} = \frac{1}{3} (g_1 + 2g_\perp) = 1.961 \pm$
0.0005, in essential agreement with the above summarized magnetization measurements $g_{iso} = 1.843$. Angular dependence on a single crystal was done at Q-band frequency (Fig. 8). The crystal was rotated from the $c$-axis to the $a$-axis. The solid line corresponds to the fit of $g_{eff}^2 = g_{\|}^2 \sin^2 \theta + g_{\perp}^2 \cos^2 \theta$, giving $g_{\perp} = 1.9844 \pm 0.0005$ and $g_{\parallel} = 1.9522 \pm 0.0005$ which correspond well with the values calculated from the different frequencies measured. The line-width-at-half-height of the Q-band spectrum at 200 K, 9.84 gauss, allows calculation of an upper bound of the transverse relaxation; $T_2 = 5.8 \text{ ns}$ from the equation: $T_2 = \frac{1}{2\pi \Delta H_{pp}}$, where $\Delta H_{pp}$ is the width-at-half-height of the EPR peak. Further studies are needed to gain additional insight into the dynamics of this molecule. It is known that for a 3$d^1$ ion in tetrahedral coordination the ground state can either be $d_{z^2}$ or $d_{x^2-y^2}$ [10,15]. For the case of tetragonal elongation, $d_{x^2-y^2}$ is the ground state with $g_{\parallel} \approx g_e - \frac{2\lambda}{\Delta E}$ and $g_{\perp} \approx g_e - \frac{2\lambda}{\Delta E}$, where $g_e$ is the free-electron $g$-value of 2.0023, and $\lambda$ is the spin–orbit coupling constant. Thus, determination of the $g$-values will yield the ground state of this molecule. It was found for (NH₄)₃CrO₈ that $g_{\perp} > g_{\parallel}$ thus demonstrating that the ground state is indeed $d_{x^2-y^2}$ [7,8,15]. It should also be noted that no hyperfine interactions are seen as expected from the low percentage (9.50%) of Cr nuclei with nuclear spin.

![Fig. 6. EPR spectra of (NH₄)₃CrO₈ at: (a) X-band, 9.5 GHz; (b) Q-band, 34.5 GHz and (c) W-band, 94.5 GHz.](image)

![Fig. 7. Temperature dependence of Q-band EPR spectra for (NH₄)₃CrO₈. No change is noticeable at the phase transition temperature of 137.5 K.](image)

![Fig. 8. Angular dependence of Q-band EPR spectra for (NH₄)₃CrO₈. Rotation is from the $c$-axis to the $a$-axis and was performed at 200 K.](image)
4. Conclusion

The compound (NH₄)₃CrO₈, newly reported here, behaves as a simple \( S = 1/2 \) paramagnetic system, largely free from hyperfine and exchange interactions. Heat capacity, susceptibility, and EPR measurements support the hypothesis that the peak in the heat capacity is an order–disorder transition with no magnetic origin. Calculation of the entropy gives nice agreement to the theoretical prediction of a mixed two state system. This compound could serve as a model system and be a simple replacement for materials like \( V_{15} \). Further studies along these lines should be fruitful.

Acknowledgements

This work was partially supported by the NSF Grant DMR 0103290 (NIRT).

K.A.A. acknowledges the National Science Foundation and the University of Florida for funding of the purchase of the X-ray equipment.

References