The results presented here show that the maltose unit in glycophane **2** is rather flexible and that temperature and solvent, in conjunction with the presence of defined sugar–arene interactions influence its conformational equilibrium. Cyclodextrins together with glycophanes **1** and **2** are good examples of the existence of different conformers of the same disaccharide. It follows that the maltose units in these three compounds should also show different conformational entropies. This may have consequences in the thermodynamics of binding[5] of these maltose-containing compounds to a receptor, for example, the maltose-binding protein.

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$[\mathrm{M^{II}(tcne)_2}] \cdot x\,\mathrm{CH_2Cl_2}$ (M = Mn, Fe, Co, Ni) Molecule-Based Magnets with T_c Values Above 100 K and Coercive Fields up to 6500 Oe**

Jie Zhang, Jürgen Ensling, Vadim Ksenofontov, Philipp Gütlich, Arthur J. Epstein, and Joel S. Miller*

Molecule-based magnets possessing spins on organic radicals is a growing area of increasing contemporary interdisciplinary research.[1, 2] Two classes of organic radicals have been particularly effective in stabilizing molecule-based magnets. These are the strong electron acceptors, such as tetracyanoethylene (TCNE), and dinitroxides. Several classes[2] of magnets are based on these radicals, namely, metallocene and manganoporphyrin electron transfer salts of TCNE (e.g., $[\mathrm{FeCp^*_2}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$ (Cp* = pentamethylcyclopentadienyl) and $[\mathrm{Mn(tpp)}]^{+}[\mathrm{TCNE}]^{\bullet-}$ ($\mathrm{H_2TPP}$ = *meso*-tetraphenylporphyrin)), and $[\mathrm{Mn^{II}(hfac)_2}]$ (hfac = hexafluoroacetylacetonate) adducts of dinitroxides (e.g., $\mathrm{(Me_2C_2)_2(NO)_2CR}$, R = Me, Et, *i*Pr, etc.), $[\mathrm{V(tcne)}_x] \cdot y\,$solvent,[3, 4] as well as a few dinitroxides. Unlike the other classes of molecule-based magnets, there is only one example of a room temperature magnet $[\mathrm{V(tcne)}_x] \cdot y\,$solvent, and due to its high ordering temperatures ($T_c \sim 400$ K) and unknown structure, more examples of this class of materials are necessary to understand the chemistry and physics. Herein, we report the preparation and preliminary magnetic properties of $[\mathrm{M(tcne)_2}] \cdot x\,\mathrm{CH_2Cl_2}$ (M = Fe (**1**), Mn (**2**), Co (**3**), Ni (**4**)) magnets.[5]

$[\mathrm{Fe(tcne)_2}] \cdot x\,\mathrm{CH_2Cl_2}$ (**1**) is prepared from the reaction of iron(II) iodide,[3] which was used in the form of the MeCN solvate, and TCNE. Both reactants were dissolved in $\mathrm{CH_2Cl_2}$, and upon mixing the product rapidly precipitated. After washing with $\mathrm{CH_2Cl_2}$ the material was dried in vacuo at 30 °C overnight.[6] The IR spectrum of compound **1** exhibits three sharp ν_{CN} bands at 2221 (m), 2277 (s), and 2174 (s) $\mathrm{cm^{-1}}$ (Table 1); the width of these absorptions may depend on the precursors and other conditions.[6] These absorptions are consistent with those for the coordinated radical anion $[\mathrm{TCNE}]^{\bullet-}$. They are similar to the υ_{CN} bands for $[\mathrm{V(tcne)}_x] \cdot y\,\mathrm{CH_2Cl_2}$, but are sharper and occur at higher energies. In contrast, however, to the amorphous $[\mathrm{V(tcne)}_x] \cdot y\,\mathrm{CH_2Cl_2}$, **1** is partly crystalline according to the X-ray powder pattern (Figure 1). Indexing of this pattern has been thwarted as the

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Table 1. IR ν_{CN} absorption bands, saturation magnetization M_s, ordering temperature T_c, and exchange energy J for $[M(tcne)_2]\cdot xCH_2Cl_2$ (M = V, Mn, Fe, Co, Ni).

