Lanthanide–TCNQ Magnet

A Rare-Earth Metal TCNQ Magnet: Synthesis, Structure, and Magnetic Properties of $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\}\cdot 4H_2O$**

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One of the most rapidly expanding areas of coordination chemistry research is the design of magnetic materials based on molecular building blocks.[1] A perusal of the literature reveals that a successful design strategy for preparing molecular magnets is the coordination of organic radicals such as nitronyl nitroxides[2] and organocyanides such as $TCNE^{-\bullet}$ (tetracyanoethylene)[3] and $TCNQ^{-\bullet}$ (7,7,8,8-tetracyanoquinodimethane)[4] to paramagnetic transition metal ions. The presence of both metal spins (typically $S > 1/2$) and organic spin carriers ($S = 1/2$) leads to strong local super-

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exchange interactions, the ultimate result of which is typically ferro- or ferrimagnetic ordering.

Although molecular magnetic materials based on 3d metals are quite common, analogous 4f element compounds are relatively rare. A few research groups have explored the magnetic-exchange interactions in mixed 3d–4f compounds[5] and 4f–organic radical materials. A notable example is the recently reported compound $[\{CuL\}_2Gd(TCNQ)_2]\cdot TCNQ\cdot CH_3OH\cdot 2\,CH_3CN$ (L = *N,N'*-propylenebis(3-methoxysalicylideneiminato) containing three different types of spin carriers (3d–4f–organic radical).[6] The magnetic properties of this mixed salt are indicative of ferromagnetic coupling between Cu^{II} and Gd^{III} ions with no contribution from the TCNQ radicals, presumably due the presence of $[TCNQ_2]^{2-}$ dimers.

Until recently, the issue of whether magnetic ordering is possible in 4f coordination polymers was an open question,[7] but recent work by Miller and co-workers have provided the first examples in which 4f elements coordinated to $TCNE^{-\bullet}$ yield products that undergo spontaneous magnetization after thermal annealing.[8] Unfortunately, no structural information is yet available for these phases. Herein we report a crystalline rare-earth TCNQ magnet that magnetically orders at 3.5 K.

Slow diffusion of deoxygenated water solutions of $GdCl_3\cdot 6H_2O$ and Li[TCNQ] (1:1 ratio) yields crystals of the title compound, $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\}\cdot 4H_2O$ (**1**). The unusual structure of the material consists of alternating anionic and cationic layers perpendicular to the *c* axis, both of which are based on a 2D network of Gd^{III} ions coordinated to TCNQ radical anions. The different ratios of Gd^{III} and $TCNQ^{-\bullet}$ in the two independent layers leads to the unusual situation of having both cationic and anionic networks. Thermal ellipsoid plots of both networks for the crystal are depicted in Figure 1.[9]

The cationic network, $[Gd_2(TCNQ)_5(H_2O)_9]^+$ contains two crystallographically independent Gd^{III} (Gd1 and Gd3) ions and five $TCNQ^-$ molecules. Both Gd^{III} ions are nine-coordinate, but Gd1 is coordinated to five $TCNQ^-$ radicals and four water molecules, whereas Gd3 is bound to four TCNQ and five water molecules. The $TCNQ^-$ ligands exhibit three different binding modes, namely μ_3-$TCNQ^-$ (bridging between two Gd3 and one Gd1 ions), μ_2-$TCNQ^-$ (bridging between Gd1 and Gd3) and terminal $TCNQ^-$. The result of this complicated connectivity pattern is the 2D network depicted in Figure 2a which consists of "$(Gd3)_2TCNQ_2$ dimers" connected to a third Gd atom (Gd1) by another $TCNQ^-$ bridging ligand to yield "chains" which are further stitched together by Gd1 ions to form the 2D network in the *ab* plane.

The anionic network, $[Gd(TCNQ)_4(H_2O)_3]^-$ contains one unique Gd^{III} ion (Gd2) and four $TCNQ^-$ molecules (Figure 1b). The nine-coordinate Gd2 ion is surrounded by six N atoms from $TCNQ^-$ ligands acting as nitriles and three H_2O molecules. Three of the four unique $TCNQ^-$ ligands act as μ_2-bridges and one is a terminal ligand. The result of these binding modes is a network formed by $[Gd_2TCNQ_2]$ "dimers" which are connected through perpendicularly oriented $TCNQ^-$ ligands to yield a pseudo-hexagonal motif (Figure 2b), in which each "dimer" is connected to four near neighboring dimers.

