Magnetism

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Room-Temperature Organic-Based Magnet ($T_c \approx 50\,^{\circ}C$) Containing Tetracyanobenzene and Hexacarbonylvanadate(−I)**

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The discovery of the first organic-based magnet, $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene),[1] led to the development of several new families of magnetically ordered materials based on unpaired electron spins residing in p orbitals. These include $[Mn^{II}(hfac)_2(NITR)]$ (hfac = hexafluoroacetylactonate; NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide)[2] and $[Mn^{III}(porphyrin)]^{+}[TCNE]^{\cdot-}$ [3] based ferrimagnets as well as β-*p*-

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$NO_2C_6H_4NIT$,[4] [tetrakis(dimethylamino)ethylene][C_{60}],[5] and $NCC_6F_4CS_2N_2$,[6] among others.[3b,7] The reaction of $V(C_6H_6)_2$[8a] and $V(CO)_6$,[8b] albeit by different mechanisms, formed $V[TCNE]_x{\cdot}z\,CH_2Cl_2$ ($x \approx 2$; $z \approx 0.5$), a disordered room-temperature organic magnet with $T_c \approx 400$ K.[3b] Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) studies reveal that the vanadium is divalent and surrounded by six nitrogen centers at 2.084(5) Å, Figure 1.[9]

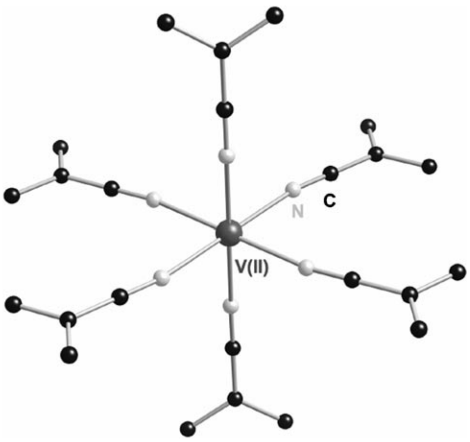
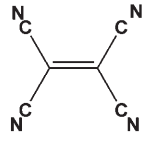


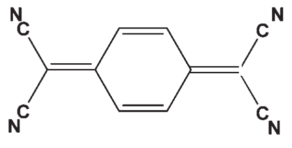
Figure 1. Local structure around each V^{II} site in $V[TCNE]_x$ deduced from XANES and EXAFS studies.

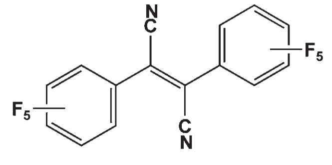
Subsequently, solvent-free thin films of $V[TCNE]_x$ have been prepared by chemical vapor deposition (CVD).[10] Use of trifluoromethylbenzene ($PhCF_3$) as the solvent, which has a slightly enhanced dielectric constant (9.2) with respect to CH_2Cl_2 (8.9),[11] led to an increase in the T_c as well as thermal stability.[12] Magnetotransport studies suggest that the electrons in the valence and conducting bands of $V[TCNE]_x$ are spin polarized,[13] and this material has potential "spintronic" applications.

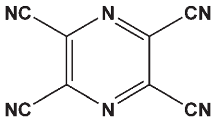
With the goal of identifying new magnetically ordered organic-based materials, the reaction of $[V(CO)_6]$ with several polynitrile electron acceptors has been studied. To date, V[α,α′-dicyanoperfluorostilbene]$_2$ ($T_c = 205$ K),[14] V-[TCNP]$_2$ (TCNP = tetracyanopyrazine; $T_c = 200$ K),[15] and V[TCNQ]$_2$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane; $T_c = 56$ K), as well as several 2,5-disubstituted TCNQs[16] are the few reported examples of magnets which are compositionally related to $V[TCNE]_x$. While these structures are unknown, based upon the composition, they are assumed to be similar to $V[TCNE]_x$, Figure 1.

