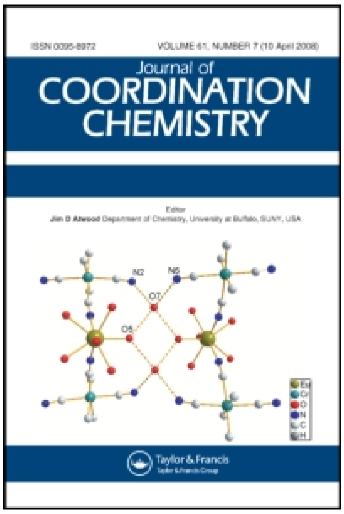

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A NOVEL ONE-DIMENSIONAL CYANO-BRIDGED CHAIN COMPLEX $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]$_n: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETOCHEMISTRY

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A NOVEL ONE-DIMENSIONAL CYANO-BRIDGED CHAIN COMPLEX $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETOCHEMISTRY

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DMF (dimethylformamide) reacts with $Gd(NO_3)_36H_2O$ and $K_3Mn(CN)_6$ to afford a novel cyano-bridged complex $[Gd(DMF)_4(H_2O)_2Mn(CN)_6] \cdot H_2O]_n$. The crystal structure of the complex (abbreviated as GdMn) has shown that it has a novel one-dimensional chain structure. The complex crystallizes in space group $P2_1/c$ with $a = 13.004(2)$, $b = 12.762(2)$, $c = 19.160(4)$ Å, $\beta = 109.51(3)°$, $V = 2997.2(9)$ Å, $D_x = 1.584\,\mathrm{Mg\,m^{-3}}$, $Z = 4$. Variable temperature (1.5-300 K) magnetism shows there exists weak antiferromagnetic interaction between Gd and Mn atoms across the cyano bridge.

Keywords: Gadolinium; Manganese; Cyano-bridged complex; One-dimensional chain; Crystal structure; Antiferromagnetic coupling

INTRODUCTION

There has been great interest in the study of magnetic properties of molecular-based compounds [1-4]. One of the main challenges in this field is the design of materials with high critical temperatures. Hexacyanometallate complexes have been widely studied in many fields such as molecular-based magnets, in which the Prussian blue analogues particularly show fascinating magnetic properties with high *Tc* values [5, 6]. In recent years, a

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lot of research on cyano-bridged complexes is related to transition metal ions [7–9]. The 4f-3d magnetic molecular complexes synthesized were mainly focussed on Ln–Cu complexes [10–13] while little attention was paid to the cyano-bridged lanthanide-transition metal complexes [14, 15]. In the present work, we employed *N,N*-dimethylformamide (DMF) as a hybrid ligand to synthesize a new kind of cyano-bridged chain complex containing rare earth and manganese in order to explore novel molecular-based magnets.

EXPERIMENTAL

Physical Measurements

Elemental analyses (C, H, N) were carried out using an Elementar Cario EL analyzer. Infrared spectroscopy using KBr pellets was performed on a Nicolet 7199B spectrophotometer in the 4000–400 cm^{-1} range.

TABLE I Crystal data and structure refinement details for $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$

Complex	$Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O$
Empirical formula	$C_{18}H_{34}GdMnN_{10}O_7$
Formula weight	714.74
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.004(2)$ Å $b = 12.762(2)$ Å $\beta = 109.51(3)°$ $c = 19.160(4)$ Å
Volume	2997.2(9) Å^3
Z	4
Calculated density	1.584 Mg/m^3
Absorption coefficient	2.665 mm^{-1}
$F(000)$	1428
Crystal size	0.20 × 0.20 × 0.10 mm
θ range for data collection	2.26 to 25.01°
Index ranges	$-15 < = h < = 14, 0 < = k < = 15, 0 < = l < = 14$
Reflections collected/unique	4340
R_{int}	0.280
Independent collection refls.	4168
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4168/12/149
Goodness-of-fit on F^2	1.034
Final R indices [$I >$ 2sigma(I)]	$R1 = 0.075$, $wR2 = 0.161$
Largest duff. peak and hole	3.882 and −2.103 e.A^−3