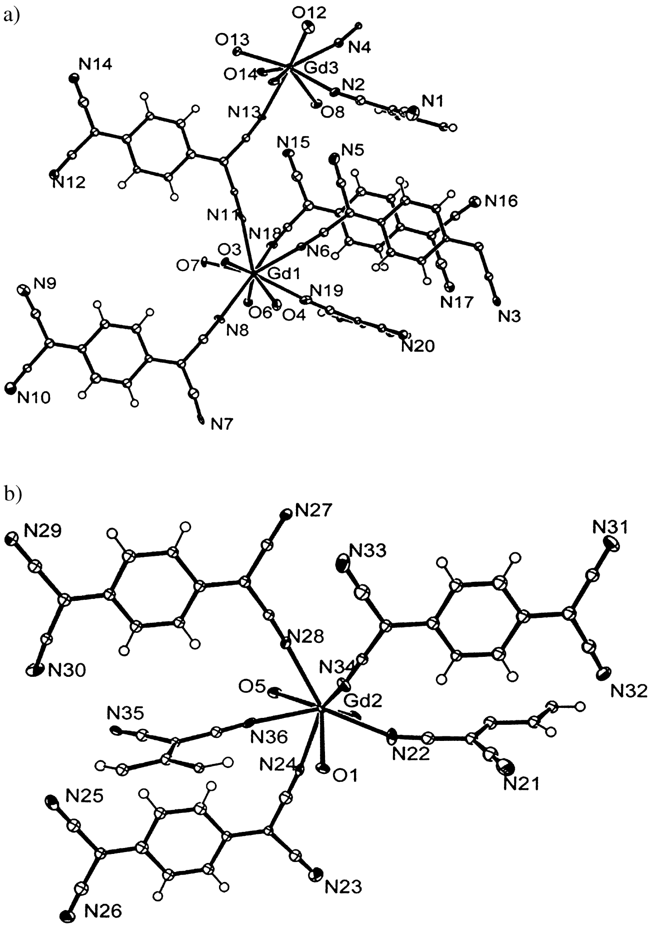

Figure 1. Structure of $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\}\cdot 4H_2O$; thermal ellipsoid representations of the cationic (a) and anionic (b) networks.

Two important supramolecular features regarding the structure of $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\}\cdot 4H_2O$ are worthy of note. The dangling nitrile substituents of the $TCNQ^-$ ligands are involved in hydrogen bonding to coordinated H_2O molecules, which affords extra stabilization to the 2D networks, and, most importantly, the anionic and cationic frameworks are involved in 1D π-stacking interactions between $TCNQ^-$ radicals. The stacking distances are uniform, (~3.2 Å) with no apparent dimerization being evident. There are also TCNQ ligands that do not participate in the stacking interactions, which lie perpendicular to these chains. Overall, it is evident that the packing is very efficient and there is little available free space.

The title compound **1** can also be prepared in bulk as a polycrystalline material from $GdCl_3\cdot 6H_2O$ and LiTCNQ. Elemental and thermal gravimetric analyses as well as powder X-ray diffraction analysis support the conclusion that this polycrystalline material is structurally very similar to the crystals obtained by slow diffusion (see Supporting Information). The IR spectrum exhibits a similar stretching frequency for the bulk material, $\nu(C\equiv N)$ 2177 cm^{-1}. That value is similar to that of the crystals, $\nu(C\equiv N)$ 2180 cm^{-1}. These values are typical for mono-reduced TCNQ. Notably, the number of