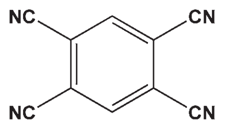
The prototype electron acceptor, TCNE, forms the magnet with the highest T_c. Modification by extension along the central C–C bond, that is, formation of TCNQ, led to a material with a substantial reduction in T_c. In contrast, use of the TCNP electron acceptor, that is, modification of TCNE by extension perpendicular to the central C–C bond leads to a material with only a mild reduction in T_c. Hence, we sought additional examples of electron acceptors with a structure related to TCNP, and preferably one that could be chemically modified or attached to a polymer backbone. Herein, we report a new, the second, room-temperature organic-based magnet prepared from the reaction of $[V^0(CO)_6]$, and 1,2,4,5-tetracyanobenzene (TCNB) as well as a magnet prepared from the reaction of TCNB and $[V^0(PhMe)_2]$.


TCNE


TCNQ


α,α′-dicyanoperfluorostilbene


TCNP


TCNB

Owing to the high oxidation potential, albeit irreversible, for $[V(CO)_6]$ ($E^{-/o} = +0.88$ V vs. saturated calomel electrode (SCE), in CH_2Cl_2[17]) or the reversible one-electron oxidation for $[V(PhMe)_2]$ ($E^{o/+} \approx -0.30$ V vs. SCE, in CH_2Cl_2[18]) both should not reduce TCNB ($E^{-/o} = -0.64$ V vs. SCE, in MeCN[19]). Nonetheless, immediate reactions occurs forming a dark, amorphous product.

The reaction of two equivalents of TCNB per $[V(CO)_6]$[18,20] in CH_2Cl_2 ($\mathbf{V_{CO}{\cdot}CH_2Cl_2}$) or $PhCF_3$ ($\mathbf{V_{CO}{\cdot}PhCF_3}$) or per $[V(PhMe)_2]$ in CH_2Cl_2[21] ($\mathbf{V_{PhMe}{\cdot}CH_2Cl_2}$) in a dry box, led to the isolation of magnetically ordered materials.[22] $\mathbf{V_{CO}{\cdot}CH_2Cl_2}$, $\mathbf{V_{CO}{\cdot}PhCF_3}$, and $\mathbf{V_{PhMe}{\cdot}CH_2Cl_2}$ exhibit a $\nu_{C\equiv N}$ absorption in at 2158 ± 3 and a shoulder at 2190 ± 4 cm^{-1} (Figure 2). These IR absorptions are lower in energy than that observed for TCNB^o (2245 cm^{-1}) and are indicative of reduced TCNB. The number and broad nature of the $\nu_{C\equiv N}$ absorptions suggest that there are multiple C≡N environments in the material. This situation is also observed for $V[TCNP]_2{\cdot}z$ solv. (solv. = solvent)[15] and $V[TCNE]_x{\cdot}z\,CH_2Cl_2$ ($x \approx 2$; $z \approx 0.5$) that have three absorptions present between 2215 and 2150 cm^{-1}.[3b,8,10]

Unprecedentedly, the materials prepared using $[V(CO)_6]$ additionally have broad absorptions at 1845 ± 4 and 1699 ± 10 cm^{-1}. The assignments of ν_{CO} and $\nu_{\mu\text{-}CO}$, respectively, are indicative of $[V^{-I}(CO)_6]^-$, which has a strong, broad ν_{CO} absorption at approximately 1845 cm^{-1}. Additionally, an absorption at 649 ± 1 cm^{-1} ascribed to ν_{VC} which is also observed for $[V^{-I}(CO)_6]^-$, is present. The presence of $[V^{-I}(CO)_6]^-$ was confirmed by dissolution into MeCN and observation of a solution ν_{CO} absorption at 1860 cm^{-1} that is identical to an authentic sample of $[V^{-I}(CO)_6]^-$. $[V^{-I}(CO)_6]^-$ undoubtedly forms from the disproportionation of $[V^0(CO)_6]$, as has been established from the reaction with several

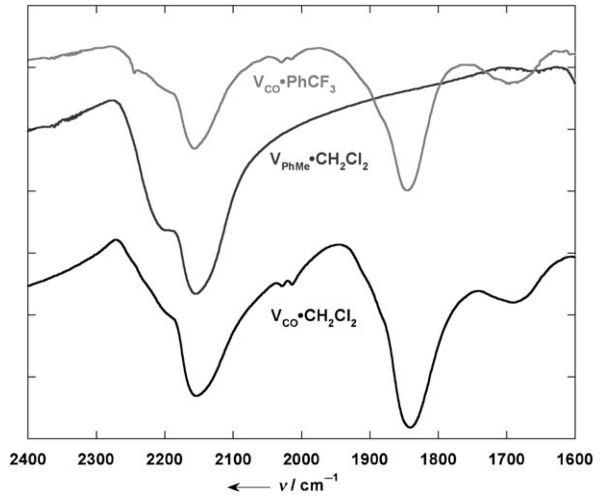


Figure 2. IR spectra of $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ in the range 1600 to 2400 cm^{-1}.

