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Organometallic magnets

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Contents

Abstract

Organometallic chemistry has enabled the discovery of the first organic magnets, i.e. those with unpaired electron spins in the p orbitals, and the first organic magnet with a magnetic ordering temperature exceeding room temperature. The reaction of $\mathrm{Fe^{II}(C_5Me_5)_2}$ and tetracyanoethylene (TCNE) forms the electron transfer salt $\mathrm{[Fe(C_5Me_5)_2]^{\bullet +}[TCNE]^{\bullet -}}$, which is a bulk ferromagnet below 4.8 K. In contrast, the reaction of either $\mathrm{V(C_6H_6)_2}$ or $\mathrm{V(CO)_6}$ and TCNE forms $\mathrm{V(TCNE)_x \cdot y(solvent)}$, which is a bulk ferrimagnet below its thermal decomposition temperature of 350 K with a $T_c \sim 400$ K. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organic magnets; Ferromagnetic; Magnetic ordering temperature

1. Metallocene-based magnets

Magnets have comprised of a number of metals (or their oxides) with the essential electron spins solely residing in d- or for some materials in f-orbitals.

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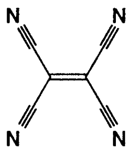
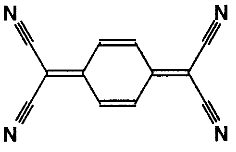
Magnets based on p-orbital spin-bearing organic radicals were fleetingly dismissed [1], or only proposed theoretically [2], but their realization was achieved a few decades later. The first organic magnet was $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ (TCNE = tetracyanoethylene). $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ possessed a $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structural motif, Fig. 1 [3]. Upon application of only the Earth's magnetic field (ca. 0.5 Oe) a spontaneous magnetization characterizing this material was observed [4]. The saturation magnetization, M_s, for single crystals aligned parallel to the chain axis exceeds that of iron metal by 32% on a per Fe or g-atom basis. This is in excellent agreement with the calculated M_s for ferromagnetic alignment of the donor and the acceptor [5]. The critical (Curie) or magnetic ordering temperature, T_c, is 4.8 K. The magnetization as a function of applied field data, $M(H)$, for $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ exhibits hysteresis loops, Fig. 2, with a large coercive field of 1000 G at 2 K [4].



TCNE



TCNQ

To understand the magnetic interactions leading to the observed bulk magnetic behavior the magnetic susceptibility was analyzed using several different physical models. Independent spins are evident as above 130 K the susceptibility fits the Curie–Weiss law with $\theta = +30$ K [4,5]. A one-dimensional Heisenberg model with a ferromagnetic exchange coupling, J, of 19 $\mathrm{cm^{-1}}$, however, better accounts for the data down to 16 K [4]. These models fail to account for the magnetic behavior below 16 K, as long range spin and three-dimensional spin interactions become increasingly significant. This continues until three-dimensional ferromagnetic ordering occurs at 4.8 K. The intrachain coupling is attributed to the configuration admixing of an excited state with the ground state, which has been reported as the mechanism for stabilizing ferromagnetic interactions within donor–acceptor (D/A) complexes and a paradigm to make some predictions as to the magnetic coupling of new materials within this class of materials [6,7].

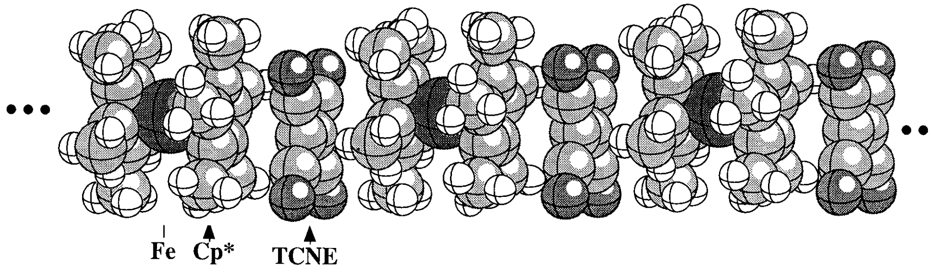


Fig. 1. A segment of the parallel chain for $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$.