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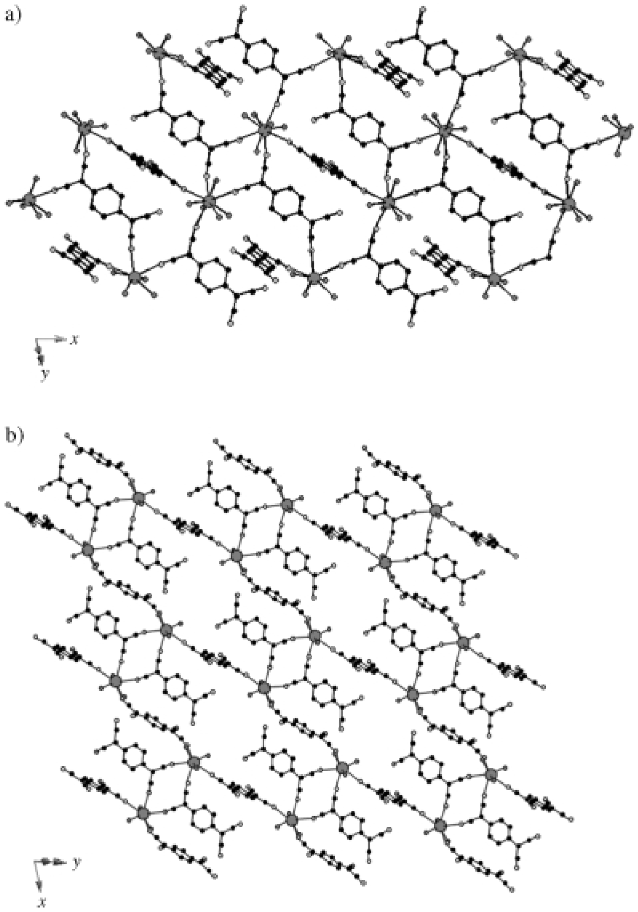

Figure 2. a) Top view of the tetrameric chains (terminal TCNQ ligands have been omitted for clarity) in the cationic network of **1**. b) Top view of the 2D anionic network (terminal TCNQ ligands have been omitted for clarity) in **1**.

water molecules present in the bulk material varies with the extent of drying as supported by TGA analysis.

The magnetic properties of **1** were investigated over the temperature range 2–300 K at 1000 G. The $\chi_m T$ product shows a slight decrease from a room-temperature value of 27.3 emu K mol^{-1}, down to 25.6 emu K mol^{-1} at 50 K. The high-temperature data were fit to a Curie–Weiss law, with a Curie constant of 27.1 emu K mol^{-1}, which is in good agreement with the expected value for three isolated Gd^{III} ions ($S = 7/2$) and nine TCNQ$^-$ radical anions ($S = 1/2$) in a magnetically dilute sample (27 emu K mol^{-1} for $g = 2$). The Weiss constant ($\theta = -5.07$ K) is small and negative, indicative of antiferromagnetic interactions between spin carriers. At temperatures near 10 K, the value of $\chi_m T$ begins to increase, and at 2 K the value abruptly increases, which is an indication of the onset of spontaneous magnetization. In accord with the conclusion that magnetic ordering is occurring, AC magnetic susceptibility measurements were performed. The results are plotted in Figure 3 where it can be clearly seen that the material exhibits an out-of-phase signal (χ''_m) at T_c ~3.5 K. No AC frequency dependence of the AC signal was observed up to 1000 Hz.

The presence of antiferromagnetic interactions, as hinted by the thermal dependence of the DC susceptibility, was confirmed by the field dependence of the magnetization at 1.8 K. The magnetization increases rapidly at low fields, and at $H > \sim 4$ T, the signal reaches saturation at a magnetization value of 18.1 μB, or 18 spins, which represents an intermediate value from the total 30 spins present. This result supports the conclusion that the nature of the magnetic ordering is, indeed, ferrimagnetic, and arises from the non-compensated spins in an antiparallel spin alignment. Notably, magnetically, this material is actually three-dimensional with multiple interactions. The structure renders it very difficult to provide a simple rationalization of the magnetic data. In addition to the intra-layer interactions, including direct exchange (Gd-TCNQ) and superexchange (between TCNQ groups through the Gd bridges, and vice versa); there are also strong magnetic interactions between layers through the short π–π contacts between TCNQ units in adjacent layers. It is well known that the latter type of interaction is antiferromagnetic. Unfortunately, the complexity of the system does not allow further magnetic analysis at this point, including the sign and strength of every single magnetic interaction present in the compound. But the magnetic data clearly indicate that some of the magnetic interactions are antiferromagnetic, a situation that leads us to define the material as a ferrimagnet. The preparation of molecular model compounds (dimers) is needed to reach a better understanding of this material. The material behaves as a soft magnet and does not show hysteretic behavior at 1.8 K.

