

Magnetic Ordering in Self-assembled Materials Consisting of Cerium-(III) Ions and the Radical Forms of 2,5-TCNQX₂ (X = Cl, Br)**

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Unlike transition metals, rare earth elements do not engage in appreciable magnetic superexchange due to the highly contracted nature of the 4f orbitals and strong shielding effects of the outer 5d and 6s shells. This situation notwithstanding, the co-assembly of d- as well as p-orbital based spins with lanthanide ions has been a fruitful approach to magnetic heterospin systems with interesting properties.^[1] The majority of reports involving molecular magnetism of lanthanide elements focus on trivalent Sm, Eu, Gd, Tb^[2] and, especially, Dy compounds.^[3] Extraordinary properties have been reported for diverse families of compounds from a number of leading research groups beginning with the pioneering results of Rey and Gatteschi who began publishing research on lanthanide nitronyl-nitroxide materials as early as 1989.^[1a] In terms of recent milestones, the discovery of slow paramagnetic relaxation for single ion sandwich complexes such as (BuN₄)[Tb(Pc)₂] (Pc = phthalocyanine anion)^[4a] and for square,^[3d] triangular^[3e,4b,d] as well as other polynuclear Dy compounds^[3] is infusing molecular magnetism research with renewed optimism in regard to the potential for realizing high-temperature single molecule magnets (SMMs). The most recent report in this vein of a Dy₅ pyramidal complex with blocking temperatures as high as 40 K and a thermal barrier for magnetization reversal of ca. 540 K is a particularly promising finding.^[4c] Another recent remarkable report with regard to the use of radical bridges in rare earth magnetism has also appeared, that is, that the N₂³⁻ radical bridge leads to the strongest magnetic coupling on record for a Gd^{III} complex and a blocking temperature of 8.3 K at a sweep rate of 0.08 T s⁻¹ for a Dy^{III} analogue.^[5]

Among the lanthanides, examples of the use of Ce^{III} are scarce in molecular magnetism research, presumably because there is only one spin on this ion.^[6] Cerium-containing

magnetic materials have been reported with Mn ions and phosphonate ligands; these include a discrete cluster dominated by ferromagnetic superexchange and a one-dimensional polymer that exhibits antiferromagnetic interactions.^[6c] Of further note is the work of Christou and co-workers who prepared unusual compounds including two Mn^{IV}₈Ce^{III} clusters that behave as SMMs, one of which is the first example of a loop-based SMM.^[6c] A series of mixed chromium–lanthanide ladder-type polymers was prepared with La^{III}, Pr^{III}, Nd^{III}, Ce^{III} and [Cr^{III}(ox)₃]³⁻ with antiferromagnetic coupling being observed for the Ce analogue.^[6a] Finally, 4f/3d compounds of general formula [Ln(DMF)₄(H₂O)₅(μ-CN)M(CN)₅]_nH₂O₅ (Ln = La^{III}, Ce^{III}; M = Fe^{III}, Co^{III}) were prepared and antiferromagnetic coupling between the Fe^{III} and Ce^{III} centers was observed.^[6b,d] Detailed EPR analyses of the Ce–Fe, La–Fe and Ce–Co analogues provides additional evidence for the exchange coupling.

