

Room temperature and near-room temperature coordination polymer magnets



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ABSTRACT

Four new vanadium-based coordination polymers that exhibit high magnetic ordering temperatures (T_c) have been synthesized. Magnetic measurements show that these polymers are soft ferrimagnets. The IR shows a reduced nitrile environment in these polymers, elemental analysis reveals that the compositions of the polymers are 2:1 acceptor to vanadium ratio. An electrochemical measurement of acceptors shows a weak correlation between T_c and the redox potentials. Change in the dihedral angle of an acceptor with the substitution in a specific position of the phenyl ring alters the magnetic ordering temperature in these polymers. Calculated electron affinity and Mulliken spin densities on acceptors, either in the neutral or in the anionic form, shows no relationship with the observed trend in T_c . These compounds are analogues to $V[TCNE]_2$ complexes with varying degree of solvent of coordination.

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1. Introduction

The synthesis of molecule-based magnets with an ordering temperature above the room temperature has received renovated interest with special regards to their suitability for the use in devices. The first such molecule-based magnet with the magnetic ordering temperature above room temperature was $V[TCNE]_2 \cdot xCH_2Cl_2$ prepared by the reaction of vanadium bis benzene, $V(C_6H_6)_2$, with tetracyanoethylene (TCNE) [1]. 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 [2]. Magneto transport studies by Epstein group revealed that the electrons in the valance and conducting bands of $V[TCNE]_2$ are spin polarized [3] and this material has potential “spintronic” applications.

With the goal of identifying the new magnetically ordered organic-based material we [4,5] and others [6] have reported additional organic one electron acceptors and their vanadium complexes. Based upon their composition, these are assumed to be similar to $V[TCNE]_2 \cdot xCH_2Cl_2$ (Fig. 1). Unfortunately these TCNE analogue complexes with vanadium are not better than the original complex in terms of air sensitivity and the magnetic ordering temperature [7]. This necessitated the systematic study of these

tunable TCNE analogues with respect to their geometric and electronic properties with the goal of uncovering the mechanism of magnetic ordering temperature. We hope to understand the magnetic ordering temperature and the air sensitivity of the complexes by synthesizing the number of TCNE analogues and its model complexes that might give further insight in to the phenomenon of magnetism. The results of several such studies that we have undertaken are presented.

In particular, we report the synthesis and a property of magnets constructed from four new acceptors which are all related structurally but exhibit different magnetic ordering temperatures (Fig. 2). Attempts have also been made to correlate the observed trends in the magnetic ordering temperature with calculated and experimentally determined properties of the acceptors, with limited success.

2. Experimental section

Preparations of air sensitive compounds were carried out in a nitrogen-filled vacuum atmospheres glove box. Vanadium hexacarbonyl was made from $[V(CO)_6] [(Et)_4N]^+$ according to a literature procedure [8]. Malanonitrile, N-chlorosuccinimide, potassium cyanide, and piperidine were purchased from Aldrich. All fluorinated benzaldehydes are purchased from Acros or elsewhere. Reagents were used as received except as noted below. Dichloromethane was distilled from P_2O_5 and degassed with glove box nitrogen prior to use. Acetonitrile was distilled from P_2O_5 followed by distillation from CaH_2 under argon prior to use. 1H and ^{19}F NMR were carried out on Varian Inova –400 MHz or Unity

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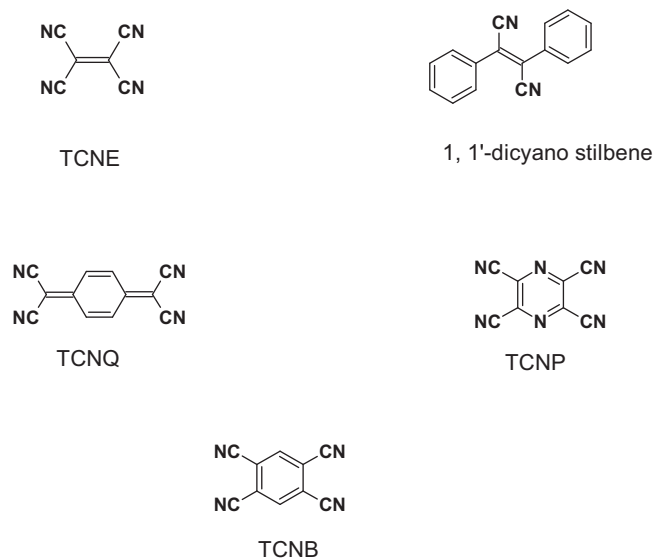


Fig. 1. TCNE and other similar acceptors used for the coordination polymer magnet.

–400MHz NMR instruments. FTIR performed on MIDAC M-1700. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Magnetic measurements were performed on a 7 T Quantum Design MPMS SQUID magnetometer. Measurements of field-cooled magnetization as a function of temperature were performed from 5 to 325 K as indicated. Powder samples were cooled in 100 G applied field and measured upon warming in 5 G applied field. Measurements of magnetization as a function of applied magnetic field were performed at 5 K. The amplitude of oscillating magnetic field used for ac susceptibility measurement was 3.5 Oe with zero dc bias fields and at frequencies of 1, 10, and 100.

Electrochemistry measurements were recorded using CH Instruments model 600A potentiostat. Measurements were performed on 10 mM solutions in acetonitrile and 0.1 M *n*-tetrabutylammonium tetrafluoroborate as a supporting electrolyte. All measurements were recorded between the potential range of 0 and –400 mV at a scan rate of 100 mV/s using a carbon electrode with Ag/AgCl as the reference. Solution resistance was compensated 95% using positive feedback IR compensation.

