Solvent Dependence of the Magnetic Ordering Temperature for Decamethylferrocenium Tetracyanoethenide, $[Fe^{III}(C_5Me_5)_2][TCNE]\cdot$Solvent

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The magnetic properties of monoclinic $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}\cdot$MeCN (**1**·MeCN) have been measured and compared to that of orthorhombic $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ (**1**). Peaks in both $\chi'(T)$ and $\chi''(T)$ are observed verifying that antiferromagnetic ordering is not present in either **1** or solvated **1** (**1**·*S*). **1**·MeCN facilely loses MeCN and both desolvated **1**·MeCN and **1** have the same magnetic behavior ($T_f = 4.96 \pm \leq 0.03$ K). In contrast, solvated **1**·MeCN has a reduced T_f of 2.87 ± 0.02 K. This is ascribed to the layers of MeCN that separate the pairs of layers of parallel chains of $[Fe(C_5Me_5)_2][TCNE]$, which reduce the 3-D magnetic coupling leading to a lower ordering temperature. Formation of other magnetically ordered solvates, **1**·*S* (*S* = EtCN, PrCN, PhCN, 1,2-$C_6H_4Cl_2$, NCC_4H_8CN), with $2.87 < T_f < 4.82$ K, which, except for *S* = PrCN, also have $T_f = 4.96 \pm \leq 0.03$ K upon desolvation. Addition of THF to **1** leads to an enhanced T_f of 5.50 ± 0.11 K, which is attributed to an external pressure (ca 2.5 kbar) induced by the THF solvent that does not occur for the nitrile-based solvents. The desolvated materials exhibit a small frequency dependence in the ac susceptibility, $\chi'(T,f)$. This is typically an order of magnitude lower than the frequency dependence for the solvated species, which is indicative of enhanced glassiness and disorder.

Introduction

The study of magnetically ordered molecule-based materials is a growing area of contemporary chemistry.[1,2] $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$, $[Fe^{III}Cp^*_2]^{\bullet+}[TCNE]^{\bullet-}$, (Cp* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene) (**1**), was the first organic-containing magnet characterized, and has an ordering temperature, T_c, of 4.80 K.[3] Improvements led to the discovery of $V(TCNE)_x\cdot y(CH_2Cl_2)$, the first room-temperature organic magnet ($T_c \sim 400$ K).[4] The structures of orthorhombic **1** (Figure 1a) and monoclinic $[FeCp^*_2]^{\bullet+}[TCNE]^{\bullet-}\cdot$MeCN (**1**·MeCN) (Figure 1b) were determined and both were composed of parallel linear chains of alternating radical cations (**C**) and radical anions (**A**), that are either in-registry or out-of -registry (Figure 2) with intrachain Fe···Fe separations of 10.621 and 10.415 Å, respectively.[3b] The structure of **1**·MeCN differs from **1** as the MeCN separates pairs of rows of the parallel chains. The structure of **1**·MeCN is well ordered. In contrast, due to severe disorder, the location of $[TCNE]^{\bullet-}$ could not be determined for **1**. Nonetheless, due to the facile loss of the solvent, unless in equilibrium with *S* **1**·MeCN rapidly desolvates upon harvesting to form polycrystalline **1**.[3b] As a consequence of the ease of studying **1** with respect to **1**·MeCN, all the physical studies to date were performed on **1**.[3,5] Herein, we report the magnetic ordering behavior of **1**·MeCN as well as that of other solvates.