Given the success of the Ln^{III}/nitronyl-nitroxide radical systems in yielding both discrete complexes and extended structures,^[1a–d,h,2a,3a–c,7] it is of obvious interest to pursue the combination of trivalent lanthanide ions with other organic radicals. To date, TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) has yielded several interesting compounds with trivalent lanthanide atoms such as [Ln(N–N)_x(TCNQ)₃] (Ln = Pr, Nd; N–N = 1,10-phenanthroline, dipyrindylamine; x = 2, 4) and [Ln(N–N)₄(TCNQ)₄],^[8] a 2-D material [[Gd₂(TCNQ)₅(H₂O)₉]{Gd(TCNQ)₄(H₂O)₃·4H₂O}_∞] composed of interpenetrating anionic and cationic networks that exhibits ferromagnetic ordering at 3.5 K,^[1j] and a family of Ln^{III}/[TCNQF₄]⁻ (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) molecular magnets,^[11] among which is a Tb analog which exhibits a fascinating interplay between SMM and phonon bottleneck (PB) behavior. Of additional note is the interesting report by Miller and co-workers of magnetic ordering in the rare earth series [Ln(TCNE)₃] (TCNE = tetracyanoethylene) with Gd^{III} and Dy^{III} ions.^[12] These previous examples notwithstanding, there is very little rare earth organocyanide radical chemistry in the literature.

As part of a broad effort in our group to investigate the properties of TCNQ radicals coordinated to rare earth metal ions, we investigated the chemistry of Ce^{III} with TCNQ and derivatives. Earlier, the compound [Ce₂(TCNQ)₄(H₂O)₁₂]-[TCNQ]₂·MeOH·3H₂O was reported along with its electrochemical properties, but no magnetic studies were included.^[9] Herein we report the syntheses, structures, and magnetic properties of a slightly different phase of this compound, namely [Ce₂{(TCNQ)₄(H₂O)₁₀(CH₃OH)₂}[TCNQ]₂·2H₂O·2CH₃OH (**1**) and the two new compounds: [Ce₂(TCNQBr₂)₄-

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(MeOH)₉(H₂O)[TCNQBr₂]₂ (**2**) and [Ce(TCNQCl₂)₂(MeOH)₉(H₂O)][TCNQCl₂]₂ (**3**).

Compound **1** crystallizes in the triclinic space group $P\bar{1}$, the asymmetric unit of which contains one [Ce(TCNQ)₂(H₂O)₅(CH₃OH)]⁺ formula unit as well as two halves of uncoordinated TCNQ radical anions, two molecules of methanol and one molecule of water (Figure 1a). In the

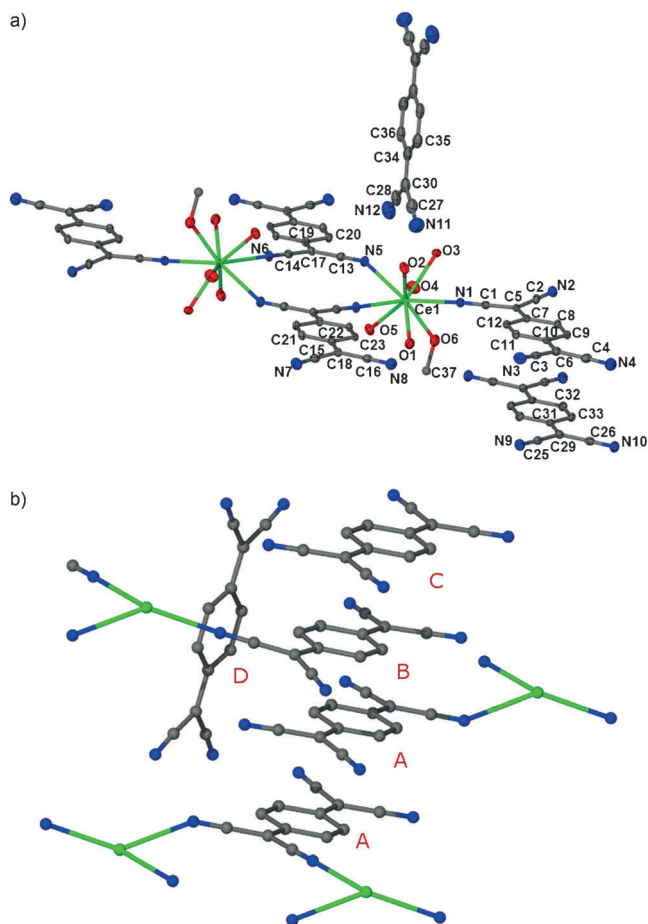


Figure 1. a) Coordination sphere of **1** revealing the dinuclear nature of the cation and emphasizing the different types of TCNQ radicals. b) A portion of the structure of **1** that emphasizes the different types of TCNQ and their arrangements.

