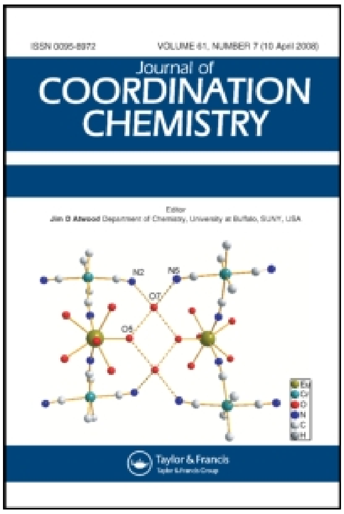

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Synthesis, Crystal Structures and Magnetic Properties of Ion-Pair Complexes with Hydrogen Bonding Network: $Ln(DMA)_n(H_2O)_m Cr(CN)_6 \cdot xH_2O$($Ln$ = Sm, Gd: n = 4, m = 3, x = 2; Ln = Er: N = 3, m = 4, x = 0)

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SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF ION-PAIR COMPLEXES WITH HYDROGEN BONDING NETWORK: $\mathbf{Ln(DMA)_n(H_2O)_m\ Cr(CN)_6 \cdot xH_2O}$ ($\mathbf{Ln = Sm, Gd: n = 4, m = 3, x = 2; Ln = Er: n = 3, m = 4, x = 0}$)

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Three ion-pair Ln–Cr complexes $[Sm(DMA)_4(H_2O)_3][Cr(CN)_6] \cdot 2H_2O$, $[Gd(DMA)_3(H_2O)_4][Cr(CN)_6] \cdot 2H_2O$ and $[Er(DMA)_3(H_2O)_4][Cr(CN)_6]$ (DMA = dimethylacetamide) have been synthesized. X-ray structure analyses of the title complexes revealed that there is a hydrogen-bonding network through CN groups and H_2O molecules. Variable temperature magnetic susceptibilities indicate weak antiferromagnetic interactions between cation and anion pairs moderated through the hydrogen bonding network.

Keywords: Ion-pair complexes; Hydrogen bonding network; Crystal structures; Magnetic properties; Lanthanide compounds

INTRODUCTION

In recent years, much research work has been carried out on molecular-based magnets [1–7], which have great advantages over traditional magnetic alloys (small volume, low density, varied structure, easy recombination,

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processing and shaping). However, it is rather difficult to design and synthesize target molecular-based magnets. In order to keep the magnetic domain parallel in the crystal lattice, the first step is molecular engineering, i.e., to prepare molecules with the highest possible spin multiplicity in chain-like or layer-like structure. The second step is crystal engineering, i.e., to assemble a macroscopic three-dimensional system by means of ferromagnetic coupling. There are several ways to achieve crystal magnetic engineering; one is direct assembly from chemical reaction [8], another is to assemble the magnetic molecules through hydrogen bonding or organic ligands [9,10]. In the present work, using dimethylacetamide (DMA) as a ligand, three ion-pair complexes with a hydrogen bonding network were synthesized, $Sm(DMA)_4(H_2O)_3][Cr(CN)_6]\cdot 2H_2O$, $[Gd(DMA)_3(H_2O)_4][Cr(CN)_6]\cdot 2H_2O$ and $[Er(DMA)_3(H_2O)_4][Cr(CN)_6]$. Their detailed crystal structures and magnetochemical properties are reported below.

EXPERIMENTAL

Synthesis of $Ln(DMA)_n(H_2O)_mCr(CN)_6\cdot xH_2O$

To a solution of $Ln(NO_3)_3\cdot 6H_2O$ (0.222 g (Sm), 0.226 g (Gd), 0.232 g (Er), 0.5 mmol) containing dimethylacetamide (2 cm^3), $K_3[Cr(CN)_6]$ (0.164 g, 0.5 mmol) in a minimum amount of water was slowly added with stirring. The resulting solution was filtered and the filtrate allowed to stand at room temperature in the dark. After two days, well-shaped, light-yellow, single crystals were obtained. Anal. Calcd. for $C_{22}H_{46}CrSmN_{10}O_9$ (SmCr%): C, 33.12, H, 5.77; N, 17.57. Found: C, 33.44; H, 5.61; N, 17.88. For $C_{22}H_{46}CrGdN_{10}O_9$(GdCr): C, 32.84; H, 5.72; N, 17.41. Found: C, 33.41; H, 5.49; N, 17.75%. For $C_{18}H_{35}CrErN_9O_7$ (ErCr): C, 30.48; H, 4.94; N, 17.78. Found: C, 30.40; H, 4.71; N, 17.93%. IR spectra exhibit a complicated pattern of bands in the range 4000–400 cm^{-1}. For SmCr: 2133 cm^{-1} (m), 2113 cm^{-1} (s), 1672 cm^{-1} (m), 1651 cm^{-1} (s); for GdCr: 2129 cm^{-1} (m), 2114 cm^{-1} (s), 1670 cm^{-1} (m), 1654 cm^{-1} (s); for ErCr: 2129 cm^{-1} (m), 2114 cm^{-1} (s), 1670 cm^{-1} (m), 1654 cm^{-1} (s), which are ascribed to $\nu_{C\text{–}N}$ and $\nu_{C\text{–}OO}$, respectively.