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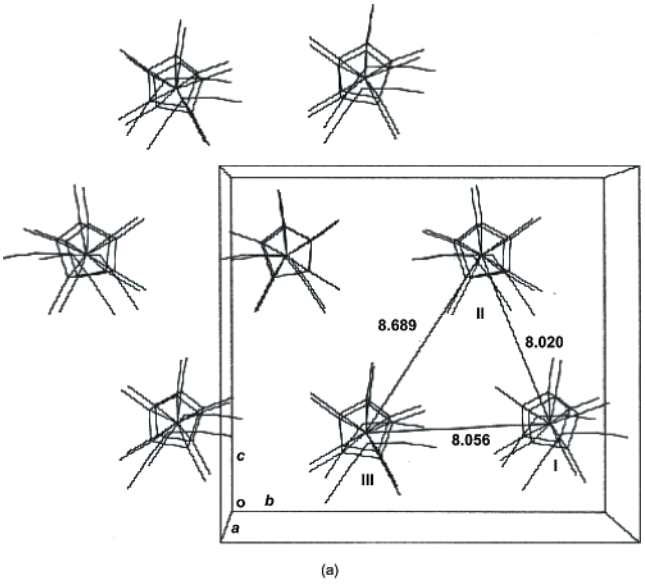

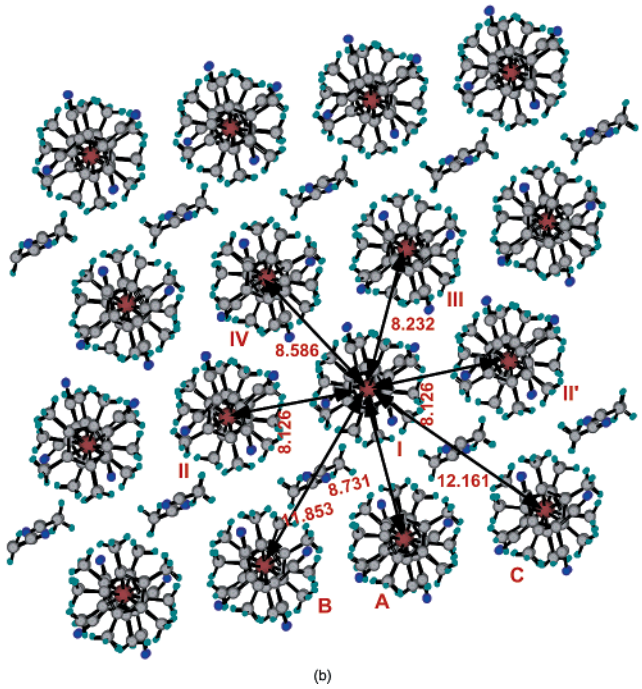

Figure 1. Structures of **1** (a) and **1**·MeCN (b) along the chain axis (*a*-axis for **1** and *b*-axis for **1**·MeCN) showing the unique nearest-neighbor chains and the interchain separation. The interchain distances are the shortest distance between the parallel Fe···Fe chains.

Experimental Section

Synthesis. All solvents were distilled under nitrogen from the appropriate drying agents before use, and the syntheses of the electron-transfer salts were carried out in an inert atmosphere (DriLab). TCNE (Aldrich) and $FeCp^*_2$ (Strem) were sublimed prior to use. **1**·MeCN and **1** were prepared as previously described.[3b] The other solvates of **1**, **1**·*S* (*S* = EtCN, PrCN, PhCN, 1,2-$C_6H_4Cl_2$, NCC_4H_8CN) were prepared via the same procedure, except *S* was the solvent.

Physical Methods. Thermal properties were studied on a TA Instruments model 2050 thermogravimetric analyzer (TGA) located in a Vacuum Atmospheres DriLab under argon to protect air and moisture sensitive samples. The compounds, however, desolvated so quickly that neither elemental analyses nor TGA could be obtained, even for the high-boiling solvents. The ac susceptibilities were determined on a Quantum Design MPMS-5XL 5 T SQUID magnetometer.[6,7] Solids were loaded in airtight Delrin holders, and samples containing solvent were sealed in quartz EPR tubes under vacuum, and because the amount of material studied was unknown the data are reported as arbitrary units. Infrared spectra (600 to 4000 ± 1 cm^{-1}) were obtained on either Bio-Rad FT-40 or Bruker Tensor 37 spectrophotometers as potassium bromide pellets. All compounds exhibit υ_{CN} at 2144 and 2183 cm^{-1} indicating that only unbound $[TCNE]^{\bullet-}$ was present.