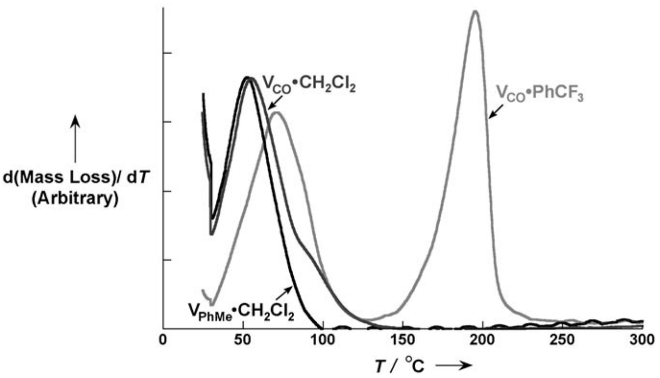


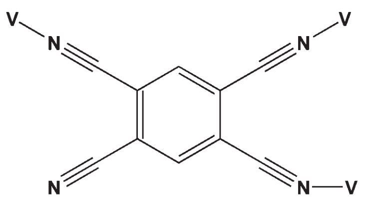
Figure 3. Derivative [d(mass loss)/d*T*] of the TGA traces for $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$.

bases.[23] Nonetheless, absorptions in these regions were not observed for the reaction of $[V(CO)_6]$ and TCNE,[3b,8,10] TCNQ,[16] TCNP,[15], and others[14] as CO is facilely lost.[18] Heating the $\mathbf{V_{CO}\cdot solv.}$ samples leads to an attenuation of both the $\nu \approx 1845$ and 1699 cm^{-1} absorptions in accord with CO loss, and growth of a peak at $\nu = 2211$ cm^{-1} arising from an increased intensity of the absorption of the band that forms the shoulder.

The 1699 cm^{-1} absorption is assigned to a bridging isocarbonyl, V−C≡O−V. Albeit rare, this linkage has been structurally characterized for $[(OC)_5V^{-I}(\mu\text{-}CO)V^{II}(thf)_4(\mu\text{-}CO)V^{-I}(CO)_5]$,[24a] whose 1684 cm^{-1} absorption is assigned to $\nu_{\mu\text{-}CO}$.[23] Likewise, $[(C_5Me_5)_2V^{II}(\mu\text{-}OC)V^{-I}(CO)_5]$ has a broad absorption at 1708 cm^{-1},[24b] which is in good agreement with the observed values for $\mathbf{V_{CO}\cdot solv}$. Hence, the $\mathbf{V_{CO}\cdot solv.}$ (**solv.** = CH_2Cl_2, $PhCF_3$) materials are proposed to have $[V^{-I}(CO)_6]^-$ centers with bridging isocarbonyl units. The presence of one ν_{CO} absorption, albeit broad, suggests that the $[V^{-I}(CO)_6]^-$ has high symmetry as $[(C_5Me_5)_2V^{II}(\mu\text{-}OC)V^{-I}(CO)_5]$ and $[(OC)_5V^{-I}(\mu\text{-}CO)V^{II}(thf)_4(\mu\text{-}CO)V^{-I}(CO)_5]$ with a single bridging isocarbonyl have multiple ν_{CO} absorptions.[23,24b]

Thermogravimetric analysis (TGA)[25a] of $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{CO}\cdot CH_2Cl}$ reveal mass-loss events (Figure 3). For $\mathbf{V_{CO}\cdot CH_2Cl_2}$ the CO and CH_2Cl_2 losses overlap in temperature and occur below 140 °C, with the shoulder at approximately 100 °C attributed to CO loss. This assignment is supported by the trace for $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ in which this shoulder is not present and the CH_2Cl_2 loss occurs below 100 °C. For $\mathbf{V_{CO}\cdot PhCF_3}$ the CO loss occurs below 120 °C, and the $PhCF_3$ loss occurs between 125 and 230 °C. This result is consistent with the lower volatility of $PhCF_3$ (b.p. = 102 °C) with respect to CH_2Cl_2 (b.p. = 40 °C). To confirm the presence of CO and its facile loss, high-resolution mass spectra[25b] as a function of heating were obtained for these samples, and a significant amount CO was detected when the samples were heated to 33 °C.