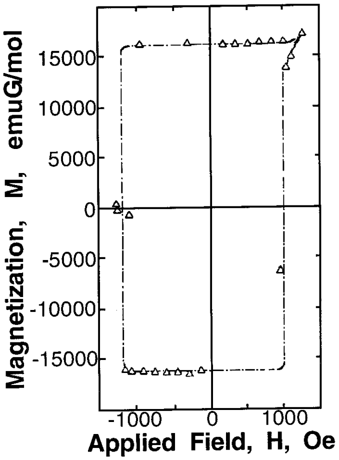


Fig. 2. Hysteresis, $M(H)$, of $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ at 2 K.

Several related compounds were studied to identify a structure–function relationship that could be used to aid in preparing new magnets with higher critical temperatures. Three approaches were investigated: (a) substitution of Fe^{III} with other metal ions; (b) Me groups with H and Et; and (c) $[TCNE]^{\bullet-}$ with other radical anion acceptors.

Replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[A]^{\bullet-}$ [A = TCNE, TCNQ] with triplet Mn^{III}, and quartet Cr^{III} leads to compounds exhibiting ferro-, and ferromagnetic coupling, respectively, Table 1. For M = Mn, the T_c increases from 4.8 [3,4] to 8.8 K [10] for A = TCNE {and from 3.1 [11] to 6.3 K [10] for A = TCNQ}. This is expected from mean-field theory where $T_c \propto S(S+1)$ [11]. In contrast, $[Cr^{III}(C_5Me_5)_2]^{+}[TCNE]^{\bullet-}$ [7] and $[Cr^{III}(C_5Me_5)_2]^{+}[TCNQ]^{\bullet-}$ [12] behave unexpectedly, i.e. although $S = 3/2$ for Cr^{III}, and a further increase in T_c is expected, their respective T_c values are 3.65 and 3.1 K substantially reduced from that of

Table 1
Summary of the critical temperatures (T_c) and coercive fields (H_{cr}) for $[M^{III}(C_5Me_5)_2][A]$ (M = Fe, Mn, Cr; A = TCNE, TCNQ)

	$[TCNE]^{\bullet-}$			$[TCNQ]^{\bullet-}$		
	Fe	Mn	Cr	Fe	Mn	Cr
S, cation	1/2	1	3/2	1/2	1	3/2
S, anion	1/2	1/2	1/2	1/2	1/2	1/2
T_c (K)	4.8	8.8	3.65	3.0	6.1	3.1
θ (K)	+16.9	+22.6	+22.2	+3.8	+10.5	+11.6
H_{cr}, Oe (K)	1000 (2)	1200 (4.2)	[a]	[a]	3600 (3)	[a]
Ref.	[3,4]	[8]	[7]	[9]	[10]	[12]

[a] Not reported.

$[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ [3,4] and $[Fe^{III}(C_5Me_5)_2]^{+}[TCNQ]^{\bullet-}$ [9]. Hence, the mean-field prediction fails, suggesting competition from another mechanism. Finally, attempts to prepare $[M^{III}(C_5Me_5)_2]^{+}[TCNE]^{\bullet-}$ (M = Ru, Os) have been unsuccessful [13] (Fig. 3).

Substituted C_5-rings may maintain the fivefold symmetry needed to form a radical cation with degenerate partially occupied MOs and a Kramer's doublet ground state as reported for $[Fe^{III}(C_5Me_5)_2]^{\bullet+}$. Hence, ferrocene, 1,2,3,4,5-pentamethylferrocene, and decaethylferrocene were also studied. Ferrocene, however, is significantly more difficult to oxidize than $Fe^{II}(C_5Me_5)_2$, and is not oxidized by TCNE [14]. Nonetheless, $[Fe^{III}(C_5H_5)_2][TCNE]$ has been reported and has the same structure type [15], Fig. 1, but is diamagnetic [15b]. In contrast, $Fe^{II}(C_5H_5)(C_5Me_5)$ is able to reduce TCNE and the one-dimensional salt in addition to other phases were prepared [16]. This one-dimensional material exhibits weak ferromagnetic coupling ($\theta = +3.2$ K), and does not exhibit magnetic ordering above 2 K [16]. $[Fe^{III}(C_5Et_5)_2][TCNE]$ has been made and has a proposed one-dimensional structure. Likewise, this electron transfer salt also exhibits ferromagnetic coupling ($\theta = +7.5$ K), but again not three-dimensional magnetic ordering [17].