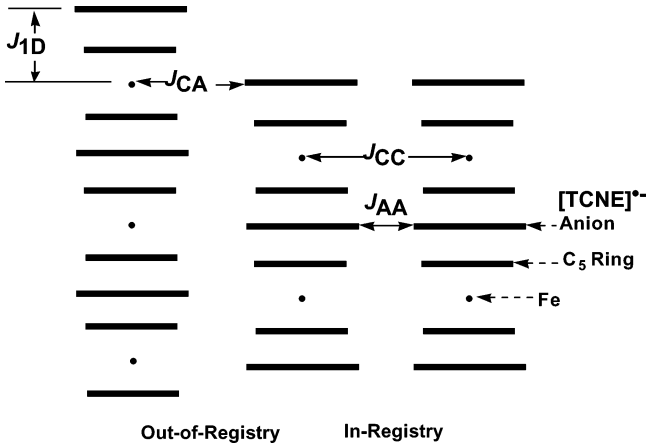

Figure 2. Schematic illustration of the structure of **1** showing intrachain pairwise out-of-registry (**I**−**II** and **I**−**III**) and in-registry (**II**−**III**) interactions. The same diagram depicts the pairwise out-of-registry (**I**−**II**, **I**−**II′**, and **I**−**III**) and in-registry (**I**−**V** and **I**−**A**) interactions for **1**·MeCN.

Results and Discussion

The reaction of $FeCp^*_2$ and TCNE in THF leads to formation of crystals of nonsolvated $[FeCp^*_2][TCNE]$ (**1**) that possess an orthorhombic unit cell (Figure 1a). In contrast, the reaction in MeCN forms monoclinic **1**·MeCN (Figure 1b). Isolation of the crystals of the solvate leads to rapid desolvation and only isolation of the nonsolvated orthorhombic **1**.[3b] To extend this family of solvates, **1**·*S* (*S* = EtCN, PrCN, PhCN, 1,2-$C_6H_4Cl_2$, and NCC_4H_8CN) have been prepared and their magnetic ordering has been studied by in- and out-of-phase ac susceptibilities [$\chi'(T)$ and $\chi''(T)$] for both the dry, crystalline material and as solvated crystals in equilibrium with the solvent. As occurs for **1**·MeCN, only the nonsolvate, **1**, is isolated as a dry solid.

Structure. The structure of **1**·MeCN lacks disorder, while that of **1** has sufficient disorder that while the cation is determined, the location of the anion is unknown.[3b] Hence, only Fe···Fe and interchain separations are known for the nonsolvated materials, Table 1. Both **1** and **1**·MeCN are composed of parallel chains of alternating $[FeCp^*_2]^{\bullet+}$ cations, **C**, and $[TCNE]^{\bullet-}$ anions, **A**, with intrachain Fe···Fe separations of 10.621 and 10.415 Å, respectively.

Each parallel chain in **1** has six nearest neighbor chains to interact in a pairwise manner, Figure 1a. Due to symmetry there are two interchain separations each of 8.020 (**I**−**II**), 8.056 (**I**−**III**), and 8.689 Å (**II**−**III**) (average = 8.26 Å) and corresponding Fe···Fe separations, defined as the perpendicular distance between

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(7) In several cases identical data were obtained for solvated samples on a 9 T PPMS susceptometer.

Table 1. Inter- and Intrachain and Inter- and Intrachain Fe···Fe Distances for [FeCp*$_2$][TCNE] 1, and 1·MeCN[a]

	intrachain	I−II[b]	I−III[b]	II−III[c]	I−A[c]	I−B[b]	I−C[b]
			[FeCp*$_2$][TCNE] **1**				
Chain···Chain		8.020	8.056	8.689			
Fe···Fe	10.621	9.618	9.649	8.689			
		9.618					
			[FeCp*$_2$][TCNE]·MeCN **1**·MeCN				
Chain···Chain		8.126	8.232	8.586	8.731	11.853	12.161
Fe···Fe	10.415	9.650	9.473	8.602	8.731	12.796	13.229
		9.652	10.029	13.102	13.591	12.796	13.229
				13.904	13.591		

[a] References 3a and 14. [b] Out-of-registry. [c] In-registry.