case of the related structure by Cheng et al.,^[9b] the basic structure is the same except that only H₂O molecules are bound to the Ce^{III} ions. One of the coordinated TCNQ radicals is a monodentate N-bonded ligand (Type B) while a second coordinated TCNQ⁻ adopts a geminal μ_2 -bridging mode (Type A; Figure 1b). The trivalent cerium atom is nine-coordinate and lies in a slightly distorted square-face monocapped square-antiprismatic environment of nitrogen and oxygen atoms consisting of three nitrogen atoms from the cyano groups of two TCNQ ligands, five oxygen atoms from coordinated water molecules and one oxygen atom from a statistically disordered water/methanol ligand. The two square faces of the coordination polyhedron are tilted 43.3° with respect to each other and are quasi-parallel (angle

9.42(9)°). The nitrogen atoms form nearly planar arrays (average displacements of 0.01 and 0.42 Å for the N₁O₃ and N₂O₂ faces, respectively) with the cerium atom lying 0.828(2) Å above the N₁O₃ face and 1.522(2) Å below the N₂O₂ face. The Ce–O₈_{water/methanol} bond lies nearly perpendicular to the N₁O₃ face (angle 88.2°) with a bond distance of 2.508(3) Å between the cerium and oxygen atoms.

In the three-dimensional packing arrangement, the two coordinated TCNQ⁻ moieties (A and B) and one of two free TCNQ radical anions (Type C) lie nearly parallel to one another with angles of 1.7(2), 2.4(2), and 0.7(2)° occurring between them. Along the [22 $\bar{1}$] direction, a one-dimensional chain structure containing both bound and free TCNQ radical anions, with the repeat pattern ...AABCBA..., propagates along this stacking axis (Figure 2). Closer inspection of this one-dimensional stack reveals nearly uniform spacing between the radicals as the centroid–centroid distances between the A...A, A...B, and B...C pairs are 3.899(2),

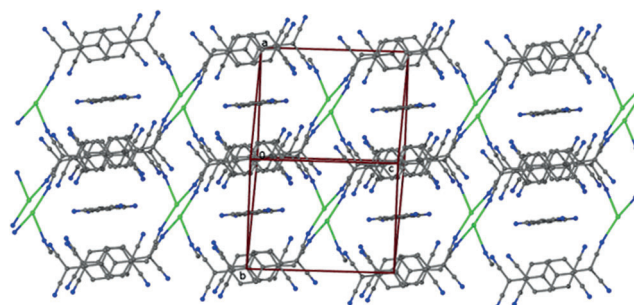


Figure 2. Packing diagram of **1** viewed diagonally to emphasize the TCNQ stacking interactions.

3.829(2), and 3.728(3) Å, respectively. Despite a small ring slippage of 2.159 Å within the A...A pair, the nearly perfect eclipsed stack for the A...B and B...C pairs combined with the approximate uniform spacing between the radicals suggest a one-dimensional chain structure with π ... π interactions. When one further considers the nearly perpendicular orientation of the second free TCNQ molecule (Type D) to A, B, and C at angles of 87.0(2), 87.7(2), and 87.7(2), it can be seen that the Type D acceptors form an extensive network of hydrogen bonds with the donor pairs.

