



$(\text{NH}_4)_3\text{CrO}_8$: A new $S = 1/2$ system exhibiting no magnetic transition down to 0.3 K

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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, $(\text{NH}_4)_3\text{CrO}_8$, a new compound of Cr(5+), with a $3d_{x^2-y^2}$, $S = 1/2$ 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 NH_4^+ 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.

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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 $\text{K}_6[\text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$, commonly abbreviated as V_{15} , with its ground state spin $S = 1/2$ is a case in point [3–5]. V_{15} 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, ^{51}V , 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, $(\text{NH}_4)_3\text{CrO}_8$, a new compound based on Cr(5+), a $3d^1$ 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, ^{52}Cr , 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 $(\text{NH}_4)_3\text{CrO}_8$ were synthesized via modification of the method of Riesenfeld [6]. Specifically,

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$(\text{NH}_4)_3\text{CrO}_8$ was synthesized by dissolving $(\text{NH}_4)_2\text{CrO}_4$ or CrO_3 in NH_4OH at room temperature. This solution was then cooled to -5°C at which point H_2O_2 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 $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 $\bar{4}$ symmetry center thus only one H atom exists in the asymmetric unit, and it was refined freely. N2 is located on a $\bar{4}2m$ 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 $1/8 \text{ CrO}_8^{3-}$ (located on a $\bar{4}2m$ center), $1/8 \text{ NH}_4^+$ (located on a $\bar{4}2m$ center), and another NH_4^+ ion located on a $\bar{4}$ symmetry element (1.4 in the asymmetric unit). Thus, the stoichiometry is $\text{CrO}_8(\text{NH}_4)_3$. The structure was also solved and refined in sub space groups of $I42m$ 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 $I > 2\sigma(I)$ to yield R_1 and wR_2 of 1.70% and 5.00%, respectively. Refinement was done using F^2 .

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 ($\sim 9.5 \text{ GHz}$), Q-band (35 GHz) and W-band ($\sim 93.5 \text{ GHz}$) 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 were done using a goniometer and the Q-band setup. The measured Zeeman splitting constants, g -values, clearly identified the compound as containing the $\text{Cr}(5+)$ ion, based on our earlier reports [7,8,11–14].

3. Results and discussion

Fig. 1 shows a schematic of the CrO_8^{3-} moiety [11], which is the central part of our compound. Fig. 2 depicts the unit cell of $(\text{NH}_4)_3\text{CrO}_8$, based on our X-ray diffraction data as discussed above. The structure consists of essentially isolated $\text{Cr}(5+)$, $3d^1$ ions and one thus expects little or no magnetic exchange interaction between the $\text{Cr}(5+)$ 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