Table 2. T_f Values for 1 and 1·*S* (*S* = THF, MeCN, EtCN, PrCN, PhCN, NCC$_4$H$_8$CN, and 1,2-C$_6$H$_4$Cl$_2$)

	desolvated		solvated	
solvent	T_f, K [a,b]	ϕ [c]	T_f, K [a]	ϕ
THF	4.95	0.0081	5.50 ± 0.11	0.082 ± 0.006
MeCN	4.96	0.0060	2.87 ± 0.02	0.19 ± 0.01
EtCN	4.98	0.0085	2.98 ± 0.06	0.18 ± 0.02
PrCN	5.12	0.021	4.23 ± 0.07	0.097 ± 0.004
PhCN	4.95	0.0051	4.56 ± 0.09	0.065 ± 0.011
NC(CH$_2$)$_4$CN	4.95	0.0071	4.82	0.025
1,2-C$_6$H$_4$Cl$_2$	4.94	0.0062[d]	3.29	0.10

[a] T_{max} for $\chi'(T, 10\ Hz)$. [b] ±≤0.03 K. [c] ±≤ 20%. [d] ± 30%.

parallel chains, of 9.618, 9.649, and 8.689 Å (average = 9.32 Å). The former pair is out-of-registry, whereas the latter pair is in-registry (Figure 2). In contrast, due to every second layer of parallel chains of **1** being separated by layers of MeCN, each chain in **1**·MeCN has five nearest neighbor chains less than 11 Å to interact in a pairwise manner, Figure 1b, with interchain separations of 8.126 (**I**−**II**), 8.126 (**I**−**II′**), 8.232 (**I**−**III**), 8.586 (**I**−**IV**), and 8.731 Å (**I**−**A**) (average = 8.36 Å) and corresponding Fe···Fe separations of 9.650, 9.650, 9.473, 8.602, and 8.731 Å (average = 9.22 Å). The first three pairs are out-of-registry, whereas the latter pairs are in-registry. Additionally, each chain has two out-of-registry chains separated by 11.853 (**I**−**B**) and 12.161 Å (**I**−**C**) with corresponding shortest Fe···Fe separations of 12.796 and 13.229 Å, but because of the substantial increase in distance (56% greater) their contribution to T_c is anticipated to be small and is neglected.

Magnetic Behavior. The in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility in the range of 2 to typically 7 K were measured in a zero applied field ($H_{ac} = 0$). The temperature at which the 10 Hz $\chi'(T)$ has a maximum value is taken as the T_f, which differs from the magnetic ordering temperature (T_c = 4.82 K) ascertained from fitting the magnetization, $M(T)$, to an equation for the β critical exponent and an extrapolation as the temperature at which $M(T) \rightarrow 0$,[8] and 4.80 K reported from specific heat data.[9] Earlier T_f was reported to be ~5 K for **1** in a pressure dependence study.[10]