Ab initio calculations were performed using the B3LYP functional with the 6–31**G(d,p) basis set within Gaussian-03 [9]. Both the neutral and anionic form of each acceptor was geometrically

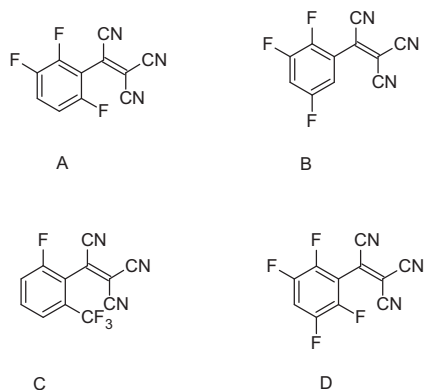


Fig. 2. Substituted phenyl tricyano ethylene, TCNE analogue compounds. (A) 2-(2,3,6-Trifluorophenyl)-1,1,2-tricyanoethylene. (B) 2-(2,3,6-Trifluorophenyl)-1,1,2-tricyanoethylene. (C) 2-(2-Fluoro-6-trifluoro methyl phenyl)-1,1,2-tricyanoethylene. (D) 2-(2,3,5,6-Tetrafluorophenyl)-1,1,2-tricyanoethylene.

optimized and based off of the optimized unsubstituted acceptor structure. During the geometry optimizations, the acceptor energies (both neutral and anionic) and Mulliken spin densities were calculated.

2.1. Syntheses

2.1.1. Synthesis of V[2-Fluoro-6-trifluoromethylphenyl tricyanoethylene]₂

Under a nitrogen atmosphere, Vanadium hexacarbonyl (25 mg, 0.111 mmol) dissolved in dichloromethane (2 mL) was added drop wise to a 2 mL solution containing 2-fluoro-6-trifluoromethylphenyl tri cyanoethylene (76 mg 0.33 mmol) while stirring. After 15 min, a black precipitate was collected on a medium frit, rinsed with dichloromethane (3 × 2 mL) and dried under vacuum for one hour. Yield: 56 mg IR (KBr): 2212 and 2127 cm⁻¹ Anal. Cal for C₂₄F₈N₆H₆V%: C, 49.59; H, 1.03; N, 14.46 found; C, 49.51; H, 1.06; N, 14.40.

2.1.2. Synthesis of V[2,3,5,-Trifluorophenyl tricyanoethylene]₂

Under a nitrogen atmosphere, Vanadium hexacarbonyl (25.6 mg, 0.112 mmol) dissolved in dichloromethane (2 mL) was added drop wise to a 2 mL solution containing 2, 3, 5 tri fluoro phenyl tricyano ethylene (76 mg, 0.34 mmol) while stirring. After 15 min, a black precipitate was collected on a medium frit, rinsed with dichloromethane (3 × 2 mL) and dried under vacuum for one hour. Yield: 61 mg. IR (KBr): 2210 and 2129 cm⁻¹. Anal. Cal for C₂₂H₄N₆F₆V 0.1CH₂Cl₂%: C, 50.51; H, 1.0; N, 15.98; found; C, 50.42; H, 1.0; N, 15.81.

2.1.3. Synthesis of V[2,3, 6, Trifluorophenyl tricyanoethylene]₂

Under a nitrogen atmosphere, Vanadium hexacarbonyl (26 mg, 0.112 mmol) dissolved in dichloromethane (2 mL) was added drop wise to a 2 mL solution containing 2, 3, 6 trifluoro phenyl tri cyanoethylene (76 mg, 0.34 mmol) while stirring. After 15 min, a black precipitate was collected on a medium frit, rinsed with dichloromethane (3 × 2 mL) and dried under vacuum for one hour. Yield: 58 mg 70% IR (KBr): 2210 and 2135 cm⁻¹. Anal. Cal for C₂₂H₄N₆F₆V 0.2CH₂Cl₂%: C, 50.60; H, 1.0; N, 15.93; found; C, 50.22; H, 1.0; N, 15.71.

2.1.4. Synthesis of V[2,3, 5, 6-Tetrafluorophenyl tricyanoethylene]₂

Under a nitrogen atmosphere, Vanadium hexacarbonyl (27.2 mg, 0.119 mmol) dissolved in dichloromethane (2 mL) was added drop wise to a solution containing 2,3,5,6 tetrafluoro phenyl tricyanoethylene (76 mg, 0.357 mmol in 2 mL) while stirring. After 15 min, a black precipitate was collected on a medium frit, rinsed with dichloromethane (3 × 2 mL) and dried under vacuum for one hour. IR (KBr): 2212 and 2130 cm⁻¹.

Anal. Cal for C₂₂H₂N₆F₈V.0.4CH₂Cl₂%: C, 45.83; H, 1.00; N, 14.31; Found; C, 45.51; H, 1.00; N, 14.31.

3. Results and discussions

3.1. Synthesis of acceptors and their coordination polymers

The acceptors were prepared from a three step synthesis starting from substituted benzaldehyde. Depending on the purity of the starting material purchased, we were purified the intermediates of the acceptors before taking in to the next step reaction. Final acceptors were purified by column chromatography and recrystallized from pentane prior to use. The overall yield obtained in all cases was above 70%.

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