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Magnetic Ordering in the Rare Earth Molecule-Based Magnets, Ln(TCNE)$_3$ (Ln = Gd, Dy; TCNE = Tetracyanoethylene)

James W. Raebiger and Joel S. Miller*

Department of Chemistry, University of Utah, 315 S. 1400 E. RM 2124,
Salt Lake City, Utah 84112-0850

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The reaction of $LnI_3 \cdot x MeCN$ (Ln = Gd, Dy) and TCNE (tetracyanoethylene) in acetonitrile forms $Ln_2[C_4(CN)_8]_3 \cdot x MeCN$. These paramagnetic light-colored solids contain the $S = 0$ octacyanobutandiide dianion, $[C_4(CN)_8]^{2-}$, which upon desolvation of these products forms dark green Ln(TCNE)$_3$. In these compounds the central C–C σ bond in $[C_4(CN)_8]^{2-}$ is broken, re-forming $S = 1/2$ $[TCNE]^{\bullet-}$. as evidenced by the color change and the infrared spectra. Ln(TCNE)$_3$ exhibit coupling between Ln^{3+} and $[TCNE]^{\bullet-}$ and magnetically order as ferrimagnets at 8.5 (Dy) and 3.5 (Gd) K.

Introduction

In the pursuit of new molecule-based magnets,[1] the rare earth ions provide an interesting complement to the transition metal ions. While much effort has been focused on the transition metals, rare earths, Ln, have unique properties that make them desirable for use in magnetic materials. Rare earth ions generally have large anisotropic magnetic moments arising from a large number of spins and strong spin−orbit coupling such that *J*, not *S*, is a good quantum number, high coordination numbers, as well as the trivalent ions, being stable and readily available. In the mean field model where $T_c = 2JzJ(J + 1)/3k_B$ (k_B = Boltzmann's constant, J is the spin coupling between nearest neighbor spin sites, T_c is the magnetic ordering temperature, and *z* is the number of nearest neighbors) enhanced T_c is expected for systems with larger values of *z* and *J*, which is anticipated for Ln^{3+} with respect to the first-row transition metal dications.

There have been a number of reports on materials containing both rare earth and transition metal ions.[2] Recently, Kahn and co-workers reported on the detailed magnetic coupling, but not ordering, for rare earth complexes with spin-bearing nitronyl nitroxide-containing ligands,[3] and mono- and dinuclear complexes of Gd^{3+} with semiquinones were prepared by Gatteschi and co-workers to examine a stronger rare earth−radical interaction.[4] The coupling (J/k_B) in the Gd−radical monomers is −10.1 K for the nitronyl nitroxide[3a] and −16.4 K for the semiquinone.[4a] A series of rare earth metal nitronyl nitroxide chains was also investigated by Gatteschi's group and was found to magnetically order at a maximum critical temperature of 4.3 K for the late rare earth ions.[5] Weaker coupling of −2.0 K (Gd) and −0.43 K (Dy) is observed in these compounds. These linear chains are the sole examples of molecule-based magnetic materials where the only metal ions present are rare earth ions.

Previously, we have investigated the magnetic properties of the coordination polymers between transition metal ions

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* To whom correspondence should be addressed. E-mail: jsmiller@chem.utah.edu.

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and the radical anion of tetracyanoethylene (TCNE), $M^{II}(TCNE)_x \cdot yS$ (S = solvent). $V(TCNE)_x \cdot y(CH_2Cl_2)$ is a magnet at room temperature, and this result sparked much interest in molecule-based magnets.[1b,6] Subsequently magnets of $M^{II}(TCNE)_2$ (M = Mn, Fe, Co, Ni) composition were prepared using the divalent metal iodides, eq 1.[1b,7]

$$MI_2 \cdot x(MeCN) + 2\ TCNE \rightarrow M(TCNE)_2 + I_2 + x\ MeCN \quad (1)$$

These materials exhibit magnetic ordering temperatures between 44 and 121 K and like $V(TCNE)_x \cdot y(CH_2Cl_2)$ are ferrimagnets.[1b] To investigate the interaction between $S = 1/2$ $[TCNE]^{\bullet-}$ and the rare earth ions, we have now extended this general method to include Gd^{3+} and Dy^{3+}. Gadolinum(III) is a spin-only rare earth ion with $J = S = 7/2$. Dysprosium(III) has the highest moment of the trivalent rare earth ions due to its spin and its spin−orbit coupling, i.e., $J = 15/2$.[8] Herein, we report the preparation and magnetic characterization of $Ln(TCNE)_3$ [Ln = Dy (**1**), Gd (**2**)].