As noted above, the T_f for **1** prepared via desolvation **1**·MeCN is 4.96 ± ≤0.03 K (Figure 3a), and it is the same when prepared from **1**·S (*S* = EtCN, PhCN, 1,2-C$_6$H$_4$Cl$_2$, NCC$_4$H$_8$CN, THF), but it is 5.12 K when desolvated from **1**·PrCN. Hence, essentially no difference in T_f is evident with an average T_f of 4.96 K, except for when S = PrCN. A small frequency dependence, $\chi'(T,f)$, is present (Figure 3a). The frequency dependence of the ac susceptibility is parametrized with ϕ, $\phi = \Delta T_f / [T_f \Delta \log f]$, and ranges from 0.005 to 0.0085, except for *S* = PrCN (ϕ = 0.021), consistent with a weak spin glass behavior, as disordered spin systems display $0.1 < \phi < 0.01$ as found in the alloys of PdMn (ϕ = 0.013) and NiMn (ϕ = 0.018) while the superparamagnet α-(Ho$_2$O$_3$)-(B$_2$O$_3$) has ϕ = 0.28.[11] One source of spin glass behavior is disorder, as structurally established for the [TCNE]$^{\bullet-}$ in [FeCp*$_2$]$^{\bullet+}$[TCNE]$^{\bullet-}$·MeCN.[3b] Hence, the magnetic properties of **1** are essentially invariant to the preparation route, and exhibit a small frequency dependence of the ac susceptibility, as noted for solvent-free **1** prepared from THF or MeCN (Figure 3a). This is attributed to the structural disorder in the anion present in **1**.[3b]

In contrast, the T_f for **1**·*S* [*S* = MeCN (Figure 3b), EtCN, PhCN, C$_6$H$_4$Cl$_2$, NCC$_4$H$_8$CN] are significantly reduced by as much as 2.09 K (42%) for *S* = MeCN (Table 2), and as little as 0.13 K for *S* = NCC$_4$H$_8$CN. This reduction in T_f is attributed to solvent inclusion between layers of the parallel chains and its associated disruption of the structure, as established for **1**·MeCN, and discussed in more detail below.[3a] Furthermore, ϕ ranges from 0.025 to 0.19 indicating a substantial increase in spin-glassiness and in disorder attributed to the solvent. Qualitatively, the larger the solvent the less is the reduction in T_f and the less is the enhancement in ϕ. This most likely indicates less inclusion of the solvent.

As a control, the $\chi'(T)$ and $\chi''(T)$ for **1** prepared from THF in the presence of THF was studied expecting behavior identical to that of dry **1** as the structure of **1** lacks THF.[3b] Unexpectedly, T_f differed and increased with respect to that of the T_f of **1** (Figure 3c) to 5.5 K, an increase of 0.55 K (11%). Furthermore, ϕ increasesd by an order of magnitude. This enhancement of T_f is attributed to pressure induced by the THF solvent that does not occur for 1,2-dichlorobenzene or the nitrile-based solvents, except perhaps for *S* = PrCN. To confirm this the T_c of the YBa$_2$Cu$_3$O$_7$ superconductor was measured with THF solvent present and compared to the T_c of the dry sample. An increase in the T_c was observed for YBa$_2$Cu$_3$O$_7$ with THF consistent with its

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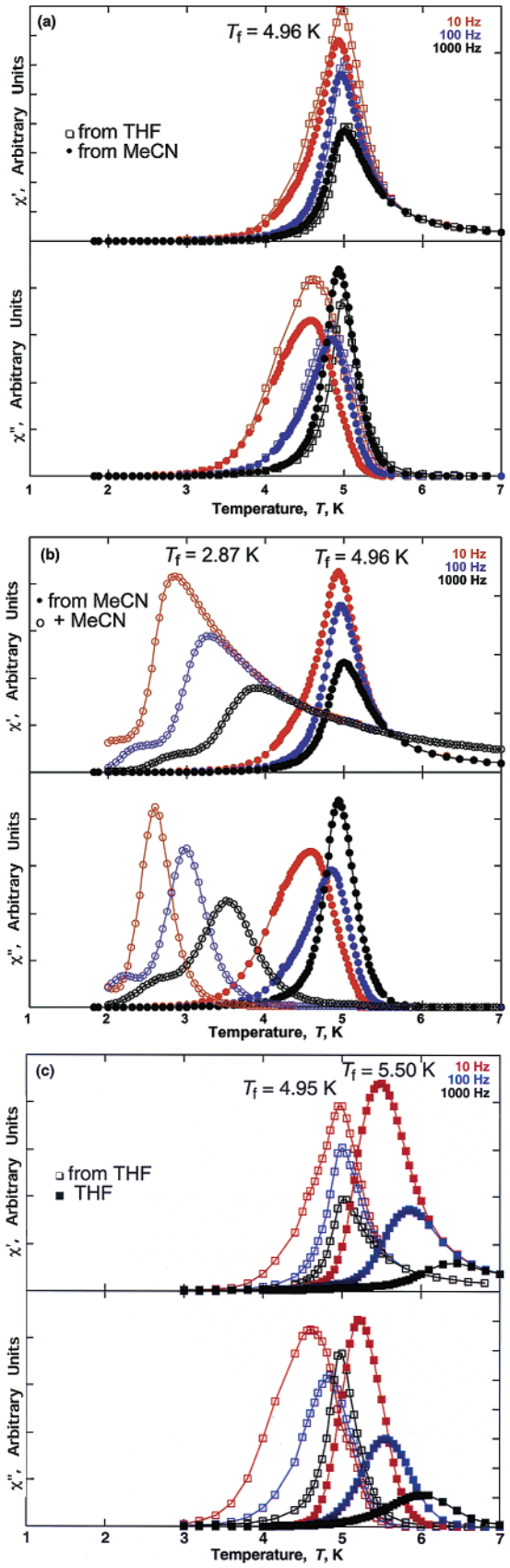

