Polyhedron 28 (2009) 1596–1605

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Oliver Kahn Lecture: Composition and structure of the $V[TCNE]_x$ (TCNE = tetracyanoethylene) room-temperature, organic-based magnet – A personal perspective

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A R T I C L E  I N F O

*Article history:*
Available online 23 January 2009

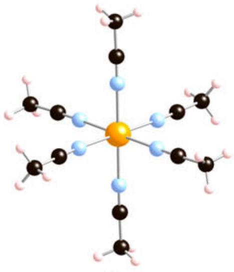
*Keywords:*
Magnetic ordering
TCNE
Organic-based magnet
Porous structure

A B S T R A C T

$V^{II}[TCNE]^{\cdot-}_z[TCNE]^{2-}_{1-z/2}$ ($1 < z < 2$) is the simplest formulation for the inhomogeneous and nonstoichiometric $V[TCNE]_x$ ($x = 1 + z/2$) room temperature magnet. This is based upon consideration of all of the surface, IR, elemental composition, and magnetic data. A limiting $z = 1$ 2-D, layered structural motif with layers of $\mu_4$-$[TCNE]^{\cdot-}$ bonded to four $V^{II}$ sites bridged by diamagnetic $\mu_4$-$[TCNE]^{2-}$ is described, and is sufficient to account for the observed $T_c$ exceeding room temperature and the observed relatively high conductivity. The $z = 2$ limiting structure with the same layers, but bridged by $S = 1/2$ $\mu$-$[TCNE]^{\cdot-}$ is identified and provides for a 3-D magnetic structure. Nonetheless, the magnet does not diffract, and the featureless morphology observed from TEM studies suggests that it is a glassy material. Attempts to grow crystalline $V[TCNE]_x$ by several slow diffusion methods were unsuccessful, and did not result is a magnetically ordered material. This suggests that the $V[TCNE]_x$ room temperature magnet is a kinetic phase, and preparing a crystalline kinetic product will be challenging.

## 1. Introduction

The reaction of $V(C_6H_6)_2$ with TCNE (tetracyanoethylene) forms a pyrophoric material that magnetically ordered as a ferrimagnet above room temperature [1]. The amorphous and disordered as well as inhomogeneous and nonstoichiometric nature of the material has thwarted its detailed structural characterization, and it was reported to be of nominal $V[TCNE]_x \cdot yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$) composition. Subsequently, a material of similar composition was reported from the reaction of $V(CO)_6$ with TCNE in dichloromethane [2], and later solvent-free thin films of the room temperature $V[TCNE]_x$ ($x \sim 2$) magnet were prepared via chemical vapor deposition (CVD)s using these reactants [3]. X-ray photoelectron spectroscopy (XPS) [3a], extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) studies of these films revealed the presence of $V^{II}$ surrounded by six nitrogen atoms with average V–N distances of 2.084 (5) Å at 300 K and 2.076 (4) Å at 10 K [4]. The V–N distance is in accord with that reported for $[V^{II}(NCMe)_6]^{2+}$ (**1**) with local $O_h$ symmetry (2.11 Å average at room temperature [5]). In addition, numerous studies indicate that electrons in valence and conducting bands of the $V[TCNE]_x$ films are spin polarized [6]; thus, this magnet is an appealing material for future generations of magnetic applications such as spintronics [7].



**1**

Albeit relatively well characterized from a magnetic perspective [1c], it is poorly characterized from composition, structural, and theoretical perspectives, although a computational study based on an idealized, octacoordinated $V^{II}[TCNE]_2$ has be reported [8], and this has limited the understanding the material. As noted above, EXAFS, XPS, and XANES results provided key information with respect to the oxidation state of vanadium as well as its first coordination sphere (not its geometry), but details as to its second nearest neighbor bonding and its extended structure have yet to be elucidated. The recently reported 2-D layered structures of $Fe^{II}[TCNE]_2 \cdot yCH_2Cl_2$ ($y \sim 0.5$) ($T_c = 100$ K) [9] and $[Fe^{II}[TCNE](NCMe)_2][Fe^{III}Cl_4]$ ($T_c$ = 90 K) [10], however, reveal clues for the extended framework motif of $V[TCNE]_x$ ($x \sim 2$).

