

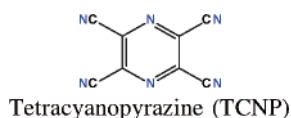
Magnetically Ordered ($T_c = 200$ K) Bis(tetracyanopyrazine)vanadium, $V[\text{TCNP}]_2 \cdot y\text{CH}_2\text{Cl}_2$

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Since the report of the first organic-based magnet, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{+}\text{[TCNE]}^{-}$ (TCNE = tetracyanoethylene),¹ new molecule-based materials have been synthesized with enhanced and controllable magnetic properties.^{2,3} The reaction of $\text{V}^0(\text{C}_6\text{H}_6)_2^{4a}$ and $\text{V}^0(\text{CO})_6^{4b}$ with TCNE formed $\text{V}[\text{TCNE}]_x \cdot y\text{CH}_2\text{Cl}_2$ ($x \approx 2$; $y \approx 0.5$), an amorphous, disordered room-temperature organic magnet ($T_c \approx 400$ K). Recently, solvent-free thin films of $\text{V}[\text{TCNE}]_x$ with a small coercive field (<1 Oe) at room temperature have been prepared via chemical vapor deposition.⁵ Magnetotransport studies indicate that electrons in valence and conducting bands of $\text{V}[\text{TCNE}]_x \cdot y\text{CH}_2\text{Cl}_2$ are spin polarized, suggesting potential “spintronic” applications.⁶ With the goal of identifying new acceptors to stabilize magnetically ordered molecule-based materials, we and others⁷ have studied the reaction of $\text{V}(\text{CO})_6$ with several polynitrile electron acceptors. To date, the only other magnet reported via the reaction of either $\text{V}(\text{C}_6\text{H}_6)_2$ or $\text{V}(\text{CO})_6$ is with α, α' -dicyanoperfluorostilbene ($T_c = 205$ K).⁷ Herein, we report a new molecule-based magnet prepared from the reaction of $\text{V}^0(\text{CO})_6$ and tetracyanopyrazine (TCNP).



Typically, 2 equiv of TCNP^8 per $\text{V}(\text{CO})_6^9$ were each dissolved in a minimum amount of CH_2Cl_2 in a drybox. The $\text{V}(\text{CO})_6$ solution was added dropwise into a stirred solution of TCNP for 5 min and was then stirred for an additional 15 min, liberating CO. The dark product was filtered, washed with CH_2Cl_2 , and dried in vacuo (yield $\sim 80\%$). Anal. Calcd for $\text{V}[\text{TCNP}]_2 \cdot 0.83\text{CH}_2\text{Cl}_2$: C, 41.57; H, 0.31; N, 35.24. Found: C, 41.97; H, 0.35; N, 34.90. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{N}}$ 2223 (s), 2188 (m), 2136 (m).

The reaction of $\text{V}^0(\text{CO})_6^{4b}$ or $\text{V}^0(\text{C}_6\text{H}_6)_2^{4a}$ and TCNE forms magnetically ordered $\text{V}[\text{TCNE}]_x$. Mechanistic studies with $\text{V}(\text{C}_6\text{H}_6)_2$ reveal that two TCNEs are reduced to $[\text{TCNE}]^{+}\text{[TCNE]}^{-}$ and $\text{V}(\text{II})$ forms.¹⁰ Due to the high oxidation potential, albeit irreversible, for $\text{V}(\text{CO})_6$ [$E^{-/0} = +0.88$ V vs SCE (CH_2Cl_2)¹¹], it should not reduce TCNP [$E^{-/0} = -0.31$ V vs SCE (CH_2Cl_2)¹²]. Nonetheless, an immediate reaction occurs, forming a dark, amorphous product (eq 1).



Hence, unlike the reaction of $\text{V}(\text{C}_6\text{H}_6)_2$ and TCNE, the reaction of $\text{V}(\text{CO})_6$ and TCNP must initially proceed not by electron transfer,¹³ leading to intermediates that reduce the oxidation potential of the V.