Figure 3. Temperature dependencies of the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility for **1** made from THF (□) and desolvation of **1**·MeCN (●) (a), **1**·MeCN (o) and desolvated **1**·MeCN (●) (b), and **1** made from THF (□) and **1** with added THF (■) (c). Note that the lines are guide for the eyes.

previously reported pressure dependence.[12] Furthermore, **1** coated in Apiezon N grease, which is known to induce a pressure of ~0.3 kbar at cryogenic temperatures,[13] shows an increase of T_c to 5.08 K. Previously, the pressure dependence of $\chi'(T)$ shows that T_f for **1** increases with increasing pressure up to 14 kbar at 0.22 K/kbar.[10] Hence, this 0.55 K increase corresponds to a local pressure of 2.5 kbar.

Magnetic Coupling. The pairwise spin couplings for the structural motif of **1** includes two intrachain coupling, J_{1D}, one interchain coupling between out-of-registry (OR) chains, J_{CA}, and two interchain couplings between in-registry (IR) chains associated with the $[FeCp^*_2]^{\bullet+}\cdots[FeCp^*_2]^{\bullet+}$, J_{CC}, and $[TCNE]^{\bullet-}\cdots[TCNE]^{\bullet-}$, J_{AA}, Figure 2.[14] The mean field model provides a relationship of T_c as a function of pairwise spin coupling, J:

$$T_c = 2zJS(S+1)/3\,k_B \qquad (1)$$

where z is the number of nearest neighbors, S the spin quantum number ($^1/_2$), and k_B is the Boltzmann constant. Using the schematic structure, Figure 2, zJ can be rewritten as

$$zJ = (zJ)_{\text{intrachain}} + \Sigma(zJ)_{\text{interchain}} \qquad (2)$$

and

$$(zJ)_{\text{intrachain}} = 2\,J_{1D} \qquad (3a)$$

$$[(zJ)_{\text{interchain}}]_{IR} = J_{CC} + J_{AA} \qquad (3b)$$

$$[(zJ)_{\text{interchain}}]_{OR} = J_{CA} \qquad (3c)$$

Hence,

$$T_c = [2J_{1D} + z_{OR}J_{CA} + z_{IR}(J_{CC} + J_{AA})]/2k_B \qquad (4)$$

Using a McConnell model to evaluate the sign of the pairwise spin couplings [ferro- ($J > 0$) or antiferromagnet ($J < 0$)][15] and J_{1D}, J_{CC}, and J_{CA} are ferromagnetic, whereas J_{AA} is expected to be antiferromagnetic.[14] Hence, both $J_{\text{intrachain}}$ (J_{1D}) and $[J_{\text{interchain}}]_{OR}$ (J_{CA}) are ferromagnetic. In contrast, $[J_{\text{interchain}}]_{IR}$ is expected to be lower in magnitude due to the competition of ferromagnetic J_{CC} and antiferromagnetic J_{AA}, i.e., $[J_{\text{interchain}}]_{IR} \sim 0$. However, due to the distance dependence of J [$\propto r^{-n}$; $n \geq 3$)][14] and the Fe···Fe separation is 2.5 times greater than the N···N $[TCNE]^{\bullet-}\cdots[TCNE]^{\bullet-}$