TABLE II Atomic coordinates (x 104) and equivalent isotropic displacement parameters (10^3 Å^2) for $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Gd(1)	1941(1)	771(1)	2238(1)	19(1)
Mn(1)	−2189(2)	1444(2)	2408(2)	18(1)
C(1)	−707(12)	948(11)	2490(9)	18(4)
N(1)	128(11)	668(11)	2440(9)	32(4)
C(2)	−2610(17)	1388(16)	1298(15)	51(6)
N(2)	−2667(17)	1375(15)	692(14)	76(7)
C(3)	−3701(15)	1844(13)	2274(11)	30(5)
N(3)	−4628(13)	1995(12)	2215(10)	45(5)
C(4)	−2637(13)	−32(12)	2404(10)	16(4)
N(4)	−2862(12)	−921(12)	2410(9)	44(5)
C(5)	−1778(11)	2916(10)	2489(8)	4(3)
N(5)	−1643(11)	3845(10)	2602(8)	26(4)
C(6)	−1762(13)	1560(12)	3499(11)	22(4)
N(6)	−1503(15)	1745(14)	4122(12)	60(5)
O(11)	2033(11)	1766(11)	3298(8)	51(4)
C(11)	1930(5)	2460(4)	3460(2)	220(2)
C(12)	2918(19)	3160(3)	4570(2)	180(18)
C(13)	1080(2)	3740(2)	4104(19)	130(13)
N(11)	1859(13)	2990(13)	4084(10)	50(5)
O(12)	3449(11)	224(10)	3248(8)	42(4)
C(21)	4408(19)	101(15)	3374(12)	61(7)
C(22)	4622(19)	−1168(17)	4354(13)	74(8)
C(23)	6187(14)	−730(2)	4048(18)	109(10)
N(12)	5073(11)	−564(11)	3916(9)	38(4)
O(13)	1040(11)	2284(10)	1666(8)	47(4)
C(31)	185(15)	2786(11)	1487(9)	31(5)
C(32)	−951(13)	4278(16)	885(12)	55(6)
C(33)	789(17)	3895(19)	719(13)	80(9)
N(13)	6(11)	3677(10)	1052(8)	33(4)
O(14)	3094(9)	−16(9)	1647(7)	34(3)
C(41)	3388(12)	−881(15)	1554(9)	33(5)
C(42)	4544(18)	−217(15)	897(12)	60(7)
C(43)	4388(17)	−2094(12)	1063(12)	53(6)
N(14)	4113(11)	−1057(10)	1178(8)	36(4)
O(21)	866(10)	349(9)	990(7)	36(3)
O(22)	3243(12)	2057(11)	2157(9)	61(4)
O(23)	−1062(10)	3692(9)	4963(7)	36(3)

Variable-temperature magnetic susceptibilities (4.2−300 K) were measured with a vibrating sample magnetometer. All data were corrected for diamagnetism of the constituent atoms with Pascal's constants.

Synthesis of $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$

$K_3[Mn(CN)_6]$ was prepared according to a published report [16]. Hydrated Gd(III) nitrates were prepared by general methods. All the other starting materials were used without purification. Since $K_3[Mn(CN)_6]$ has a tendency to hydrolyze on heating, the synthesis was carried out at room temperature and the crystals grown in refrigerator. To a DMF solution of $Gd(NO_3)_3 \cdot 6H_2O$ was added an equimolar amount of $K_3[Mn(CN)_6]$ in a minimum amount of water. The resulting mixture was kept undisturbed in a refrigerator. After about one week, well-shaped light brown crystals were obtained; there were suitable for X-ray diffraction analysis. *Anal.*, Calc. For $C_{18}H_{34}N_{10}O_7GdMn$ (%): C, 30.55; H, 4.76; N, 19.59. Found: C, 30.34; H, 4.50; N, 18.92.

X-ray Crystallography

Data from a light brown crystal of dimensions 0.20 × 0.20 × 0.10 mm for GdMn was collected using graphite-monochromated MoKα radiation on a Siemens P4 four-circle diffractometer. Some 4039 intensity data, of which 3197 were unique collected by the ω-2θ scan mode. The structure was solved by direct methods and 2044 intensity reflections with $I \geq 2\sigma(I)$ were used in the refinements. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. The final R and Rw values were 0.075 and 0.126, respectively. All calculations were performed on a 586PC computer using SHELXS-90 and SHELXL-97. A summary of crystallographic data and additional data collection parameters is given in Table I. Final atomic coordinates are listed in Table II.