Compounds **2** and **3** are isomorphous, crystallizing in the monoclinic space group $C2/c$ with a nine-coordinate Ce^{III} ion residing on a special position of C_2 symmetry and an uncoordinated TCNQX₂ radical residing on an inversion center (Figure 3). Both compounds consist of a ribbon coordination polymer featuring five-coordinate methanol molecules (two of which are disordered) and two *anti*- μ_2 -TCNQX₂ radical anions bridging two identical, slightly distorted square-face monocapped square-antiprismatic Ce^{III} centers. In the case of **1**, the two square faces (N₂O₂ and N₁O₃) of the coordination polyhedron are tilted 36.7° with respect to each other and are parallel. Due to methanol molecule disorder, the Ce–O₃_{methanol} bond is oriented at an angle of 75.9° with respect to the N₁O₃ face, deviating considerably

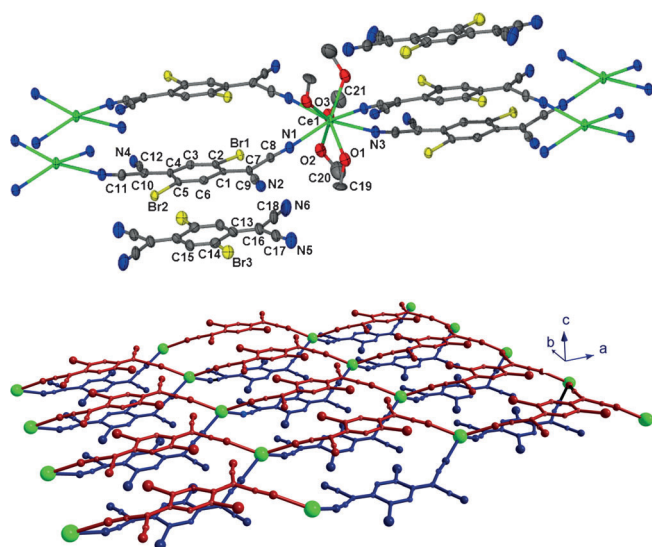


Figure 3. Structure of **2** with the atoms labeled (top) and extended structure of the Ce–TCNQ₂ network (bottom).

from the expected perpendicular value of 90°. Each formula unit of the polymer is flanked by two centrosymmetric uncoordinated TCNQ₂^{•−} moieties stacked in a nearly eclipsed fashion with coordinated radical anions at centroid–centroid distances of 3.303(5) and 3.290(7) Å for **2** and **3**, respectively. A two-dimensional supramolecular structure manifests itself as parallel ribbons that extend along the crystallographic *c*-axis and which are connected by hydrogen bonds between the coordinated methanol molecules and terminal cyanide groups of the TCNQ₂^{•−} radical anions.

Another aspect of the structures that is worth noting is that close inter-halogen contacts involving coordinated TCNQ₂^{•−} radical anions occur at distances of 3.769 Å between neighboring bromine atoms for **2** and between chlorine atoms at distances of 3.556 Å for **3**. In both instances, those inter-halogen distances observed are slightly shorter than the sum of their corresponding van der Waals radii (Br⋯Br 3.80 Å, and Cl⋯Cl 3.60 Å).^[10] All crystallographic and refinement data for **1–3** as well as their corresponding bond distances in tabular format have been deposited in the Supporting Information.

The infrared spectral data for the three compounds revealed two $\nu_{(\text{CN})}$ stretching modes for each compound: 2198 and 2165 cm^{−1} (**1**); 2192 and 2162 cm^{−1} (**2**); 2193 and 2158 cm^{−1} (**3**). In all cases, these occur at lower energies than the corresponding stretches of neutral TCNQ (2222 cm^{−1}), TCNQCl₂ (2224 cm^{−1}), and TCNQBr₂ (2218 cm^{−1}). The similarity of the observed cyanide stretching modes for **1–3** to those for LiTCNQ (2196 and 2154 cm^{−1}), LiTCNQCl₂ (2189 and 2165 cm^{−1}), and LiTCNQBr₂ (2191 and 2157 cm^{−1}), suggest that only TCNQ^{•−} and TCNQ₂^{•−} radical anions are present in the title materials and that there has not been any disproportionation.