Synthesis[a]	ν_{CN} [cm^{-1}] vw	ν_{CN} [cm^{-1}] m	ν_{CN} [cm^{-1}] s	ν_{CN} [cm^{-1}] s	M_s[b] [emu Oe mol^{-1}]	T_c [K]	J[c] [K]
$[V(CO)_6]$[6]			2189	2153	10300	ca. 400	53
$MnI_2\cdot 0.75\,CH_3CN$	2280	2224	2181	2171	19000	107	6.1
$FeI_2\cdot 0.75\,CH_3CN$	2279	2221	2177	2174	16900	121	10
$CoI_2\cdot 1.67\,CH_3CN$	2284	2230	2187	2167	8000	44	5.9
$NiI_2\cdot 1.05\,CH_3CN$	2290	2237	2194	(shoulder)	15800	44	11

[a] The given reactant was allowed to react with TCNE in CH_2Cl_2. [b] At 2 K and 5 T. [c] See text.

unit cell and space group for the low-symmetry pattern has yet to be identified. Elemental and thermal gravimetric analyses are consistent with the formulation in which x lies between 0.4 and 1.1.

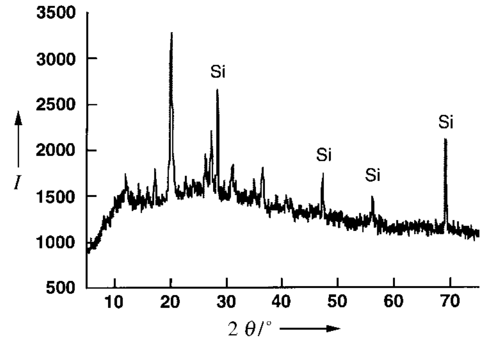

Figure 1. X-ray powder diffraction pattern[10] for $[Fe(tcne)_2]\cdot 0.75\,CH_2Cl_2$. The reflections marked with Si are attributed to an internal Si standard. I = relative intensity.

The oxidation and spin state of **1** was determined by ^{57}Fe Mössbauer spectroscopy. Within the detection limits only one iron site is observed. Above 95 K the sample shows absorptions with large chemical shift ($\delta = 1.23(1)$ mms^{-1}) and quadrupole coupling ($\Delta E_q = 3.26(1)$ mms^{-1}) indicative of penta- or hexacoordinate, high-spin Fe^{II} compounds[7] (Figure 2). As the sample is cooled below 95 K, the spectra become more complex due to magnetic splitting ($\delta = 1.24(1)$ mms^{-1}; $\Delta E_q = 3.31(1)$ mms^{-1}, $H_{int} = 229(1)$ KOe, Figure 2). The onset of the magnetic splitting is in agreement with the critical temperature determined by magnetic studies (vide infra).

Preliminary magnetization studies show that $[Fe(tcne)_2]\cdot 0.75\,CH_2Cl_2$ has a complex magnetic behavior that is essentially independent of the method of preparation and the amount of solvent.[6] The susceptibility cannot be fit to the Curie–Weiss law, $\chi \propto (T-\theta)^{-1}$, as expected for high-spin d^6 Fe^{II} centers in an octahedral environment with spin-orbit coupling.[8] A spontaneous magnetization occurs at temperatures below a T_c of 121 K as determined from the intercept of the slope of the magnetization as a function of temperature (Figure 3). At 2 K the magnetization shows complex, poorly understood responses to the field, reminiscent of metamagnetic behavior (Figure 4). At 5 T and 2 K the observed magnetization is about 16900 emu Oe mol^{-1}; however, higher fields are necessary to achieve saturation. This value of saturation magnetization corresponds to three $S = 1/2$ spins and is 63 % larger than the value for $[V(tcne)_x]\cdot yCH_2Cl_2$ (10300 emu Oe mol^{-1}) prepared from $[V(CO)_6]$.[4] It also exceeds the value (11200 emu Oe mol^{-1}) expected from antiferromagnetic coupling between an $S = 2$ Fe^{II} site and two $S = 1/2$ $[TCNE]^{\bullet -}$ ions. In addition it is substantially less than the value expected from ferromagnetic coupling (33500 emu Oe mol^{-1}). Although the T_c value shows little or no dependence on the synthetic route, the hysteresis loops taken at 2 K, which again are indicative of metamagnetic behavior, show a strong variation in the coercive field H_c, ranging from 300 to 3000 G (Figure 4). The detailed behavior