To check the need for a Kramers doublet ground state, $[Fe^{III}(C_5Me_4H)_2][TCNE]$ with the reduced symmetry cation was prepared [18]. Here θ is ca. 0 K. The lack of either three-dimensional ferro- or antiferromagnetic ordering above 2.2 K in $[Fe^{III}(C_5Me_4H)_2][TCNE]^{-}$ is in sharp contrast with the behavior of $[Fe^{III}(C_5Me_5)_2][TCNE]^{-}$ supporting that a Kramer's doublet ground state is needed.

Replacement of $[TCNE]^{\bullet-}$ with diamagnetic $[C_3(CN)_5]^{-}$ also leads to the formation of a $\cdots D^{\bullet+}A^{-}D^{\bullet+}A^{-}\cdots$ structured phase; but it exhibits only Curie susceptibility ($\theta = -1$ K) [3]. The $[Co^{III}(C_5Me_5)_2]^{+}[TCNE]^{-}$ complex with a diamagnetic donor has been prepared and exhibits essentially the Curie susceptibility anticipated for $[TCNE]^{\bullet-}$ radicals separated by diamagnetic ion spaces [3]. This demonstrates the necessity of having both the D and A radicals for stabilizing ferromagnetic coupling in the linear chain alternating $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ motif.

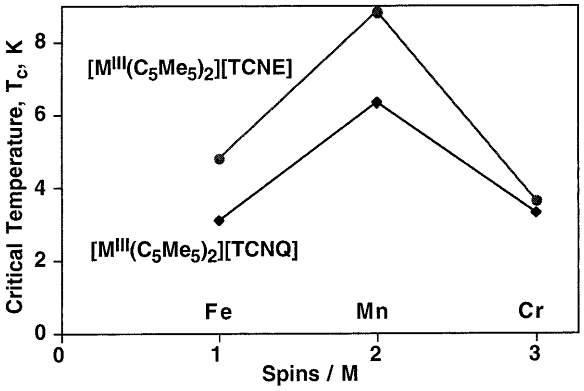


Fig. 3. The variation of T_c with increasing the spin number per metal in $[M^{III}(C_5Me_5)_2]^{+}[TCNE]^{\bullet-}$.

It is important to note that $[Fe^{III}(C_5Me_5)_2]^+[TCNQ]$, DA, has been isolated as three polymorphs, Fig. 4, each with differing magnetic properties. The monoclinic, paramagnetic purple phase forms upon fast cooling in acetonitrile [19]. It has a herringbone array of isolated DAAD units [19], Fig. 4(a), such that each repeat unit has one independent spin. Additionally upon slow cooling, two a phases consisting of parallel ···DADADA··· one-dimensional chains form [9,19]. Slow cooling to room temperature from acetonitrile leads to the isolation of the green triclinic, metamagnetic phase (Fig. 4(b)) [19]. In contrast, cooling to −20°C leads to the monoclinic, ferromagnetic phase (purple parallelepipeds) (Fig. 4(c)) [9]. Both one-dimensional phases have two spins per repeat unit. Magnetic ordering only occurs for the one-dimensional phases with the former having a transition to a antiferromagnetic state at a T_c of 2.55 K [19], while the latter has a transition to a ferromagnetic state at a T_c of 3.0 K [9]. The ferromagnetic behavior is attributed to shorter (3.609 versus 3.635 Å) and hence stronger ferromagnetic coupling between adjacent Fe(III) sites as well as longer (3.625 versus 3.478 Å) and hence weaker antiferromagnetically coupling between adjacent $[TCNE]^{\bullet-}$ groups.