The magnetic properties of **1–3** were studied on batches of single crystals. DC data were collected in the 2–300 K temperature range in an applied magnetic field of 5000 G. Room temperature χT values for compounds **1**, **2**, and **3** are

1.04, 1.02, and 1.04 emu mol^{−1} K, respectively, values slightly lower than those expected for one uncoupled Ce^{III} ion ($S = 1/2$, $L = 3$, $J = 5/2$, $g_J = 0.857$, $\chi T = 0.8$ emu mol^{−1} K) and one [TCNQX₂]^{•−} ($S = 1/2$, $\chi T = 0.375$ emu mol^{−1} K) radical anion ($\chi T_{\text{calcd}} = 1.18$ emu mol^{−1} K). As the temperature is lowered the χT value of compound **1** decreases continuously and reaches a minimum of 0.56 emu mol^{−1} K at 2 K. This behavior is attributed to antiferromagnetic interactions between the stacked TCNQ spin-carriers.

The magnetic properties of compounds **2** and **3** are quite different than that of **1**. The χT values decrease as the temperature is lowered and reach minima of 0.53 and 0.55 emu mol^{−1} K at 12 K for **2** and **3**, respectively (Figure 4). Below 12 K, the χT values increase to reach

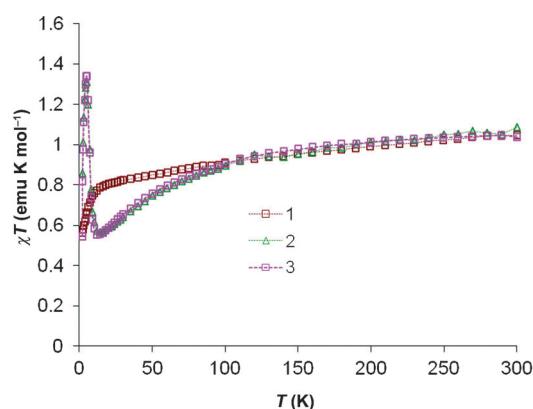


Figure 4. Temperature dependence of the χT versus T plots for **1**, **2**, and **3**.

maxima of 1.3 and 1.34 emu mol^{−1} K at 4.5 K and decrease again to 0.86 and 0.82 emu mol^{−1} K at 2 K for **2** and **3**, respectively. Hysteresis loops were observed for the magnetization versus field measurements with coercive fields of 700 Oe (**2**) and 600 Oe (**3**) (Figures 5 and S3). The zero-field-cooled (ZFC) versus field-cooled (FC) magnetizations data show bifurcations at 5.6 and 7.3 K, indicative of ferrimagnetic phase transitions at these temperatures (Figures 6 and S4).

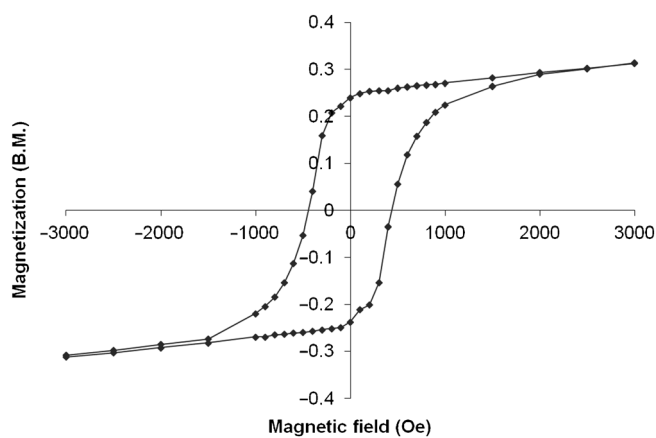


Figure 5. Hysteresis loop for [Ce(TCNQBr₂)₂(MeOH)_{4.5}(H₂O)_{0.5}] \cdot [TCNQBr₂] (**2**).