Experimental Section

All operations were carried out in an inert atmosphere box. Acetonitrile was distilled from CaH_2, then from P_2O_5. DyI_3 (Strem) and GdI_3 (Aldrich) were used as received. Tetracyanoethylene (Aldrich) was twice sublimed at 85 °C and 50 mTorr to obtain a white crystalline solid. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2050 thermogravimetric analyzer. Infrared spectra were collected on a BioRad FTS 40 FTIR spectrometer. Magnetic measurements were performed on a Quantum Design MPMS SQUID magnetometer as previously described.[9]

$LnI_3 \cdot x(MeCN)$ (Ln = Gd, Dy). LnI_3 (1.00 g) was added to 15 mL of MeCN. The solution was warmed to 50 °C to dissolve the solid. The pale yellow solution was filtered while warm and cooled to −20 °C for 3 days. The colorless needles that formed were isolated by filtration and dried under vacuum for 2 h. The white, crystalline products were then recrystallized from MeCN using the same procedure. The products were collected as white, needlelike crystals. TGA was used to determine the average acetonitrile content with values of $4 < x < 6$. IR for Ln = Dy (KBr): ν_{CN} 2306(s) and 2277(s) cm^{-1}. IR for Ln = Gd (KBr): ν_{CN} 2302(s) and 2274(s) cm^{-1}.

$Dy(TCNE)_3$. A solution of TCNE (80 mg, 0.62 mmol) in 2 mL of MeCN was added dropwise to a stirred solution of $DyI_3 \cdot 5.5(MeCN)$ (240 mg, 0.31 mmol) in 15 mL of MeCN. The reaction immediately turned orange-brown and slowly an orange-yellow precipitate formed. The mixture was stirred for 16 h and then filtered to isolate the solid. The yellow solid was washed with a minimal amount of MeCN. To remove all traces of solvent, the solid was dried at 50 mTorr and 50 °C for 6 h, during which time the solid turned from yellow to olive-green. Yield = 101 mg (92%) of a green powder. IR (KBr): ν_{CN} 2220(m), 2182(s), 2156(s, sh) cm^{-1}. TGA confirmed no MeCN present in the dried solid. Anal. Calcd (found) for $C_{18}N_{12}Dy$: C 39.54 (39.38), N 30.74 (30.48).

$Gd(TCNE)_3$. The above method using $GdI_3 \cdot 4.25(MeCN)$ was used. IR (KBr): ν_{CN} 2219(m), 2181(s), 2154(s, sh) cm^{-1}. TGA confirmed no MeCN present in the dried solid. Anal. Calcd (found) for $C_{18}N_{12}Gd$: C 39.92 (39.72), N 31.04 (30.87).

Results and Discussion

In preparing $M(TCNE)_x$, three general procedures are used, i.e., reaction of (1) M^{x+} with $[TCNE]^{\bullet-}$, (2) a metal compound that reduces TCNE and produces the desired metal ion, or (3) eq 1. The lanthanides are most commonly found in the 3+ oxidation state; thus, the first and third methods are preferred to produce $Ln(TCNE)_3$. Herein, we report the reaction of anhydrous LnI_3 (Ln = Gd, Dy) with TCNE.

Commercially available DyI_3 and GdI_3 were recrystallized from dry acetonitrile, producing colorless, needlelike crystals of $[Ln(NCMe)_x]I_3$ ($x \approx 9$). Preliminary crystallographic analysis of these crystals demonstrated the presence of nine acetonitrile molecules coordinated to the lanthanide ion in a capped trigonal prismatic arrangement, as observed for $[Ln(NCMe)_9][AlF_6]_3$ (Ln = La, Sm).[10] Upon drying the crystals under vacuum, they became opaque and lost crystallinity. Thermogravimetric analysis showed that the acetonitrile content was $4 \le x \le 6$ depending on preparation and indicates that facile loss of MeCN occurs.