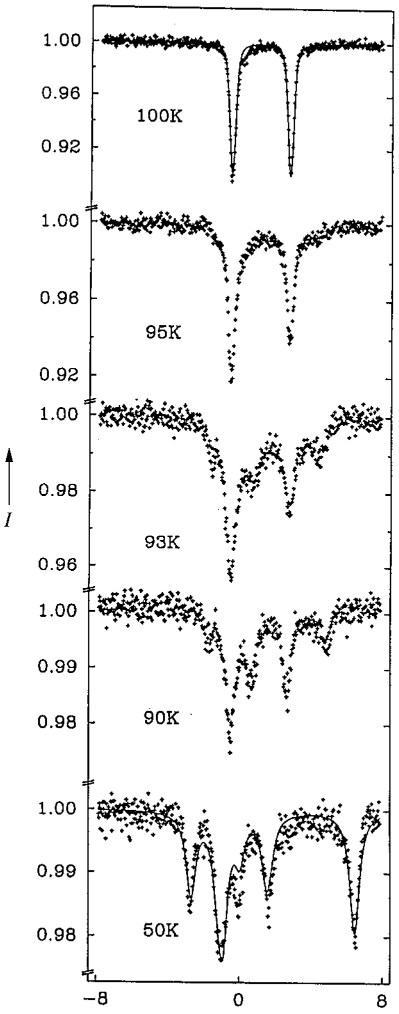

Figure 2. ^{57}Fe Mössbauer spectra of **1** at 50, 90, 93, 95, and 100 K. I = intensity.

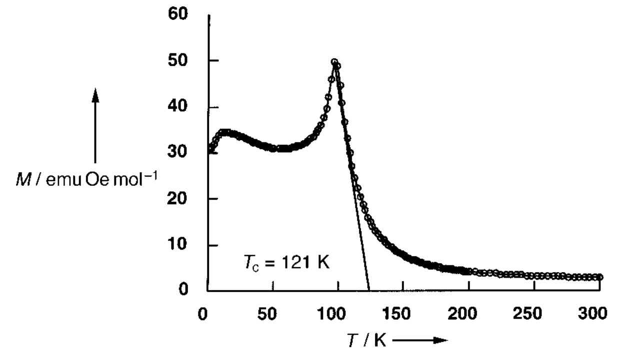

Figure 3. Zero-field cooled magnetization as function of temperature for $[Fe(tcne)_2] \cdot 0.75\,CH_2Cl_2$.

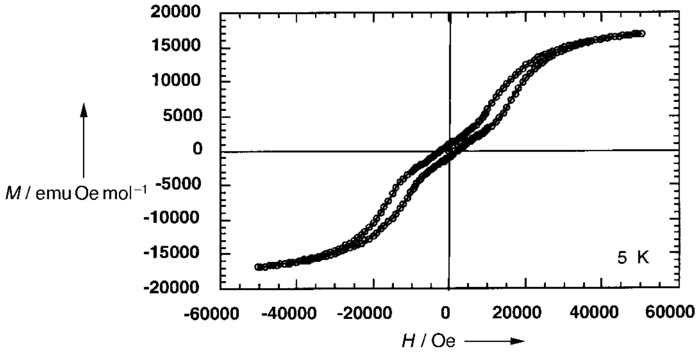

Figure 4. Representation of a hysteresis $M(H)$ for $[Fe(tcne)_2] \cdot 0.75\,CH_2Cl_2$ at 2 K. The observed coercive field for this sample is 2300 Oe, and the sample saturates to 16900 emu Oe mol^{-1}.

of the field and zero-field cooled curves also exhibits a strong dependency on reaction conditions and aging. In addition, a metastable impurity, which contributes to a broad transition around 150 K, exists for materials made from $[FeI_2] \cdot x\,CH_3CN$ and TCNE when the reaction time is less than four days.