The 2223, 2188, and 2136 cm^{-1} $\nu_{\text{C}\equiv\text{N}}$ IR absorptions indicate the presence of reduced TCNP, as these absorptions are lower in energy than those of TCNP^0 at 2254 and 2248 (sh) cm^{-1} .^{12,14} The number and broad nature of the $\nu_{\text{C}\equiv\text{N}}$ stretches suggest that there are multiple $\text{C}\equiv\text{N}$ environments in the material. This is observed

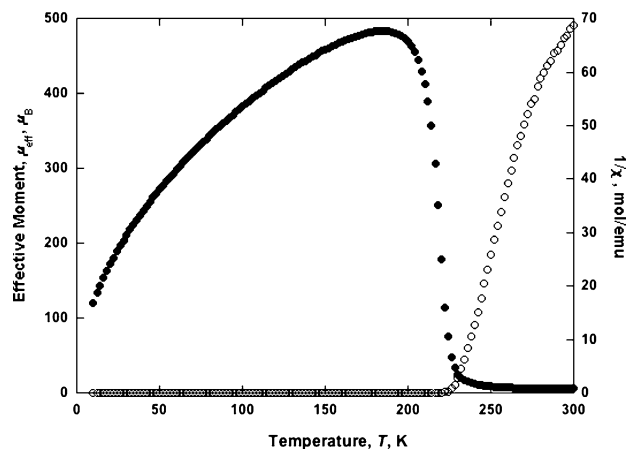
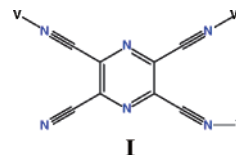


Figure 1. $\mu_{\text{eff}}(T)$ (●) and $1/\chi(T)$ (○) for $\text{V}[\text{TCNP}]_2 \cdot 0.83\text{CH}_2\text{Cl}_2$ in a 5 Oe applied field.

for $\text{V}[\text{TCNE}]_x \cdot y\text{CH}_2\text{Cl}_2$ with broad absorption at 2090 cm^{-1} and three relatively narrow features at 2214, 2191, and 2152 cm^{-1} .^{1,5b} Powder diffraction data, like those for $\text{V}[\text{TCNE}]_x$, indicate that the material is amorphous. Based on the similarity of the IR spectra to that of $\text{V}[\text{TCNE}]_x$, a similar structure is proposed. Hence, each TCNP bonds on average to three V(II)'s (I), but locally it may bond to two or four with linear as well as some bent $\text{V}-\text{N}\equiv\text{C}$ bonding. Each V(II) is proposed to be six-coordinate, with linkages to as many as six different TCNPs. Consequently, a disordered 3-D network structure forms, as proposed for $\text{V}[\text{TCNE}]_x$, except that the $\text{V}\cdots\text{V}$ separations are greater.



The 5 Oe, 10–300 K magnetic susceptibility, $\chi(T)$, was determined on a Quantum Design MPMS-5XL magnetometer, Figure 1. Above 270 K, $d[1/\chi(T)]/dT$ decreases, indicative of longer range antiferromagnetic coupling. The room-temperature moment, $\mu_{\text{eff}} [\equiv (8\chi T)^{1/2}]$, is $5.91 \mu_{\text{B}}$, which is considerably higher than the expected value of $4.58 \mu_{\text{B}}$. This is attributed to the strong effective ferromagnetic coupling and large θ of 230 K. The moment increases slowly with decreasing temperature until ~ 240 K; it then rises sharply, reaching a value of $485 \mu_{\text{B}}$ at 185 K. This peak in magnetic moment is followed by a downward curve as the temperature is further decreased to 10 K.

The zero field cooled (ZFC) and field cooled (FC) magnetization, $M(T)$, at 5 Oe show a bifurcation point at ~ 160 K (Figure 2). An ordering temperature, T_c , of 202 K is obtained from an extrapolation of the low-field $M(T)$ to the temperature at which $M(T) \rightarrow 0$ (Figure 2).