The composition of $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ was determined from elemental analyses to be $V^{II}[TCNB]_2\cdot 0.05\,CH_2Cl_2$[26a] consistent with the reported compositions of other $V[A]_2$-based (A = TCNE,[3b,8] α,α′-dicyanoperfluorostilbene,[14] TCNP,[15] TCNQ[16]) magnets. Hence, $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ is proposed to have a structure similar to $V[TCNP]_2\cdot z$ solv. (**1**), as it is has a similar composition and it magnetically orders at the same T_c (see below). In contrast, and consistent with the presence of $[V^{-I}(CO)_6]^-$, the composition of $\mathbf{V_{CO}\cdot solv.}$ as determined from elemental analyses, is $V^{II}[TCNB]_x[V^{-I}(CO)_y]_{0.5}\cdot z$ solv. ($4 > x > 3.5$; $6 > y > 3.2$; $z < 0.4$), with samples of solv. = CH_2Cl_2, $x = 3.8$, $y = 6$, $z = 0.05$,[26b] solv. = $PhCF_3$, $x = 3.8$, $y = 6$, $z = 0.1$ characterized.[26c] This non-stoichiometry and variable stoichiometry has also been observed for $V[TCNE]_x\cdot z\,CH_2Cl_2$ ($x \approx 2$; $z \approx 0.5$).[8] Owing to the time delay between their preparation and analysis, CO (and solvent) loss occurs; nonetheless, the elemental-analysis data are consistent with the presence of CO. Hence, from a charge consideration $\mathbf{V_{CO}\cdot CH_2Cl_2}$ and $\mathbf{V_{CO}\cdot PhCF_3}$ are formulated as $V^{II}[TCNB]^{-}_{1.5}\text{-}[TCNB]^{0}_{x-15}[V^{-I}(CO)_6]_{0.5}\cdot z$ solv. The presence of $TCNB^0$, however is not evident from the IR spectra as the $\nu_{C\equiv N}$ absorption expected at 2245 cm^{-1} for $TCNB^0$ is not present. The absence of a $\nu_{C\equiv N}$ absorption suggests that reduced TCNB self-associates to form a complex delocalized anionic species, as recently observed for $[TCNB]_3^{2-}$.[27] TGA analysis of percentage mass losses for the $\mathbf{V_{CO}\cdot PhCF_3}$ solv. and CO events, that is, 14.7(3) and 14.3(4)%, respectively (Figure 3), corresponds to the composition of $\mathbf{V_{CO}\cdot PhCF_3}$ being $V[TCNB]_{3.8}[V(CO)_{5.4}]_{0.5}\cdot PhCF_3$ suggestive of further loss in transit for elemental-analyzed samples. The composition of $\mathbf{V_{CO}\cdot CH_2Cl_2}$ is less definitive owing to the overlap of the solv. and CO mass-loss events. The composition of $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ from elemental analysis as well as solv. mass loss in the TGA is $V[TCNB]_2\cdot z\,CH_2Cl_2$ $z = 0.7$ and 0.05, respectively.



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Powder diffraction data, like those observed for V[TCNZ]$_x$ (Z = E, P, Q), indicate that each of these materials is amorphous. Unlike $\mathrm{V^{II}[TCNB]_2\cdot 0.05\,CH_2Cl_2}$, which is compositionally similar to several V[A]$_2$-based magnets, and, as discussed above, is proposed to be structurally similar, $\mathbf{V_{CO}\cdot solv.}$ (solv. = $\mathrm{CH_2Cl_2}$, $\mathrm{PhCF_3}$) of $\mathrm{V^{II}(TCNB^{-})_{1.5}(TCNB^{0})_{\mathit{x}-1.5}[V^{-I}(CO)_{\mathit{v}}]_{0.5}\cdot \mathit{z}\,solv.}$ composition represents a new family of organic-based magnets. The structure of $\mathbf{V_{CO}\cdot solv.}$ is elusive and perplexing. Based upon the similarity of the IR spectra with that of V[TCNE]$_x$ in the ν_{CN} region, a similar structure is proposed, containing TCNB radical anions that are nitrile bound to V$^{\mathrm{II}}$. However, the structure is distinct in that $\mathrm{[V^{-I}(CO)_6]^{-}}$ is present, and possesses symmetrical isocarbonyl bridging to the V$^{\mathrm{II}}$ center as well as additional TCNB being present. Studies aimed at further elucidating the structure of $\mathbf{V_{CO}\cdot solv.}$ are in progress; herein the focus is on its reproducible magnetic ordering.