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Table 3. Number of Nearest-Neighbor In-Registry, z_{IR}, and Out-Of-Registry, z_{OR}, Chains Present for [FeCp*$_2$][TCNE], 1 and 1·MeCN

z	[FeCp*$_2$][TCNE]·MeCN, **1**·MeCN	[FeCp*$_2$][TCNE], **1**
z_{IR}	2	2
z_{OR}	3[a]	4

[a] Two additional out-of-registry chains are present, but due to the substantially larger separation are not included (see text).

separation {for **1**·MeCN[3b]}, $|J_{AA}| > |J_{CC}|$; hence, $[J_{interchain}]_{IR} < 0$ and antiferromagnetic.

Using the structures of **1**·MeCN and **1**[3b] the values of z_{IR} and z_{OR} can be determined (Table 3), and in conjunction with the predicted signs of the differing pairwise coupling, their relative T_c values can be compared. First, the 0.206-Å shorter intrachain separation of **1**·MeCN with respect to **1** suggests a greater J_{1D} for the solvated material, which, assuming all of the remaining J values to be the same, the T_c of the solvate should exceed that of the nonsolvated material.

The interchain interactions are more complex to evaluate. Because every second layer of the parallel chains of **1** is separated by MeCN for **1**·MeCN, each chain is in close proximity to three out-of-registry chains that provide ferromagnetic coupling. In contrast, each chain of **1** has four other out-of-registry chains in the nonsolvated material for ferromagnetic coupling. Hence, T_c should be reduced for the solvate because of less coupling. Finally, both **1** and **1**·MeCN have two in-registry sets of interactions, which, as discussed above, provide competitive antiferromagnetic coupling. Thus, due to the reduced ferromagnetic coupling, the antiferromagnetic coupling component in eq 4 is larger and a reduced T_c is expected for **1**·MeCN with respect to **1**, as observed. Likewise, although the structures of the other solvates are unknown, their reduced T_c values with respect to **1** are thought to be a consequence of differing interchain couplings and the number of couplings.

Conclusion

Isolation of crystalline solvates or even partial solvates of **1**, **1**·*S*, have yet to be achieved due to the rapid loss of the solvate from **1**·*S*. However, **1**·*S* (*S* = MeCN, EtCN, PrCN, PhCN, 1,2-$C_6H_4Cl_2$, NCC_4H_8CN) formed and can be studied in situ as crystals in equilibrium with *S*, and like nonsolvate **1** magnetically ordered similar to **1**, but with reduced T_f values [taken as the temperature at which the maximum in $\chi'(T$, 10 Hz) occurs] that range from 2.87 to 4.82 K. Peaks in both $\chi'(T)$ and $\chi''(T)$ are observed verifying that antiferromagnetic ordering is not present for both **1** and **1**·*S*. The nonsolvates all exhibit a T_f of 4.96 $\pm$ $\leq$0.03 K, and disorder/spin glass behavior as evidenced by the observed frequency dependencies of $\chi'(T)$ and $\chi''(T)$. However, the degree of glassiness is low, as evidenced by the low value of the figure of merit, ϕ, i.e., ≤ 0.01. Except for *S* = PrCN in contrast, ϕ is an order of magnitude greater for the nonsolvates indicating substantially greater disorder due to the presence of the solvent. Qualitatively, the larger the solvent the less is the reduction in T_f and the less is the enhancement in ϕ. This most likely indicates less inclusion of the solvent. Furthermore, addition of THF to crystals of **1** induces an external pressure enhancing T_f.

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