RESULTS AND DISCUSSION

IR Spectrum

The IR spectrum of the complex indicates that there exist some hydrogen bonds in the solid state. At $3000 \sim 3700\,cm^{-1}$, a broad band with a peak value at $3421\,cm^{-1}$ assigned to be the vibration of H—O is found. A strong peak at $2123\,cm^{-1}$ and a shoulder peak at $2140\,cm^{-1}$ is assigned to the stretch of CN. The characteristic CN absorption shows a red shift compared with the IR spectrum of $K_3[Mn(CN)_6]$, which indicates the formation of a cyano bridge. A strong peak at $1653\,cm^{-1}$ and a shoulder at $1672\,cm^{-1}$ is due to the C—O stretch of the coordinated DMF molecules.

Description of Structure

Table II shows the atomic coordinates and equivalent isotropic displacement parameters for the title complex. The Gd atom is eight coordinated by six oxygen atoms from four DMF molecules and two water molecules, and two nitrogen atoms from the two bridging CN ligands. The Gd—N bond distances are 2.516(16) Å (Gd—N1) and 2.522(13) Å (Gd—N5), respectively. Distances between Gd and the O atoms from H_2O molecules range from 2.393(12) to 2.401(15) Å, and from 2.335(13) to 2.382(14) Å between Gd and O atoms from DMF molecules. The bond angles consisting of the bridging CN and Gd (C1—N1—Gd and C5—N5—Gd) are 159.1(13)0°, 163.6(12)°, respectively. The bond angle N1—Gd—N5 is 76.10(5)°. Table III shows selected bond lengths and angles for GdMn.

The geometry of the $Mn(CN)_6^{3-}$ ion is approximately octahedral with the coordination of six CN ligands. Bond distances (Mn—C) range from

TABLE III Selected bond lengths (Å) and bond angles (°) for the complex

Gd(1)—O(13)	2.335(13)	Mn(1)—C(5)	1.945(13)
Gd(1)—O(11)	2.364(16)	Mn(1)—C(3)	1.963(19)
Gd(1)—O(12)	2.353(12)	Mn(1)—C(4)	1.971(16)
Gd(1)—O(14)	2.382(14)	Mn(1)—C(6)	1.98(2)
Gd(1)—O(22)	2.401(15)	Mn(1)—C(1)	1.984(16)
Gd(1)—O(21)	2.393(12)	Mn(1)—C(2)	2.01(3)
Gd(1)—N(1)	2.516(16)	N(5)—Gd(1)#2	2.522(13)
Gd(1)—N(5)#1	2.522(13)		
O(13)—Gd(1)—O(11)	80.3(5)	C(1)—Mn(1)—C(2)	89.3(8)
O(13)—Gd(1)—O(12)	141.4(4)	N(1)—C(1)—Mn(1)	171.2(16)
O(11)—Gd(1)—O(12)	70.4(5)	C(1)—N(1)—Gd(1)	159.1(13)
O(13)—Gd(1)—O(14)	115.0(5)	N(2)—C(2)—Mn(1)	169(2)
O(11)—Gd(1)—O(14)	140.9(5)	N(3)—C(3)—Mn(1)	173.9(16)
O(12)—Gd(1)—O(14)	77.4(5)	N(4)—C(4)—Mn(1)	177.4(14)
O(13)—Gd(1)—O(22)	70.0(5)	N(5)—C(5)—Mn(1)	169.2(14)
O(11)—Gd(1)—O(22)	81.6(6)	C(5)—N(5)—Gd(1)#2	163.6(12)
O(12)—Gd(1)—O(22)	81.1(5)	N(6)—C(6)—Mn(1)	172.4(16)
O(14)—Gd(1)—O(22)	71.8(5)	C(11)—O(11)—Gd(1)	143(3)
O(13)—Gd(1)—O(21)	71.5(4)	C(21)—O(12)—Gd(1)	136.9(16)
O(11)—Gd(1)—O(21)	145.5(5)	C(31)—O(13)—Gd(1)	145.9(13)
O(12)—Gd(1)—O(21)	143.4(4)	C(41)—O(14)—Gd(1)	137.7(13)
O(14)—Gd(1)—O(21)	71.4(4)	O(13)—Gd(1)—N(5)#1	142.2(4)
O(22)—Gd(1)—O(21)	106.1(5)	O(11)—Gd(1)—N(5)#1	112.7(5)
O(13)—Gd(1)—N(1)	76.5(5)	O(12)—Gd(1)—N(5)#1	74.4(4)
O(11)—Gd(1)—N(1)	71.2(5)	O(14)—Gd(1)—N(5)#1	78.1(5)
O(12)—Gd(1)—N(1)	115.1(5)	O(22)—Gd(1)—N(5)#1	144.6(5)
O(14)—Gd(1)—N(1)	145.3(4)	O(21)—Gd(1)—N(5)#1	80.8(4)
O(22)—Gd(1)—N(1)	139.7(5)	N(1)—Gd(1)—N(5)#1	75.0(5)
O(21)—Gd(1)—N(1)	82.9(5)	C(5)—Mn(1)—C(3)	89.7(6)
C(3)—Mn(1)—C(1)	175.6(7)	C(5)—Mn(1)—C(4)	175.1(8)
C(4)—Mn(1)—C(1)	88.5(6)	C(3)—Mn(1)—C(4)	88.1(7)
C(6)—Mn(1)—C(1)	91.0(7)	C(5)—Mn(1)—C(6)	82.6(6)
C(5)—Mn(1)—C(2)	95.1(7)	C(3)—Mn(1)—C(6)	91.9(8)
C(3)—Mn(1)—C(2)	87.9(9)	C(4)—Mn(1)—C(6)	93.1(7)
C(4)—Mn(1)—C(2)	89.3(8)	C(5)—Mn(1)—C(1)	93.9(6)
C(6)—Mn(1)—C(2)	177.7(7)		