The 2 to 400 K magnetic susceptibility, $\chi(T)$, was determined on a Quantum Design MPMS-5XL magnetometer, and the 300–370, 315–325, and 190–210 K data can be fit to the Curie–Weiss expression with $\theta = 326$ (for $\mathbf{V_{CO}\cdot CH_2Cl_2}$), 308 ($\mathbf{V_{CO}\cdot PhCF_3}$), and 188 K ($\mathbf{V_{PhMe}\cdot CH_2Cl_2}$), indicative of effective ferromagnetic coupling (Figure 4). At higher temperature, $\mathrm{d}[1/\chi(T)]/\mathrm{d}T$ decreases, indicative of longer range antiferromagnetic coupling. Below θ, $\chi T(T)$ increases to values as high as 17500 emu Oe mol^{-1} for $\mathbf{V_{CO}\cdot CH_2Cl_2}$, and $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$, reach maxima at $0.64 \pm 0.05\,\theta$ prior to decreasing. The behavior is suggestive of magnetic ordering. The spin-only values of χT of 2.44 (for $\mathbf{V_{CO}\cdot CH_2Cl_2}$), 2.44 ($\mathbf{V_{CO}\cdot PhCF_3}$), and 2.63 ($\mathbf{V_{PhMe}\cdot CH_2Cl_2}$) emu Oe mol^{-1} are significantly exceeded.

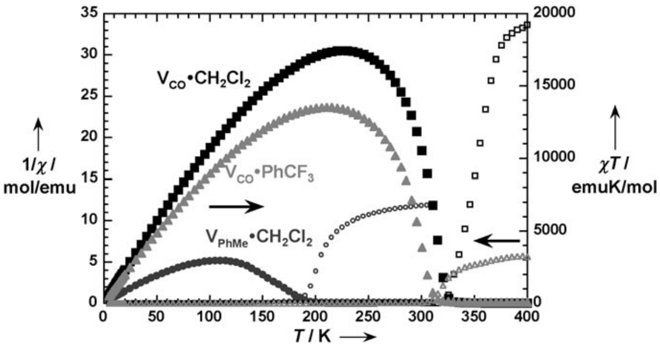

Figure 4. $\chi T(T)$ (filled symbols) and $1/\chi(T)$ (open symbols) for $\mathbf{V_{CO}\cdot CH_2Cl_2}$ (■,□), $\mathbf{V_{CO}\cdot PhCF_3}$ (▲,△), and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ (●,○) in a 100 Oe applied field.

The 5 Oe zero-field cooled (ZFC) and field-cooled (FC) magnetization, $M(T)$, have bifurcation temperatures at 311, 306, and 206 K for $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$, respectively (Figure 5). Their respective T_{c} values obtained from an extrapolation of the low-field $M(T)$ to the temperature at which $M(T)\rightarrow 0$ are 325, 305, and 200 K (Figure 5). These T_{c} values are comparable to θ in accord with mean-field theory.