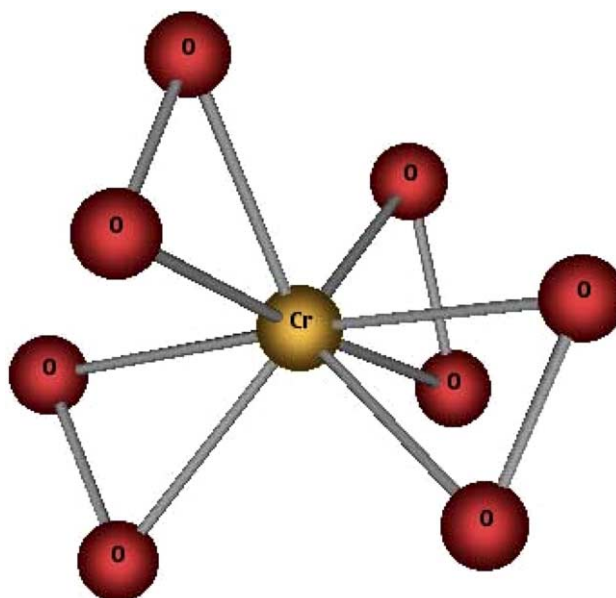
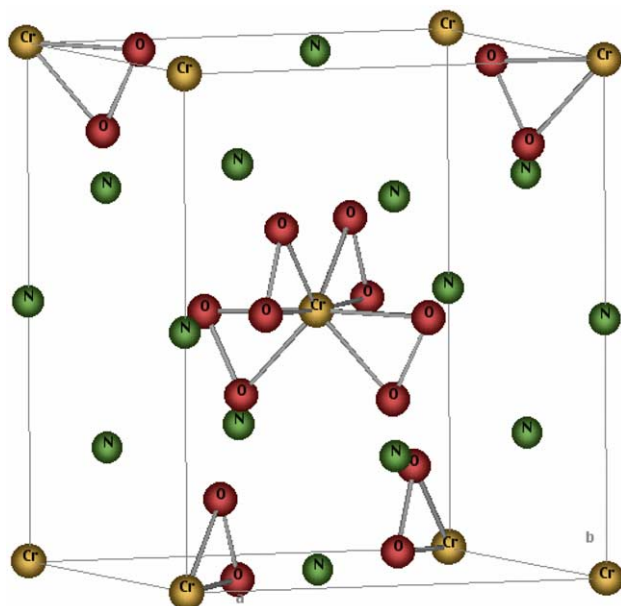
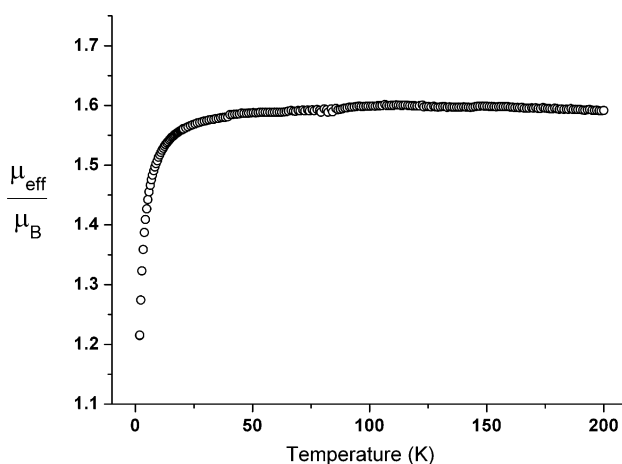
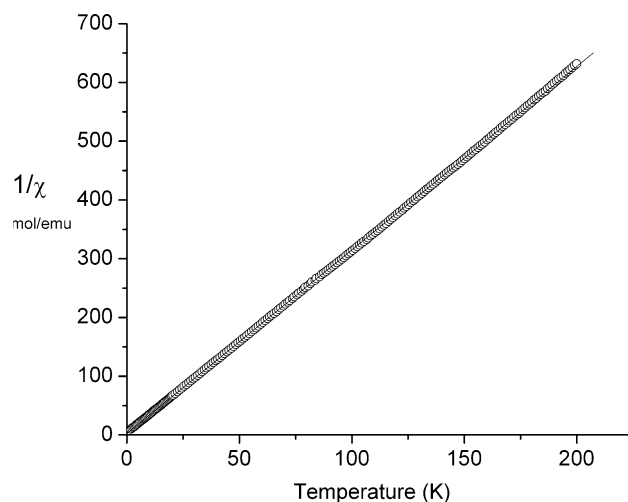
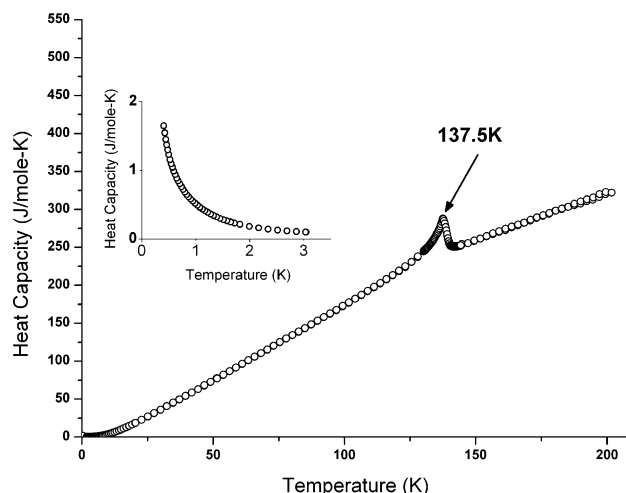


Fig. 1. Structure of CrO_8^{3-} ion.