$Dy(TCNE)_3$ (**1**) and $Gd(TCNE)_3$ (**2**) were made via eq 2. To remove residual acetonitrile, the resultant yellow powders were dried at 50 °C under vacuum for 12 h, which caused the solids to turn dark olive-green. Both compounds are amorphous powders. The products showed no MeCN by thermogravimetric analysis. Because both Ln^{3+} and $[TCNE]^{\bullet-}$ react with water, the products are extremely moisture sensitive. When removed from the inert atmosphere box, the green solids instantaneously turned purple, then slowly become brown after several hours.

$$3\ LnI_3 \cdot x(MeCN) + 6\ TCNE \rightarrow 2\ Ln(TCNE)_3 + Ln(I_3)_3 + 3x\ MeCN \quad (2)$$

The IR spectra of **1** and **2** showed three ν_{CN} absorptions at 2220(m), 2182(s), and 2156(s) cm^{-1} for **1** and at 2219(m), 2181(s), and 2154(s) cm^{-1} for **2**. These values are indicative of metal-bound $[TCNE]^{\bullet-}$ and are consistent with those reported for other $M^{II}(TCNE)_x$ compounds (Table 1). In the absence of structural information, $Ln(TCNE)_3$ are proposed to have three-dimensional (3D) extended networks, with each $[TCNE]^{\bullet-}$ binding on average to three rare earth ions, with each Ln^{3+} being nine-coordinate (as occurs for $[Ln(NCMe)_9]^{3+}$ [10]), e.g., **3**. The $[TCNE]^{\bullet-}$ binding is analogous to the $M(TCNE)_2$ family of compounds with M^{II} being

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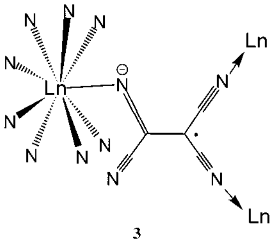
Table 1. ν_{CN} IR Absorption Bands and T_c for M(TCNE)$_x$ (M = V, Mn, Fe, Co, Ni, Gd, Dy)

M	ν_{CN}, [TCNE]$^{\bullet-}$, cm^{-1}	ν_{CN}, [C$_4$(CN)$_8$]$^{2-}$, cm^{-1}	T_c, M(TCNE)$_x$, K	J/k_B,[d] K
V	2214(m), 2191(s), 2158(s, sh)[6b]	*a*	~400[6]	53[1b]
Mn	2224(m), 2181(s), 2171(s)[7]	2212(s), 2205(s), 2153(s), 2096(sh)[12]	75[14a]	4.3[1b]
Fe	2221(m), 2177(s), 2174(s)[7]	2213(m), 2154(s), 2108(w)[12]	97[14b]	8.1[1b]
Co	2230(m), 2194(s), 2167(s)[7]	2223(m), 2179(s, sh), 2160(s), 2112(w)[c]	44[7]	5.9[1b]
Ni	2237(m), 2194(s)[7]	*a*	44[7]	11[1b]
Gd	2219(m), 2181 (s), 2154(s)[b]	2215(m), 2204(m, sh), 2176(s, sh), 2156(s), 2106(w, sh)[b]	3.5[b]	0.07[b]
Dy	2220(m), 2182(s), 2156(s)[b]	2219(m), 2206(m), 2181(s, sh), 2158(s), 2105(w, sh)[b]	8.5[b]	0.04[b]

[a] Unknown. [b] This work. [c] Results to be published. [d] Calculated from mean field model, see text.

octahedral, where the [TCNE]$^{\bullet-}$ also binds on average three metal ions.[1b,6]