In conclusion, the polymeric salt $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\}\cdot 4H_2O$ has been crystallized and shown to consist of both cationic and anionic layers that exhibit different ratios of Gd^{III} and TCNQ$^-$ radicals. This material is only the third example of a lanthanide/organic radical based magnet to our knowledge and the first lanthanide–TCNQ magnet. Efforts to incorporate more anisotropic lanthanide ions such as Eu^{3+} and Dy^{3+} into polymeric materials with TCNQ$^{-\bullet}$ are currently in progress.

Experimental Section

All reactions were performed under nitrogen using standard Schlenk techniques. Single crystals were obtained by layering a solution of

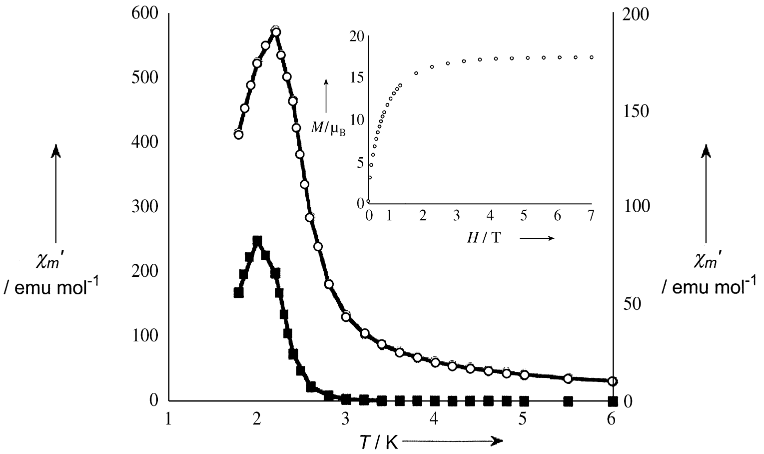

Figure 3. AC susceptibility data for **1**: (○) in-phase response (χ'_m); (■) out-of-phase response (χ''_m). The inset is the plot of magnetization versus field performed at 1.8 K.

$GdCl_3 \cdot 6H_2O$ (150 mg in 20 mL of degassed H_2O) with Li[TCNQ] (84 mg in 20 mL of degassed H_2O) in a Schlenk tube. The bulk reaction product was obtained in the form of a dark purple precipitate by adding degassed H_2O (20 mL) to a solid mixture of $GdCl_3 \cdot 6H_2O$ (220 mg, 0.59 mmol) and Li[TCNQ] (125 mg, 0.59 mmol) in a Schlenk flask. The solution was stirred for 30 min and then left undisturbed overnight. The powder was collected by vacuum filtration, washed with copious amounts of H_2O, and dried under vacuum; yield 162 mg (31 %).

DC magnetic susceptibility measurements were preformed on crushed single crystals of **1** (2.89 mg) with a Quantum Design MPMS-2 SQUID magnetometer operating in the temperature range of 1.8–300 K at 1000 G. AC magnetic susceptibility measurements were performed on the same sample with an oscillating frequency of 125 Hz.

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[9] Crystal data for $\{[Gd_2(TCNQ)_5(H_2O)_9][Gd(TCNQ)_4(H_2O)_3]\} \cdot 4H_2O$ (**1**) at 110(2) K: $C_{108}H_{68}N_{36}O_{16}Gd_3$, $M_r = 2597.73$, dark purple blocks, $0.067 \times 0.058 \times 0.030$ mm, triclinic, space group $P\bar{1}$, $a = 15.767(3)$, $b = 17.806(4)$, $c = 19.406(4)$ Å, $\alpha = 74.59(3)$, $\beta = 81.61(3)$, $\gamma = 76.64(3)°$, $V = 5089(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.695$ g cm^{-3}; $2\theta_{max} = 46.54°$; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; $T = 293(2)$ K; 20045 reflections, of which 14276 are unique, and of which 9001 were included in the refinement ($I > 2\sigma$); solution by direct methods (G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen (Germany), **1997**) and refinement on F^2 by full-matrix least-squares procedure (G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen (Germany), **1997**); 918 parameters; isotropic refinement of all C atoms, O6 and N4, the remaining non-hydrogen atoms were refined anisotropically; H atoms were included in their calculated positions, except in solvent water molecules; final values $R(F) = 0.0603$, $R_W(F^2) = 0.1136$. CCDC-199356 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).