With a 4.8 K magnetic ordering temperature $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ is the first magnet: (i) with spins residing in a p-orbital; (ii) exhibiting magnetic hysteresis; (iii) that lacked an extended one-, two,- or three-dimensional network structure;

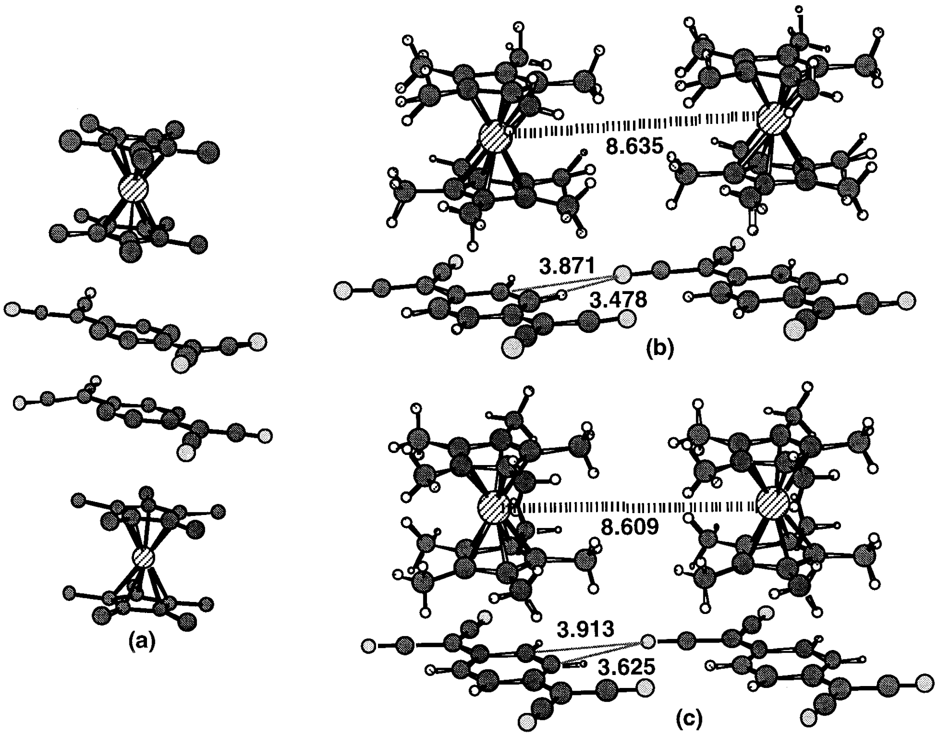
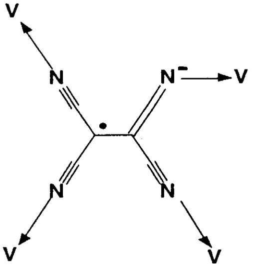


Fig. 4. Packing arrangements for three polymorphs of $[Fe^{III}(C_5Me_5)_2]^+[TCNQ]^{\bullet-}$.

that (iv) was soluble in conventional organic solvents; and (v) did not require metallurgical processing. Today, molecule-based magnets [20] include many diverse examples of materials exhibiting magnetic ordering including ferromagnets, ferrimagnets, canted/weak ferromagnets, metamagnets, and spin glasses. Materials range from organic nitroxides, mixed organic radicals/organometallic or inorganic coordination systems, to the more classical inorganic coordination compounds (e.g. mixed metal cyanides and oxalates), with several classes of the organic–metal-ion containing ones possessing $[TCNE]^{\bullet -}$ studied in our laboratory.

2. $M(TCNE)_x$ magnets

To extend our knowledge regarding the $[M^{III}(C_5Me_5)_2]^+[TCNE]^{\bullet -}$ family of magnets, the reaction of TCNE and $V^0(C_6H_6)_2$, isoelectronic with d^5 $Mn^{II}(C_5Me_5)_2$, was executed with the hope of forming another organic magnet. $[V^I(C_6H_6)_2]^+[TCNE]^{\bullet -}$ was not isolated, however, a magnet of composition $V(TCNE)_x \cdot y(CH_2Cl_2)$ ($x \sim 2$; $y \sim 1/2$) was identified [21]. This material, albeit extremely water and air sensitive, magnetically ordered below its thermal decomposition temperature (~ 350 K), and had a critical temperature ca. 400 K [21] Although the structure is unknown, the magnetic, IR, and elemental analyses data led to the formulation of $V^{II}(TCNE)_2 \cdot 1/2(CH_2Cl_2)$ possessing an $S = 3/2$ V^{II} and two $S = 1/2$ $[TCNE]^{\bullet -}$ moieties. A three-dimensional network structure, **I**, with each V surrounded by up to six ligands, primarily nitrogens from different $[TCNE]^{\bullet -}$ species, and the $[TCNE]^{\bullet -}$ moieties binding up to four different vanadium atoms via σ-N bonds is proposed.