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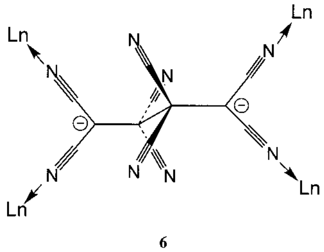
Samples of both compounds were also prepared with minimal drying in order to preserve the yellow powders initially isolated. The solids were dried for 5 min under vacuum to produce pale green-yellow (Dy, **4**) and yellow (Gd, **5**) solids of Ln(TCNE)$_3$·*x*(MeCN) composition. Thermogravimetric analysis of **4** and **5** revealed $x \approx 3$. The IR spectra have MeCN nitrile peaks at 2311 and 2283 cm^{-1} as well as reduced TCNE ν_{CN} peaks at 2219, 2206, 2181 (sh), 2158, and 2105 (sh) cm^{-1}. These ν_{CN} absorptions are inconsistent with TCNE, isolated [TCNE]$^{\bullet-}$, metal-bonded [TCNE]$^{\bullet-}$, or even π-[TCNE]$_2^{2-}$,[11] but are assigned to the diamagnetic octacyanobutanediide, the dianion-σ-bonded dimer of [TCNE]$^{\bullet-}$, [C$_4$(CN)$_8$]$^{2-}$.[12] μ_4-[C$_4$(CN)$_8$]$^{2-}$ has been structurally characterized in M[C$_4$(CN)$_8$](MeCN)$_2$ (M = Fe, Mn) and exhibits characteristic ν_{CN} absorptions at 2213, 2154, and 2108 cm^{-1} (Table 1).[12] Hence, **4** and **5** are respectively formulated as Ln$_2$[C$_4$(CN)$_8$]$_3$(MeCN)$_x$ ($x \approx 6$; Ln = Dy, Gd). The binding of [C$_4$(CN)$_8$]$^{2-}$ to four metal ions, **6**, is expected as observed in the structure of M[C$_4$(CN)$_8$](MeCN)$_2$·CH$_2$Cl$_2$ (M = Fe, Mn),[12] as they have similar IR spectra.



6

Paramagnetic M[C$_4$(CN)$_8$](MeCN)$_2$(CH$_2$Cl$_2$) (M = Fe, Mn) could be desolvated at 100 °C to produce the magnetically ordered compounds M(TCNE)$_2$ containing $S = 1/2$ [TCNE]$^{\bullet-}$.[12] Desolvation of **4** and **5** to achieve **1** and **2**, respectively, produced the same effect, with the dimer converted to [TCNE]$^{\bullet-}$, as evidenced by the color changes and the ν_{CN} IR spectra of the resulting dark green solids.

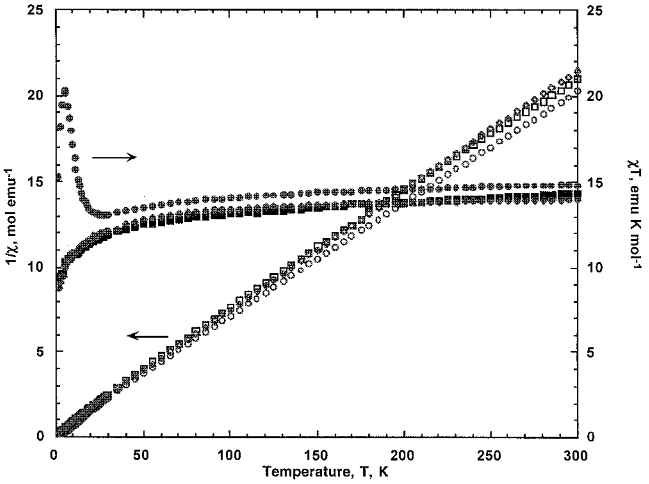


Figure 1. Plot of $\chi^{-1}(T)$ and $\chi T(T)$ for **1** (●), **3** (■), and DyI$_3$(MeCN)$_{5.5}$ (◆) measured in an applied field of 500 Oe.

The dc magnetic susceptibilities (χ) of **1**, **2**, **4**, and **5** were measured between 2 and 300 K in an applied field of 500 Oe. Compounds **4** and **5** do not show evidence of magnetic ordering. The dc magnetic susceptibility of these species was also measured in a 500 Oe field. The values of χT at 300 K are 14.0 emu K mol^{-1} (**4**) and 8.46 emu K mol^{-1} (**5**). These values are close to those expected for Dy^{3+} and Gd^{3+}, as [C$_4$(CN)$_8$]$^{2-}$ is diamagnetic. Above 50 K, the data can be fit to the Curie−Weiss expression, $\chi \propto [T - \theta]^{-1}$, with $\theta = -13$ and -18 K, for **4** and **5**, respectively. The shapes of the $\chi T(T)$ plots are nearly identical to those of the recrystallized LnI$_3$·*x*(MeCN) (Ln = Dy, Gd), Figure 1.[13] Thus, the magnetic properties of **4** and **5** are due to the rare earth ions only. This confirms the presence of diamagnetic [C$_4$(CN)$_8$]$^{2-}$ units in the light-colored, solvated materials.