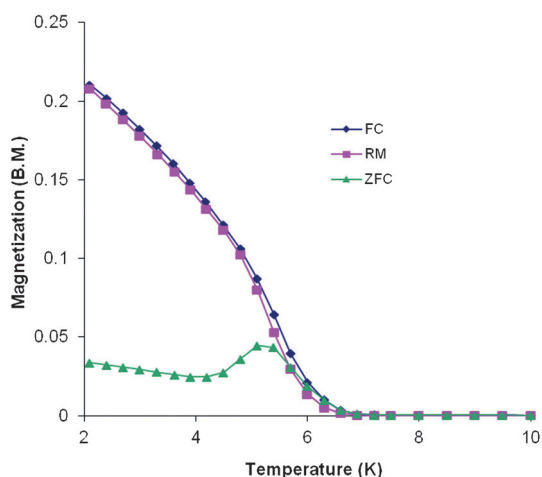


Figure 6. Field-cooled (FC), zero-field-cooled (ZFC), and remanent magnetization (RM) for **2**.

Zero-field AC susceptibility measurements were performed over the range of frequencies from 1–1000 Hz at $H_{AC} = 5$ Oe. Compounds **2** and **3** exhibit typical intensities for the AC signal for bulk magnetic ordering. The maximum of the out-of-phase signal was observed at 5.4 (Compound **2**, Figure S5) and 7.1 K (compound **3**, Figure S6) as shown in the corresponding figures.

In summary, compounds containing Ce^{III} and radical anions of TCNQ, $TCNQBr_2$, and $TCNQCl_2$ have been prepared. Magnetic studies of the compound with $TCNQ^{\cdot-}$ was found to contain two non-interacting Ce^{III} ions and magnetic contributions from a single isolated $TCNQ^{\cdot-}$ radical anion. No evidence of magnetic ordering for this compound was observed. The $TCNQX_2$ derivatives exhibit a different structure featuring a “sandwich network” based on two types of coordinated $TCNQX_2$ radicals with free $[TCNQX_2]^{\cdot-}$ radical anions residing between the layers. Evidently, the 2-D Ce^{III} - $TCNQX_2$ architecture results in stronger magnetic interactions and, surprisingly, leads to a magnetically ordered state with hysteresis. Such magnetic behavior is unexpected for Ce^{III} ($4f^1$) compounds and, indeed, these findings open up new questions about what governs the magnetism of hybrid spin $4f/3p$ molecular solids.

Experimental Section

Single crystals of **1** were obtained after one week by the following procedure: Separate solutions of $CeCl_3 \cdot 7H_2O$ (0.074 g, 0.2 mmol) in 4 mL of MeOH and LiTCNQ (21 mg, 0.1 mmol) in 6 mL of MeOH/ H_2O 1:1 v/v) were prepared. A 2 mL quantity of the LiTCNQ solution was syringed into a 6 mm OD Pyrex tube and carefully layered with 3 mL of the $CeCl_3 \cdot 7H_2O$ solution. Yield 21 mg, 66%. IR (Nujol), $\nu(C\equiv N)$: 2198, 2165 cm^{-1} .

Single crystals of **2** were obtained after one day by the following procedure. Separate solutions of $CeCl_3 \cdot 7H_2O$ (0.074 g, 0.2 mmol) in 4 mL of MeOH and $LiTCNQBr_2$ (36 mg, 0.1 mmol) in 6 mL of MeOH were prepared. A 2 mL quantity of the $CeCl_3 \cdot 7H_2O$ was syringed into a 6 mm OD Pyrex tube and carefully layered with 3 mL of the $LiTCNQBr_2$ solution. Yield 32 mg, 49%. (Nujol), $\nu(C\equiv N)$: 2192, 2162 cm^{-1} . Single crystals of **3** were obtained under analogous

conditions used for **2**. Yield 26 mg, 46%. IR (Nujol), $\nu(C\equiv N)$: 2193, 2158 cm^{-1} .

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