Both $Fe^{II}[TCNE]_2 \cdot yCH_2Cl_2$ ($y \sim 0.5$) (Fig. 1) and $[Fe^{II}[TCNE](NCMe)_2][Fe^{III}Cl_4]$ (Fig. 2) possess $S = 1/2$ $\mu_4$-$[TCNE]^{\cdot-}$ (**2**) bridging to

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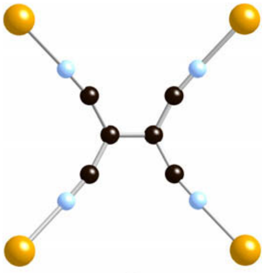
0277-5387/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.poly.2008.11.030

four $Fe^{II}$ ions in parallel, but undulating layers. These layers are connected in the former material via $S = 0$ $\mu_4$-$[C_4(CN)_8]^{2-}$ bridging to four $Fe^{II}$ ions, and capped by two $S = 0$ MeCN molecules in the latter material. Hence, both materials are layered magnets, and the presence $S = 1/2$ $\mu_4$-$[TCNE]^{\cdot-}$ bridging to four $V^{II}$ ions in parallel, but undulating layers were instantly thought to be present for $V[TCNE]_x$.



**2**

The lack of planarity of the $Fe^{II}_4[TCNE]^{\cdot-}$-based (**2**) magnetic layers that leads to the observed undulating layers is attributed to the competition between the octahedral environment about each $Fe^{II}$ ion (i.e. preferred 90° *cis*-CN–Fe–NC linkages) and linear coordination of the nitriles to the $Fe^{II}$ ions (i.e. preferred 180° sp-hybridized Fe–N–C linkages) that from simple geometrical considerations cannot coexist, as 165° Fe–N–C angles are needed (assuming 90° *cis*-CN–Fe–NC). Hence, to be more linear, i.e. Fe–N–C angle >165°, adjacent $Fe^{II}$-based octahedra cant with respect to each other and the layers buckle. This lack of planarity is also reported for some [11], but not all [11e,12], reduced $\mu_4$-TCNQ-based materials.

The factor-of-four higher $T_c$ for $V[TCNE]_x$ (400 K) with respect to these iron-containing magnets (~100 K) suggests that $V[TCNE]_x$ may have different structure that stabilizes the higher $T_c$. The Mean Field expression for $T_c$

$$T_c = \frac{2JzS(S+1)}{3k_B} \quad (1)$$

(*J* is the nearest neighbor exchange coupling, *z* is the number of nearest neighbors, and $k_B$ is Boltzmann's constant) reveals that by increasing the number of nearest neighbors (*z*) from 4 to 6, $T_c$ increases by 50%. Hence, a 3-D structural motif should have a higher $T_c$, and it is appealing to consider that $V[TCNE]_x$ has a 3-D magnetic structure, as originally postulated [1a]. For a ferrimagnet with two different spin sites, *i* and *j*, with $z_i$ and $z_j$ nearest neighbors, respectively, the Mean Field expression is expanded to Eq. (2) [13,14]

$$T_c = \frac{2|J|[z_i z_j S_i(S_i+1)S_j(S_j+1)]^{1/2}}{3k_B} \quad (2)$$

Assuming a constant *J*, increasing z from 4 to 6 for each V site (3-D) [15], and reducing *S* from 2 ($Fe^{II}$) to 3/2 ($V^{II}$) should result in a small reduction in $T_c$ by 3.2%, which is at variance to the observed factor-of-four increase. Hence, a 3-D structural motif is insufficient, and an enhanced *J* is needed to account for the factor-of-four increase in $T_c$.