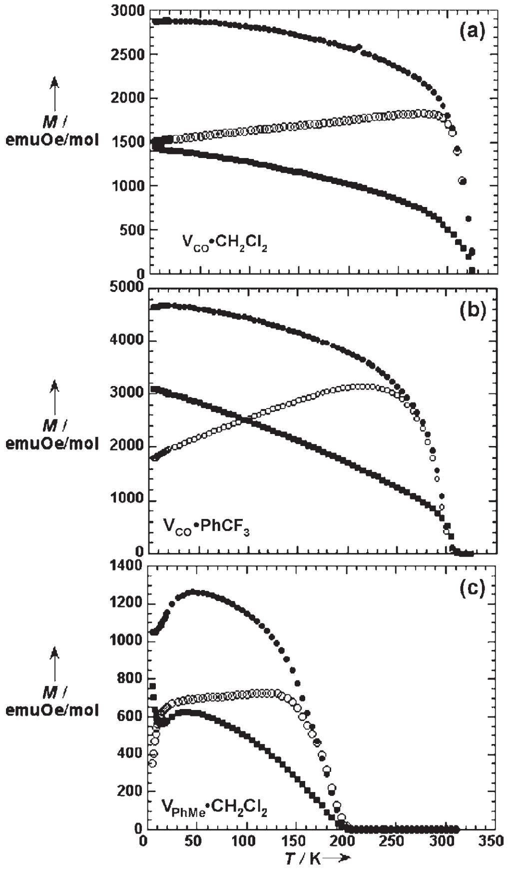

Figure 5. Zero-field (○) and field-cooled (●) (ZFC/FC) as well as remnant magnetization (■) for $\mathbf{V_{CO}\cdot CH_2Cl_2}$ (a), $\mathbf{V_{CO}\cdot PhCF_3}$ (b), and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ (c) in a 5 Oe applied field.

The 10 K field-dependent magnetization, $M(H)$, shows an immediate increase and reaches saturation at ≤ 75 Oe (Figure 6). $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$, respectively, saturate to 11400, 10700, and 4700 emu Oe mol^{-1} at 50000 Oe (not shown) For $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ this is 84 % of the expected value of 5585 emu Oe mol^{-1} for $S = 3/2$ V$^{\mathrm{II}}$ antiferromagnetically coupled to two $S = 1/2$ $\mathrm{[TCNB]^{\cdot -}}$, consistent with the system being a ferrimagnet. In contrast, antiferromagnetic coupling between an $S = 3/2$ V$^{\mathrm{II}}$ and $1.5\,S = 1/2$ $\mathrm{[TCNB]^{\cdot -}}$ both $\mathbf{V_{CO}\cdot CH_2Cl_2}$ and $\mathrm{V_{CO}\cdot PhCF_3}$ should saturate to 8378 emu Oe mol^{-1}, however approximately 11000 emu Oe mol^{-1} is observed, suggestive of more complex magnetic interactions. Each of these materials has a 7 ± 1 Oe coercive field at 10 and 280 K (Figure 6). These data indicate that they are relatively soft ferrimagnets as reported for V[TCNE]$_2$[8,10] and V[TCNP]$_2$.[15] The remnant magnetization (M_{rem}) is 1860, 3400, and 990 emu Oe mol^{-1} at 10 K for $\mathbf{V_{CO}\cdot CH_2Cl_2}$, $\mathbf{V_{CO}\cdot PhCF_3}$, and $\mathbf{V_{PhMe}\cdot CH_2Cl_2}$ (Figure 6), respectively. The in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components of ac susceptibility at 10, 100, and 1000 Hz were measured and are consistent with magnetic ordering as a ferrimagnet.

In summary, the reaction of TCNB with $\mathrm{[V^{0}(CO)_6]}$ in $\mathrm{CH_2Cl_2}$ and $\mathrm{PhCF_3}$ forms a new compositional family of magnets with T_{c} values exceeding room temperature and as high as 325 K (≈50 °C). The magnets are formulated as