Compound **1** shows remarkable thermal stability. The IR spectrum, the X-ray powder pattern, and the magnetic measurements on a sample treated at 130 °C for 38 h, suggest that the chemical and structural features of the materials are preserved after the heat treatment, except for the loss of solvent molecules. Some thermal degradation is apparent from magnetic measurements on a sample treated at 180 °C, and the IR spectrum indicates massive decomposition when the material is heated to 200 °C. The thermal gravimetric analytical data show that although desolvation starts at temperatures as low as 40 °C, it does not approach completion until the sample decomposes. As CH_2Cl_2 is a noncoordinating solvent, such high desolvation temperature may be attributed to the fact that **1** is likely a three-dimensional network, and the trapped CH_2Cl_2 can only be completely released when the structure collapses. Although **1** is not pyrophoric like $[V(tcne)_x] \cdot y$ solvent, it does decompose in air. A Fluorolube mull of **1** shows signs of H_2O absorption after being exposed to air for 40 min. Prolonged exposure to air causes the broadening and shift of the υ_{CN} to 2230 cm^{-1} and the sample also becomes amorphous.

Similar reactions of TCNE and acetonitrile solvates of MI_2 led to $[M(tcne)_2] \cdot x\,CH_2Cl_2$ (M = Mn (**2**), Co (**3**), Ni (**4**)). Preliminary studies indicate magnetic order with T_c values of 44 K for **3** and **4** and 107 K for **2** (see Table 1). These values are significantly lower than that reported for analogous vanadium compounds.[9] By using the mean-field expression $T_c = JzS(S+1)/3k_B$ (J = exchange energy, k_B = Boltzmann's constant, and z = number of nearest neighbors) for $H = -2\mathbf{J}\mathbf{S}_a \cdot \mathbf{S}_b$ and by assuming z = 6, the following order for the J values is determined: $[V(tcne)_x] \cdot y$ solvent $\gg \mathbf{4} \approx \mathbf{1} > \mathbf{2} \approx \mathbf{3}$ (see Table 1). The powder diffraction data indicate that **2** is isostructural to **1**;[10] however, for **3** and **4** the solids diffract poorly and do not appear to be isomorphous to **1**. Based upon the composition and the similarity of the υ_{CN} absorptions for **2**–**4**, we assign all the metals to the divalent oxidation state. Likewise, the previously elusive oxidation state of vanadium in the room temperature magnet $[V(tcne)_x] \cdot y\,CH_2Cl_2$ is also assigned the divalent oxidation state.

Hysteresis is observed for **1**, **3**, and **4** (but not **2**) below T_c; however, as observed for $[V(tcne)_x] \cdot y\,CH_2Cl_2$[3, 4] the coercive field varies from sample to sample. Nonetheless, we observe coercive fields ranging from 300 Oe (**4**) to a large 6500 Oe (**3**). The shape of the hysteresis curves is characteristic of metamagnetic behavior and along with more detailed magnetic studies, including ac measurements, will be the focus of future research.

Hence, a new synthetic route enabling the preparation of several new molecule-based magnets of the composition $[M^{II}(tcne)_2] \cdot x\,CH_2Cl_2$ has been identified. These new magnets have T_c values that exceed 100 K and coercive fields as great as 6500 Oe.

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[9] As observed for the preparation of $[V(tcne)_x]\cdot y$ solvent,[3, 4] reactions of $[M^{II}I_2]\cdot x$MeCN (M = Mn, Fe, Co, Ni) in MeCN led to magnetic materials with reduced T_c values.

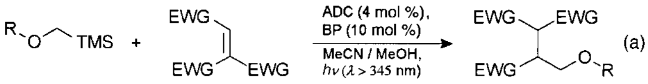
[10] Powder diffraction data: corrected d spacing [Å] (normalized intensity): M = Fe: 7.393 (38), 5.123 (25), 4.425 (100), 3.266 (25), 2.862 (21), 2.462 (21); M = Mn: 7.455 (15), 5.210 (17), 4.470 (100), 3.314 (33), 2.912 (25), 2.494 (23).