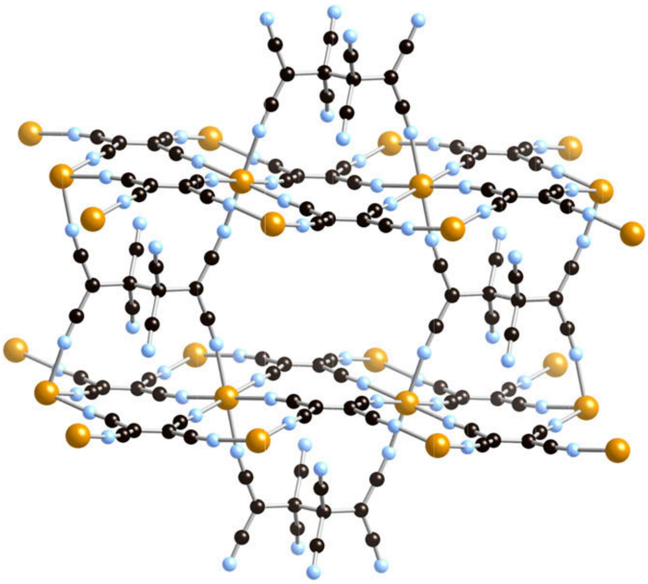


**Fig. 1.** Structure of $Fe^{II}[TCNE]_2 \cdot yCH_2Cl_2$ best formulated as $Fe^{II}[\mu_4\text{-TCNE}][\mu_4\text{-}C_4(CN)_8]_{1/2} \cdot yCH_2Cl_2$ ($CH_2Cl_2$ is disordered and resides in the channels within the porous framework structure) [9]. Each $Fe^{II}$ is bonded to 6 nitrogens, and only some $\mu_4$-$[C_4(CN)_8]^{2-}$ are shown for clarity.

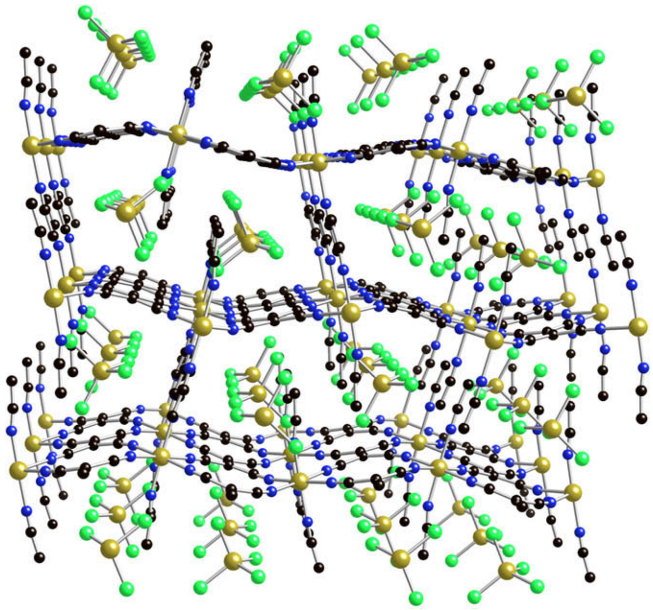


**Fig. 2.** Structure of $[Fe^{II}[TCNE](NCMe)_2][Fe^{III}Cl_4]$ [10].

### 1.1. Structural aspects

A 3-D magnetic structure can be envisaged via bridging $S = 1/2$ $\mu_4$-$[TCNE]^{\cdot-}$ magnetic layers with $\mu$-$[TCNE]^{\cdot-}$ (Fig. 3), among other possibilities [8a]. While this structural model is attractive, as it is consistent with the EXAFS and XANES data, it per se does not account for the enhanced $T_c$. Furthermore, this simplistic model is inconsistent with the diffraction data, as the structure would be ordered, and thus should diffract to some extent. Thus, the enhanced $T_c$ must arise, at least in part, from a larger exchange coupling, *J*.

From an analysis of the saturation magnetization temperature dependence, $M_s(T)$, by the Block law for spin wave theory, $J/k_B$ is estimated to be 100 K for $V[TCNE]_x$ [3]. Using Eq. (2) and $z_V = 4$ (and 6), a 447 K (and 548 K) $T_c$ is expected. While both 2- and 3-D structural models predict a $T_c$ above room temperature, the former is sufficient and closer to the observed value. While sufficient, magnetic anisotropy is needed for magnetic ordering in 2-D (Ising), which is not present for $V[TCNE]_x$.

Although the structure for $V[TCNE]_x$ is unknown, direct exchange coupling is expected to occur via V–NCCCN–V and V–NCCCCN–V spin-bearing linkages that are analogous to the Fe–NCCCN–Fe and Fe–NCCCCN–Fe linkages solely present for both layered (2-D) $Fe^{II}[TCNE][C_4(CN)_8]_{1/2}$ and $[Fe^{II}[TCNE](NCMe)_2][Fe^{III}Cl_4]$,