The value of χT at 300 K for **1** is 15.0 emu K mol^{-1} and is in good agreement for $J = 15/2$ Dy^{3+} ion (14.09 emu K mol^{-1}) and three [TCNE]$^{\bullet-}$ (0.375 emu K mol^{-1}), i.e., 15.22 emu K mol^{-1}. Above 50 K, the data can be fit to the Curie−Weiss law with $\theta = -8.5$ K, indicative of weak antiferro-

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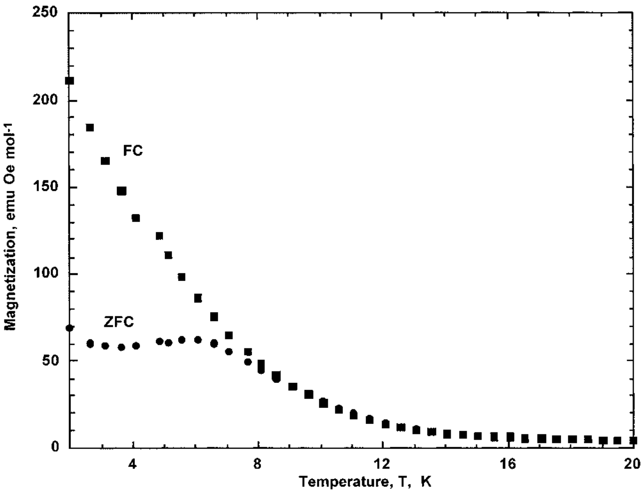

Figure 2. Plot of zero-field-cooled (ZFC, ●) and field-cooled (FC, ■) magnetization of **1** measured in a 5 Oe applied field. The low-temperature region is displayed with the bifurcation point at 8.5 K

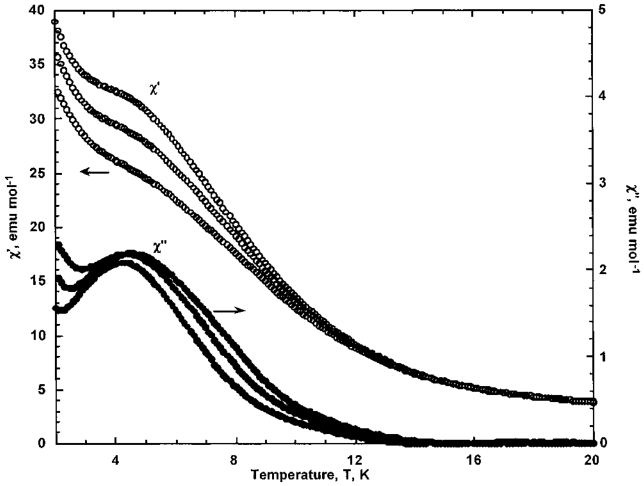

Figure 3. Plot of the in-phase (χ′, ○) and out-of-phase (χ″, ●) components of the ac susceptibility of **1** at 10, 100, and 1000 Hz.

magnetic coupling. Upon cooling, the value of χT remains constant until 30 K, at which point it gradually increases to a maximum of 19 emu K mol^{-1} at 5 K (Figure 1). The 5 Oe zero-field-cooled (ZFC) and field-cooled (FC) magnetization shows a bifurcation point at 8.5 K (Figure 2), which indicates the onset of magnetic ordering. The ac susceptibility measured in a 1 Oe field oscillating at 10, 100, and 1000 Hz has poorly defined shoulders in the in-phase, χ', signal and peaks in the out-of-phase, χ'', signal (Figure 3). The onset of the χ'' signals occurs at roughly 12 K, with the maxima at about 5 K. This behavior is indicative of long-range magnetic ordering with glassiness arising from local structural disorder. The structural disorder is consistent with its amorphous nature, as noted from powder diffraction studies. The 2 K magnetization of **1** at 9 T is 31 500 emu Oe mol^{-1} and is not saturated. This value is low, as the expected value for antiferromagnetic coupling between Dy^{3+} and the three [TCNE]$^{\bullet-}$ anions is 39 000 emu Oe mol^{-1}. Since it is not saturated but approaching the values expected for antiferromagnetic coupling, **1** is a ferrimagnet. Hysteresis at 2 K shows a small coercive field, H_{cr}, of 20 Oe.