I

$V(TCNE)_x \cdot y(CH_2Cl_2)$ ($x \sim 2$; $y \sim 1/2$) exhibits a field-dependent magnetization, $M(H)$, between 1.4 and 350 K, Fig. 5, and saturates to ca. 6000 emu Oe mol^{-1} at 2 K and 19.5 kG. The expected maximum or saturation magnetization, M_s, assuming $g = 2$, for ferromagnetic coupling between $S = 3/2$ V^{II} and the two $S = 1/2$ $[TCNE]^{\bullet -}$ moieties (i.e. $S_{total} = 5/2$) is ca. 28 000 emu Oe mol^{-1}. In contrast, antiferromagnetic coupling, leading to ferrimagnetic behavior, leads to an $S_{total} = 1/2$ with an expected M_s of 5600 emu Oe mol^{-1}. The latter is in excellent agreement with the observed value. Hysteresis with a coercive field of 60 G is observed at room temperature. The strong magnetic behavior is noted by a powder of $V(TCNE)_x \cdot y(CH_2Cl_2)$ being attracted to a permanent magnet at room tempera-

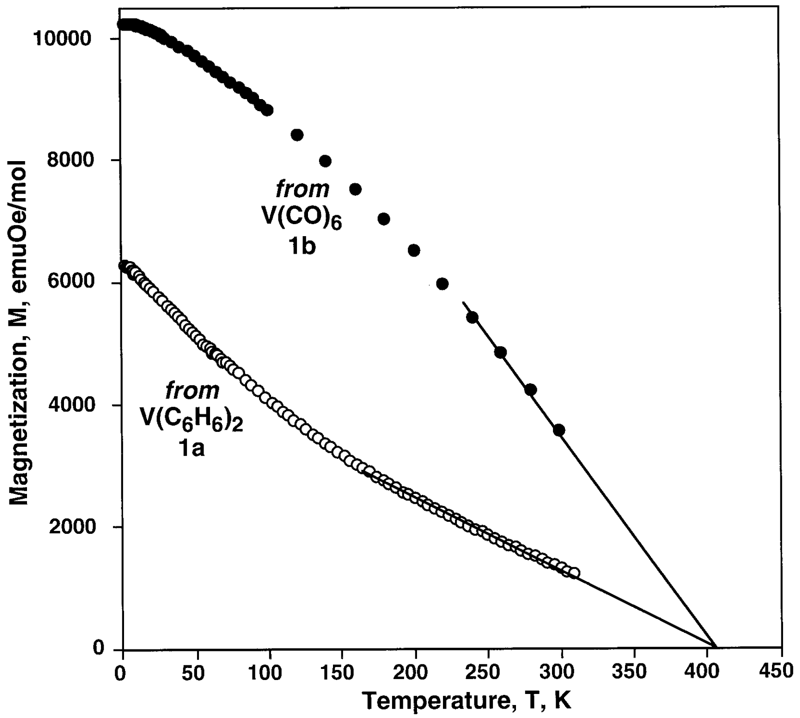


Fig. 5. Magnetization as a function of temperature, $M(T)$, at 1 kG for V(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) prepared from V(C$_6$H$_6$)$_2$ and V(CO)$_6$.

ture, Fig. 6. Hence, V(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) is the first example of an organic-based material with a critical temperature exceeding room temperature.

The reaction of V(C$_6$H$_6$)$_2$ and other strong acceptors such as TCNQ, perfluoro-TCNQ (TCNQF$_4$), C$_4$(CN)$_6$, 2,3,5,6-tetrachlorobenzoquinone (chloranil), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) led to insoluble precipitates of unknown composition, which obey the Curie–Weiss expression with $\theta < 0$ characteristic of antiferromagnetic behavior.

V(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) is structurally disordered; hence, improved preparative routes leading to less disorder as well as avoiding the difficult-to-prepare V(C$_6$H$_6$)$_2$ were sought. The reaction of TCNE with isoelectronic V^0(C$_5$H$_5$)(C$_7$H$_7$) in contrast to V^0(C$_6$H$_6$)$_2$ did form a magnet [22]. This is a consequence of the greater oxidation potential of V^0(C$_5$H$_5$)(C$_7$H$_7$) (0.34 V versus SCE) with respect to V^0(C$_6$H$_6$)$_2$ (-0.28 V). The reaction of V^0(CO)$_6$ with TCNE at room temperature led to room-temperature magnets.