Symmetry transformations used to generate equivalent at #1: $-x, y-1/2, -z+1/2$; #2: $-x, y+1/2, -z+1/2$.

1.945(13) to 2.01(3) Å, and Mnl—C1 and Mnl—C5 (bridging) are 1.984(16) Å and 1.945(13) Å, respectively. The two cyano-bridges lead to distortion of the bond angle C1—Mnl—C5 (93.9(6)°). Mn—C—N bond

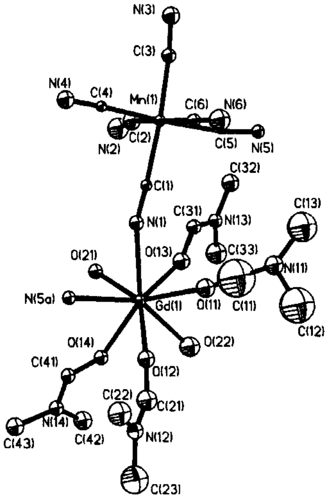

FIGURE 1 Molecular structure of $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$.

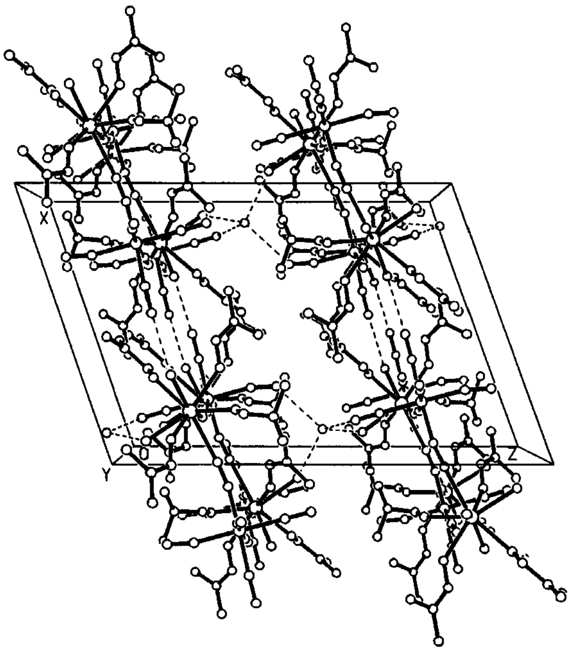

FIGURE 2 Molecular packing of $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$.