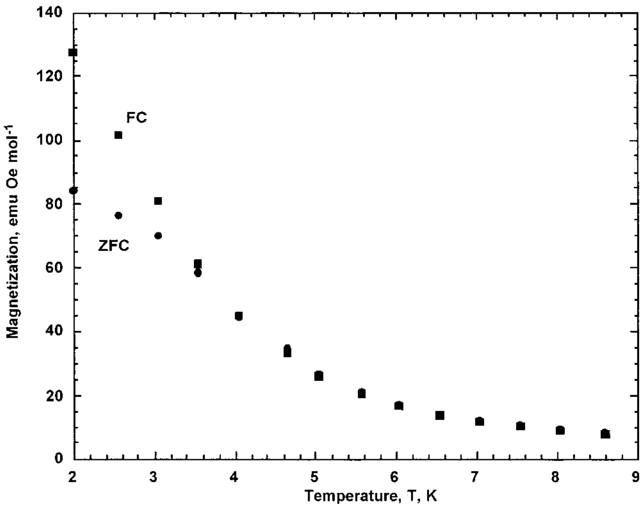

Figure 4. Plot of zero-field-cooled (ZFC, ●) and field-cooled (FC, ■) magnetization of **2** measured in a 5 Oe applied field. The low-temperature region is displayed with the bifurcation point at 3.5 K.

The value of χT at 300 K for **2** is 8.85 emu K mol^{-1}, which corresponds to a Gd^{3+} ion (7.87 emu K mol^{-1}) and three [TCNE]$^{\bullet-}$ (0.375 emu K mol^{-1}). Above 50 K, the data can be fit to the Curie−Weiss law with $\theta = -11.8$ K, indicative of antiferromagnetic coupling. Upon cooling, the value of χT remains constant until 30 K, at which point it gradually increases to about 13 emu K mol^{-1} at 2 K, which is similar to that of Dy(TCNE)$_3$ in Figure 1. The 5 Oe ZFC/FC magnetization of **2** shows a bifurcation point at 3.5 K, characteristic of magnetic ordering (Figure 4). The ac susceptibility has ill-defined shoulders in the $\chi'(T)$ and peaks in $\chi''(T)$. The onset of the χ'' signals occurs at ~6 K, with the maxima at 3.5 K. There is a very small frequency dependence of the peaks indicative of glassy behavior of the magnetically ordered state. The magnetization of **2** at 9 T and 2 K is 35 500 emu Oe mol^{-1} and is saturated above 6 T. The saturation magnetization lies between the values expected for ferromagnetic (55 850 emu Oe mol^{-1}) and for antiferromagnetic (22 340 emu Oe mol^{-1}) coupling between the Gd^{3+} ion and the three [TCNE]$^{\bullet-}$ and is being studied further. A hysteresis loop at 2 K shows a very small coercive field of 15 Oe.

Thus, both **1** and **2** possess $S = 1/2$ [TCNE]$^{\bullet-}$ that weakly antiferromagnetically couples and at low temperature exhibit a gradual magnetic phase transition to a ferrimagnetic state. The compounds are amorphous materials, and therefore the onset of magnetic ordering is not sharply defined. Compound **1** exhibits a higher T_c due to the anisotropic nature of the Dy^{3+} ion compared to isotropic Gd^{3+} found in **2**. Although the Ln^{3+} have large values of J as well as large numbers of nearest neighbors, z, the overall low T_c's of 8.5 and 3.5 K for **1** and **2**, respectively, are attributed to weak coupling (J) between the spin-nearing ions. The average value of J can be estimated from the aforementioned mean field expression relating T_c and J, Table 1. The estimated J values for **1** and **2**, 0.04 and 0.07 K, respectively, are 2 orders of magnitude lower than those for M^{II}(TCNE)$_2$ (M = Mn, Fe, Co, Ni). The weak coupling is attributed to the longer Ln−N separations with respect to $M^{II}-N$, as well as less shielding of the valence f electrons, bringing these electrons closer to the nucleus, making them available for covalent bonding. The values are also much lower than the linear chain compounds mentioned above[5] due to the radicals being shared by an average of three rare earths rather than two.

Nonetheless, the family of $M(TCNE)_x$ molecule-based magnetic materials has been extended to include those with rare earth ions. The temperatures of the magnetic phase transitions are higher than those reported for the 1D nitronylnitroxide chains[5] presumably due to the 3D nature (greater z) of the $Ln(TCNE)_3$ species.

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