The elemental analyses suggest that the magnets prepared from V(C$_6$H$_6$)$_2$ or V(CO)$_6$ have similar compositions. The similarity of the IR spectra for the magnets prepared from V(C$_6$H$_6$)$_2$ and V(CO)$_6$ and the absence of $\nu_{C\equiv O}$ stretches in the 1800 to 2000 cm^{-1} region for the latter magnet strongly suggest that all the carbonyls are expelled from the vanadium coordination sphere upon the reaction of V(CO)$_6$

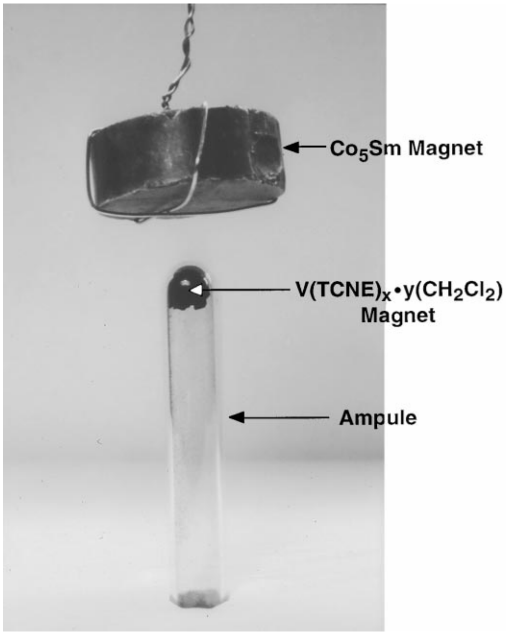


Fig. 6. Photograph of a powdered sample of the $V(TCNE)_x \cdot y(CH_2Cl_2)$ being attracted to a Co_5Sm magnet.

with TCNE [22]. This was confirmed by the loss of CO via Toepler pump measurements for: $V(CO)_6 + y TCNE \rightarrow CO + V(TCNE)_y(CO)_{6-x}$ with $x = 5.9 \pm 0.1$. Based on the lack of CO and the similarity between the IR spectra for the magnets prepared from $V(CO)_6$ and $V(C_6H_6)_2$, both are assigned the same structure. Nonetheless, differences between the ν_{CN} absorptions indicate that the two magnets are structurally inequivalent and different temperature dependence of the magnetic behavior is observed, although both have a $T_c \sim 400$ K, Fig. 5.

The magnetization for the $V(CO)_6$-prepared magnet, Fig. 5, is 10 300 emu Oe mol^{-1} at 4.2 K and 3600 emu Oe mol^{-1} at room temperature; an increase of 67 and 133%, respectively, with respect to the $V(C_6H_6)_2$-prepared magnet. The magnetization decreases monotonically with increasing temperature for the $V(C_6H_6)_2$-prepared magnet, this is less pronounced or the $V(CO)_6$-prepared magnet. The unusual linear decrease of magnetization with increasing temperature is characteristic of extensive disorder, suggesting that the $V(CO)_6$-prepared magnet is less disordered. Hysteresis with a coercive field of 15 Oe is observed at 4.2 K and at room temperature for the $V(CO)_6$-prepared magnet. This is significantly lower than the value of 60 Oe observed for the $V(C_6H_6)_2$-prepared magnet [21]. The extrapolated T_c values for both magnets are ~ 400 K, Fig. 5 [21].

The magnetic properties of these magnets suggest that more organometallic-prepared magnets with higher T_c values are achievable. Using cyanide ligands additional room temperature magnets also based on vanadium, even with $T_c \sim 100$°C have recently been reported [23].

Due to T_c exceeding room temperature, applications for this magnet can be envisioned [24]. One application is for magnetic shielding, the attenuation of magnetic fields found in many electronic applications, e.g. high voltage lines or near cell phones. The feasibility of using $V(TCNE)_x \cdot y$solvent for these applications has been reported [25].

Acknowledgements

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