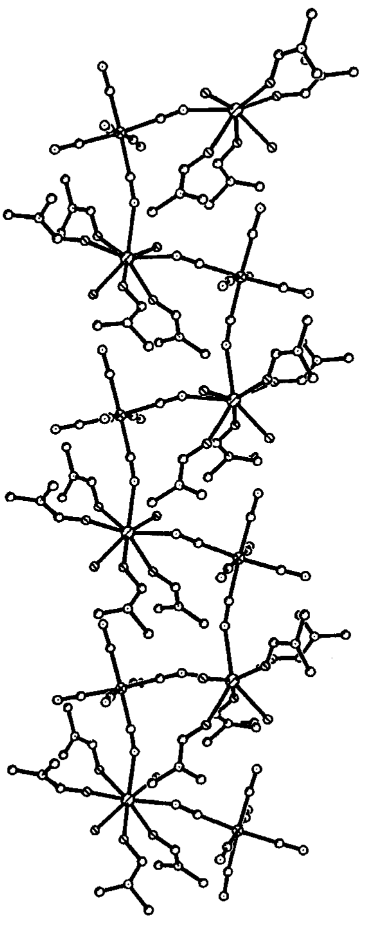

FIGURE 3 One-dimensional structure of $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$.

angles range from 169(2)° to 174.4(14)° and C—N bond distances range from 1.141(9) to 1.162(9) Å. Although both the Mn—C and C≡N distances vary, they are considered normal. Mn—C—N bond angles do not significantly deviate from 180°. However, the bridging CN ligand is coordinated to the Gd atom in a bent mode, which may be due to the steric effects involving coordinated DMF molecules around the Sm atom.

There exist two types of hydrogen bonding; one is intermolecular hydrogen bonding between the coordinated water molecule of one complex unit and the CN of another complex unit. Another is the intramolecular hydrogen bonding involving the uncoordinated water molecule. The O atom of the uncoordinated water molecule forms a hydrogen bond with the H atom of a coordinated water molecule, while the H atom of the

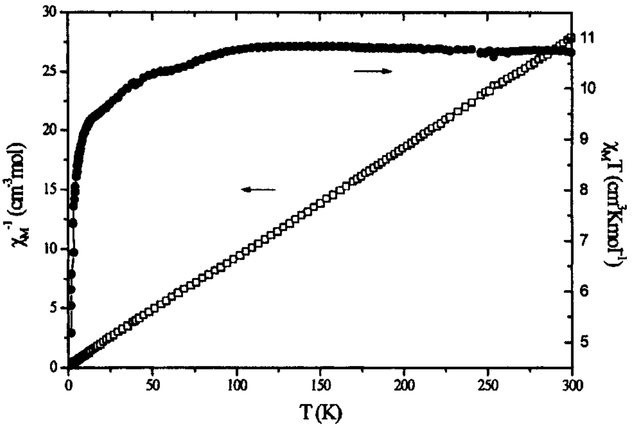

FIGURE 4 Variable-temperature magnetic susceptibility of $[Gd(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$ (1.5 ~ 300 K).

uncoordinated water molecule forms another hydrogen bond with the bridging CN. Because there exist two approximately perpendicular CN bridges between Mn and Gd atoms, a one-dimensional chain structure, —Mn—C1N1—Gd—N5C5—Mn—C1N1—Gd—, is formed, which seems akin to the β-folding of protein molecules (illustrated in Fig. 3). The one-dimensional chain structure is significantly different from other lanthanide heterocyanometallates which consist of only one CN bridge.

Magnetic Properties

The variable temperature magnetic susceptibility (1.5–300 K) of the complex (as shown in Fig. 4) has been determined, in the form of χ_M^{-1} and $\chi_M T$ *vs.* T plots, where χ_M is the magnetic susceptibility per mol of complex unit and T is the absolute temperature. Susceptibility (1.5 K ~ 300 K) was measured by a SQUID magnetometer under an applied magnetic field of 1.0 T (Fig. 4). The inverse plot is nearly a straight line, corresponding to the Curie-Weiss law. The constants C (the spin-only value) and θ for the complex have been obtained based on the Curie-Weiss law $\chi_M = C/(T - \theta)$. The negative θ constant suggests an antiferromagnetic interaction between metal ions Gd^{III} and Mn^{III} ($S = 1/2$).

Supplimentary Material

H atom positions, anisotropic thermal parameters and lists of observed and calculated structures are available from the authors on request.

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