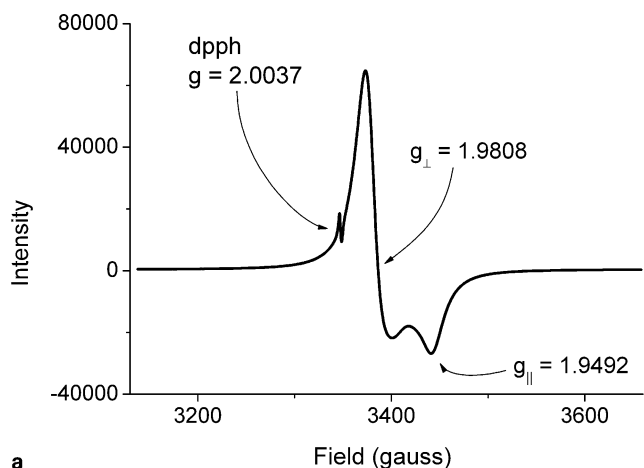
Fig. 2. Unit cell for $(\text{NH}_4)_3\text{CrO}_8$.

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 peroxochromates [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).

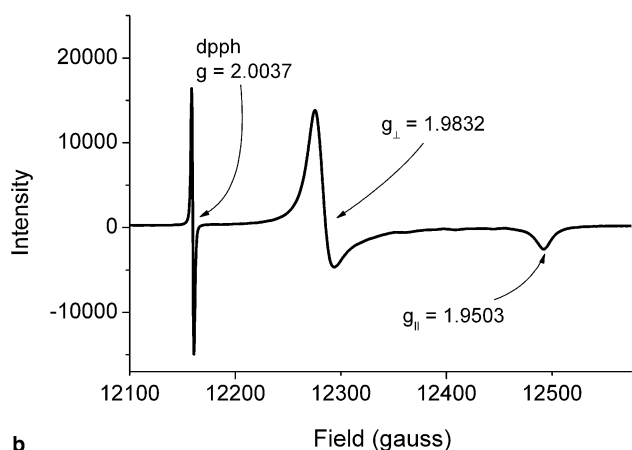
Heat capacity data (Fig. 5), on the other hand, exhibited a small but sharp peak at 137.5 K, which indicated the presence of some form of an order–disorder phase transition. $\Delta S = 4.70$ J/mol K was calculated over the peak by graphing $C_p * T$ versus T and then integrating; $\Delta S = \int C_p \frac{dT}{T}$. For a two state mixed system, the theoretically expected value is $\Delta S = R * \ln(2) = 5.76$ J/mol K,

Fig. 3. Temperature dependence of magnetic moment of $(\text{NH}_4)_3\text{CrO}_8$.Fig. 4. Temperature dependence of $1/\chi$ for $(\text{NH}_4)_3\text{CrO}_8$. Red line is the fit to the Curie–Weiss Law.Fig. 5. Temperature dependence of heat capacity for $(\text{NH}_4)_3\text{CrO}_8$. The arrow highlights the solid–solid phase transition at 137.5 K. Inset shows heat capacity from 3 to 0.4 K.

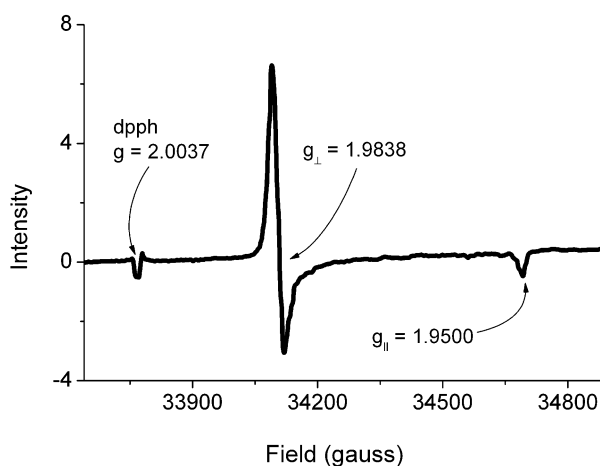
which indicates that the phase transition can be ascribed to an order–disorder mechanism. The order–disorder process must involve the reorientational motion of the NH_4^+ groups. We rule out the order–disorder change in the CrO_8^{3-} units because other isostructural peroxochromates do not exhibit any 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 $g_{\parallel} = 1.983 \pm 0.0005$ and $g_{\perp} = 1.950 \pm 0.0005$. These data yield $g_{\text{iso}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 1.961 \pm$