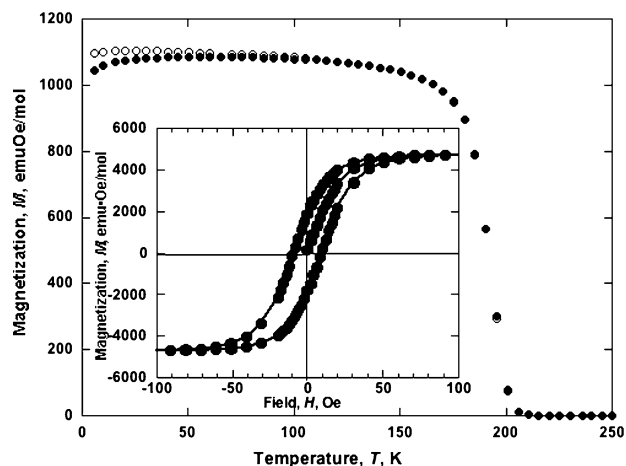


Figure 2. Zero field (●) and field cooled (○) (ZFC/FC) $M(T)$ for $V(\text{TCNP})_2 \cdot 0.83\text{CH}_2\text{Cl}_2$ in a 5 Oe applied field. Inset is $M(H)$ showing hysteretic behavior for $V(\text{TCNP})_2 \cdot 0.83\text{CH}_2\text{Cl}_2$ at 2 K.

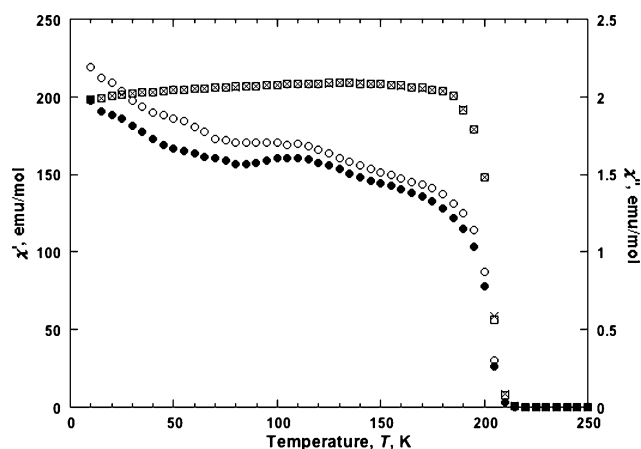
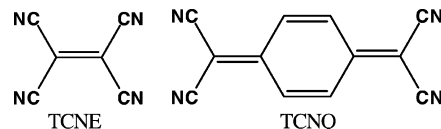


Figure 3. Real, $\chi'(T)$ (□, ×), and imaginary, $\chi''(T)$ (●, ○), ac susceptibilities for $V(\text{TCNP})_2 \cdot 0.83\text{CH}_2\text{Cl}_2$ at 33 (□, ●) and 100 (×, ○) Hz.

Field-dependent magnetization, $M(H)$, at 2 K shows a sharp increase below 20 Oe followed by a gentle upward slope to 5 T, at which point the magnetization reaches a near-saturation value of 5200 emu·Oe/mol (Figure 2, inset). This is 93% of the expected value of 5585 emu·Oe/mol for $S = 3/2$ V^{II} antiferromagnetically coupled to two $S = 1/2$ $[\text{TCNP}]^{+}$, consistent with the material being a ferrimagnet. This value is in good agreement with that reported for $V[\text{TCNE}]_2 \cdot y\text{CH}_2\text{Cl}_2$ ⁴ and $V[\text{TCNE}]_2$.⁵ The system shows a coercive field of 8 (Figure 2), 9, and 9 Oe at 2, 5, and 180 K, respectively, suggesting that it is a relatively soft ferrimagnet. The remanent magnetization (M_{rem}) is 1860 (Figure 2 inset), 1825, and 385 emu·Oe/mol at 2, 5, and 180 K, respectively.

The in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components of ac susceptibility at 33 and 100 Hz¹⁵ were measured below 250 K (Figure 3). The $\chi'(T)$ curve is relatively flat below 180 K, and then decreases to zero with increasing temperature between 180 and 210 K, in accord with the magnet ordering. Likewise, $\chi''(T)$ shows a gradual decrease from 10 to 195 K with increasing temperature, and then a decrease to zero between 195 and 210 K, in accord with magnetic ordering. The broadness of the peak makes it difficult to determine if the ac susceptibility is frequency dependent, but suggests that it is not.

Several approaches have been pursued to identify alternative acceptors with respect to $[\text{TCNE}]^{+}$ for stabilized magnetic ordering. The work reported herein shows that extending the distance between nitriles (and the V spin sites) as occurs by lengthening TCNE to TCNQ is not as effective³ as widening the acceptor as occurs for TCNP [i.e., the NCCCCN fragment is better than the $-\text{C}(\text{CN})_2$ fragment], and new magnets based upon substituted TCNP are being sought.



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