α-Silyl Ethers as Hydroxymethyl Anion Equivalents in Photoinduced Radical Electron Transfer Additions[**]

Guido Gutenberger, Eberhard Steckhan,[*] and
Siegfried Blechert

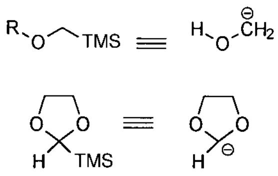
Hydroxymethyl anion equivalents (d^1-synthons) are desirable umpoled synthetic building blocks in organic chemistry.[1] In one of the very rare descriptions of its successful generation Hoppe et al. lithiated carbamates in the presence of (−)-sparteine.[2] Addition of nucleophilic hydroxy- or alkoxymethyl radicals to electron-poor alkenes can be considered as a general alternative. The oxidation of ethers, for example electrochemically,[3] provides the desired radical after one-electron oxidation and deprotonation; however, due to their high oxidation potentials ethers are difficult to oxidize. Besides, the generated alkoxy radical would be further oxidized immediately to the corresponding carbenium ion. The oxidation potential can be decreased significantly by introducing a silyl group to the position *α* to oxygen.[4] Nevertheless, also in this case further oxidation of the radical to the corresponding cation after desilylation cannot be avoided. Following our recent investigations of aminomethyl radicals[5] we are now presenting a new method for the generation of hydroxymethyl anion equivalents by photoinduced electron transfer catalysis (PET catalysis) starting from *α*-silyl ethers. This approach provides protected *α*-hydroxymethyl radicals under mild,[6] nonoxidizing conditions. A multiple-step alternative for the generation of *α*-silyloxyalkyl radicals is the radical Brook rearrangement of *β*-silylalkoxy radicals, which are accessible by radical cyclization of *ω*-bromoacylsilanes.[7]

In our method one-electron oxidation generates an intermediate *α*-silyl ether radical cation, which fragments with cleavage of the silyl group as an electrofuge. In the presence of catalytic amounts of 9,10-anthracenedicarbonitrile (ADC; 4 mol %) and biphenyl (BP; 10 mol %), irradiation with UV/Vis light leads to the addition of *α*-silyl ethers to acceptor-substituted alkenes. In this way, *γ*-acceptor-substituted ethers and alcohols can be prepared (Scheme 1).



Scheme 1. PET-catalyzed addition of *α*-silyl ethers to acceptor-substituted alkenes. EWG = electron-withdrawing group, TMS = trimethylsilyl, R = benzyl, TBDMS, methyl.

The *α*-silyl ethers **1**–**4** employed react as hydroxymethyl anion equivalents or, in the case of 2-trimethylsilyl-1,3-dioxolane (**5**), as formyl anion equivalents (Scheme 2). Consequently, this reaction can be considered to be a new route, analogous to the Michael addition, for the direct addition of hydroxymethyl groups to electron-poor alkenes.



Scheme 2. *α*-Silyl ethers and acetals as d^1-synthons.

We studied this transformation with the starting materials listed in Table 1. Methoxymethyltrimethylsilane (**1**) was successfully tested in addition reactions with methyl 2-cyanocrotonate (**6**) to give **11**. Because of the difficult cleavage of the methyl ether to generate the free OH function, trimethylsilylmethanol and other *α*-silyl ethers carrying readily cleavable protecting groups were examined. Reaction of the unprotected trimethysilylmethanol leads, according to GCMS analysis, to a product formed by addition of a trimethylsilyloxymethyl radical to the electron-poor double bond. Isolation of the product was impossible due to its instability. An explanation for the formation of this product would be deprotonation at the carbon or oxygen atom of the intermediate radical cation generated under electron transfer conditions. Subsequent Brook rearrangement[7, 8] would give the trimethylsilyloxymethyl radical.

Next we investigated the behavior of *α*-silyl ethers carrying protecting groups on oxygen that can be cleaved easily like trimethylsilyl, *tert*-butyldimethylsilyl (TBDMS; **4**), benzyl (**2**), and triisopropylsilyl (TIPS; **3**). The addition product obtained from a trimethylsilyl-protected *α*-silyl ether is identical, according to GCMS analysis, to that formed from trimethyl-

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