a



b



c

Fig. 6. EPR spectra of $(\text{NH}_4)_3\text{CrO}_8$ at: (a) X-band, 9.5 GHz; (b) Q-band, 34.5 GHz and (c) W-band, 94.5 GHz.

0.0005, in essential agreement with the above summarized magnetization measurements $g_{\text{iso}} = 1.843$. 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 $g_{\text{eff}}^2 = g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta$, 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 mea-

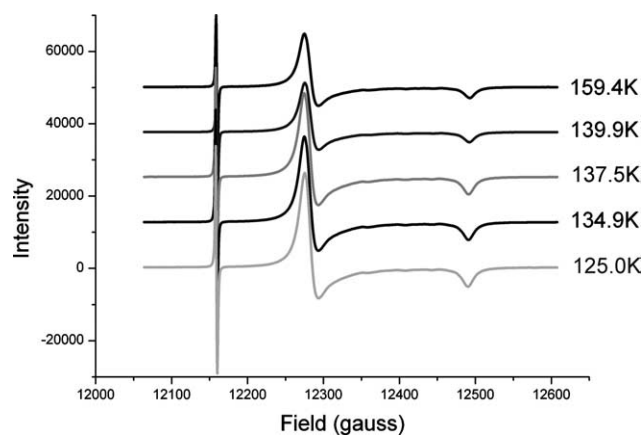


Fig. 7. Temperature dependence of Q-band EPR spectra for $(\text{NH}_4)_3\text{CrO}_8$. No change is noticeable at the phase transition temperature of 137.5 K.

sured. 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; $T_2 = 5.8$ ns from the equation: $T_2 = \frac{1.3131 \times 10^{-7}}{g \Delta H_{\text{pp}}}$, where ΔH_{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 $3d^1$ 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 $g_{\parallel} \approx g_e - \frac{8\lambda}{\Delta E}$ and $g_{\perp} \approx g_e - \frac{2\lambda}{\Delta E}$ where g_e is the free-electron g -value of 2.0023, and λ is the spin-orbit coupling constant. Thus, determination of the g -values will yield the ground state of this molecule. It was found for $(\text{NH}_4)_3\text{CrO}_8$ 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.

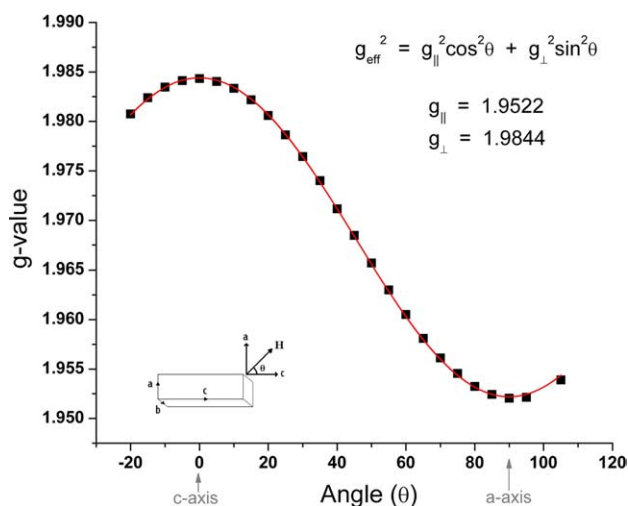


Fig. 8. Angular dependence of Q-band EPR spectra for $(\text{NH}_4)_3\text{CrO}_8$. Rotation is from the c -axis to the a -axis and was performed at 200 K.

4. Conclusion

The compound $(\text{NH}_4)_3\text{CrO}_8$, 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.

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