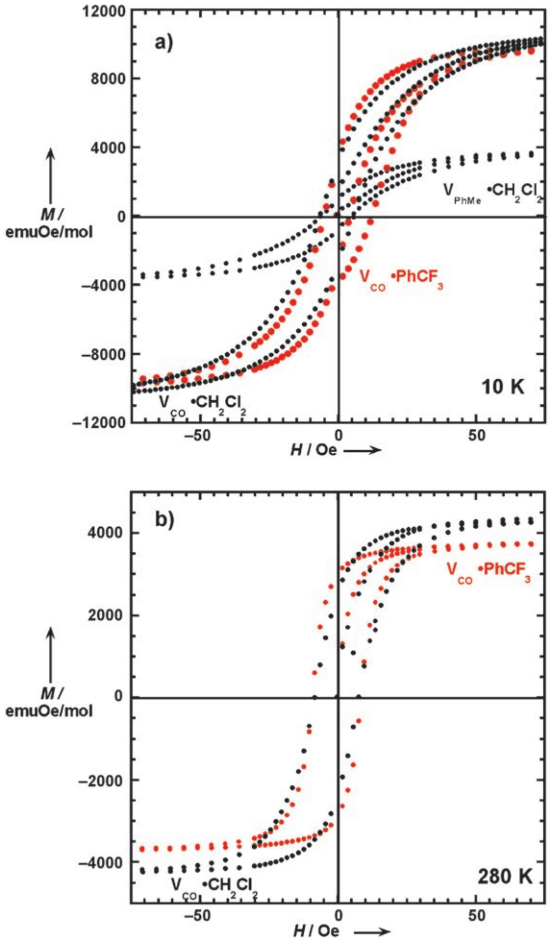

Figure 6. *M*(*H*) showing hysteretic behavior for $\mathbf{V_{CO}{\cdot}CH_2Cl_2}$, $\mathbf{V_{CO}{\cdot}PhCF_3}$, and $\mathbf{V_{PhMe}{\cdot}CH_2Cl_2}$ at 10 K (a) and $\mathbf{V_{CO}{\cdot}CH_2Cl_2}$ and $\mathbf{V_{CO}{\cdot}PhCF_3}$ at 280 K (b).

$V^{II}[TCNB]^{-}_{1.5}[TCNB]^{0}_{x-1.5}[V^{-I}(CO)_6]_{0.5}{\cdot}z$ solv. ($4 > x > 3.5$; solv. = CH_2Cl_2, $PhCF_3$), but albeit possessing TCNB and symmetric isocarbonyl bonding of $[V^{-I}(CO)_6]^-$ moieties, its structure is elusive. In contrast, the reaction of TCNB with $[V^0(PhMe)_2]$ in CH_2Cl_2 forms a magnet of $V^{II}[TCNB]_2{\cdot}z\,CH_2Cl_2$ composition that orders at 200 K. Hence, the addition of diamagnetic TCNB and $[V^{-I}(CO)_6]^-$ moieties unexpectedly and quite surprisingly leads to a 62 % increase in T_c (to 325 K; ≈50 °C). Furthermore, the values of the saturation magnetization suggest that the materials are compositionally and structurally even more complex, and this new family of magnets is the focus of studies to resolve these issues. In addition, TCNB, unlike TCNE, possesses hydrogen atoms that could be chemically substituted and perhaps attached to a polymer backbone leading to polymeric magnets.

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Keywords: cyanocarbon compounds · electron acceptors · electron transfer · organic-based magnets · vanadium

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[22] A solution of either $[V^0(CO)_6]$ or $[V^0(PhMe)_2]$ (0.150 mmol) in a minimal amount (≈5 mL) of the desired solvent was added dropwise into a stirred suspension of 2 equivalents of TCNB (0.300 mmol, ≈10 mL) under an inert atmosphere of dry nitrogen. The mixture became dark. After stirring for ca.

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20 min, the dark, amorphous precipitate was collected by suction filtration, and dried in vacuo (Yield ≈ 50 %).

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[25] a) TA Instruments 2050 TGA located in a Dry Box (< 1 ppm O_2); b) CO ($m/z = 27.98833$ amu) was distinguished from N_2 ($m/z = 28.00027$ amu) using a Finnagan MAT95 mass spectrometer.

[26] Elemental analysis (%) calcd for a) $V^{II}(TCNB)_2\cdot 0.05\,CH_2Cl_2$ ($C_{20.05}H_{4.1}N_8VCl_{0.1}$): C 58.52, H 1.00, N 27.23, V 12.38; Found: C 58.36, H 0.82, N 27.56, V 12.21; b) $V(TCNB)_{3.8}[V(CO)_6]_{0.5}\cdot 0.05\,CH_2Cl_2$ ($C_{41.05}H_{7.7}N_{15.2}V_{1.5}Cl_{0.1}$): C 58.58, H 0.92, N 25.30; Found: C 58.68, H 0.90, N 25.10; c) $V(TCNB)_{3.8}[V(CO)_6]_{0.5}\cdot 0.1\,PhCF_3$ $C_{40.07}H_{8.1}N_{15.2}V_{1.5}F_{0.3}$: C 59.32, H 0.99, N 25.84, V 9.27, F 0.69, O 3.88; Found: C 59.15, H 1.23, N 26.33, V 8.96, F 0.98, O 3.96.

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