X-ray Crystallography

Diffraction data for a crystal with dimensions 0.30 × 0.20 × 0.15 mm (SmCr), 0.35 × 0.30 × 0.30 mm (GdCr) 0.50 × 0.30 × 0.25 mm (ErCr) were obtained with graphite-monochromated Mo$K\alpha$ radiation on a Enraf-Nonius CAD4 four-circle diffractometer, and were collected by the ω-2θ scan technique. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [11,12]. A summary of crystallographic data and refinement parameters is given in Table I. Additional materials are available from the Cambridge Crystallographic Data Center (No. CCDC-146016, 146017, and 146018) comprising complete lists of atomic coordinates, equivalent isotropic displacement parameters and full lists of bond lengths and angles.

TABLE I Crystal data and structure refinement details for the complexes

Complex	*SmCr*	*GdCr*	*ErCr*
Empirical formula	$C_{22}H_{46}CrSmN_{10}O_9$	$C_{22}H_{46}CrGdN_{10}O_9$	$C_{18}H_{35}CrErN_9O_7$
Formula weight	797.04	803.94	708.81
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	*Pbca*	*Pc*
Unit cell dimensions	$a = 16.2892(15)$ Å $b = 19.6680(18)$ Å $c = 22.520(2)$ Å	$a = 16.285(3)$ Å $b = 19.596(4)$ Å $c = 22.527(5)$ Å	$a = 9.789(2)$ Å $b = 11.263(2)$ Å $c = 13.997(3)$ Å $\beta = 105.66(3)°$
Volume	7215.0(11) Å^3	7189(3) Å^3	1485.9(5) Å^3
Z	8	8	2
Calculated density	1.468 Mg/m^3	1.468 Mg/m^3	1.584 Mg/m^3
Absorption coefficient	1.968 mm^{-1}	2.187 mm^{-1}	3.219 mm^{-1}
$F(000)$	3248	3264	708
Crystal size	0.30 × 0.20 × 0.15 mm	0.35 × 0.30 × 0.30 mm	0.50 × 0.30 × 0.25 mm
θ range for data collection	1.86 to 25.03°	2.08 to 24.97°	2.82 to 25.02°
Reflections collected	28672	5939	2531
Reflections unique	6382	5939	2531
R(int)	0.0369	0.0000	0.0000
Completeness to 2θ	25.03 91.2%	24.97 85.9%	25.02 93.2%
Absorption correction	SADABS	Psi Scans	DIFABS
Goodness-of-fit on F^2	1.023	1.213	0.969
Final R indices	$R1 = 0.033$	$R1 = 0.073$	$R1 = 0.033$
For $[I > 2\sigma(I)]$	$wR2 = 0.096$	$wR2 = 0.183$	$wR2 = 0.085$
Largest diff. peak and hole	0.710 and −0.727 e/Å^{-3}	1.856 and −2.108 e/Å^{-3}	1.984 and −1.285 e/Å^{-3}

Physical Measurements

Elemental analyses (C, H, N) were carried out on a Elementar Cario EL instrument. Infrared spectroscopy using KBr pellets was performed on a Nicolet 7199B spectrophotometer in the range 4000–400 cm^{-1}. Variable-temperature magnetic susceptibilities (1.8 ~ 300 K) were measured with a MagLab-2000 magnetometer, all data being corrected for diamagnetism of all the constituent atoms with Pascal's constants.

RESULTS AND DISCUSSION

Description of the Crystal Structures

Final atomic coordinates for non-hydrogen atoms are listed in Tables II–IV. Complexes SmCr and GdCr are isomorphous. Figure 1 shows the coordination geometry and atom labelling in the crystal structure of SmCr. X-ray diffraction crystal structure analysis reveals that it consists of the ion pairs $[Sm(DMA)_4(H_2O)_3]^{3+}$ and distorted octahedral $[Cr(CN)_6]^{3-}$. In the cation $[Sm(DMA)_4(H_2O)_3]^{3+}$, the Sm atom is coordinated by seven oxygen atoms from four DMA molecules (O(11), O(21), O(31) and O(41)) and three H_2O molecules (O(1), O(2) and O(3)). The coordination polyhedron can be described as a slightly distorted pentagonal bipyramid, in which the two apices are O(31) and O(41). Selected bond distances and bond angles for SmCr and GdCr are listed in Tables V and VI. It is worth pointing out that there is a little distinction between the SmCr and GdCr complexes; one DMA molecule coordinated to Sm atom has two conformations, where the only difference is that, besides the coordinated oxygen atoms of acetamide group of DMA, the other atoms rotate 180° around the O(31)–Sm axis; this does not exist in the GdCr complex.

Figure 2 shows the coordination geometry of $[Er(DMA)_3(H_2O)_4]^{3+}$ and distorted octahedral $[Cr(CN)_6]^{3-}$. In $[Er(DMA)_3(H_2O)_4]^{3+}$, the Er atom has seven coordinated oxygen atoms from three DMA molecules (O(11), O(21) and O(31)) and three aqua ligands (O(1), O(2) and O(3)). The coordination polyhedron can be also described as a slightly distorted pentagonal bipyramid, of which the two apices are the oxygen atoms of two DMA molecules, O(21) and O(31). The Er atom has only three coordinated DMA molecules, which is probably due to the fact the ionic radius of Er^{3+} is shorter than those of Sm^{3+} and Gd^{3+}. Selected bond lengths and angles for the ErCr complex are listed in Table VII.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for SmCr. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Sm(1)	8736(1)	736(1)	6760(1)	29(1)
Cr(1)	7105(1)	1907(1)	4021(1)	28(1)
C(1)	7904(3)	1323(3)	4519(2)	35(1)
N(1)	8308(3)	980(3)	4807(2)	53(1)
C(2)	6174(3)	1315(3)	4388(2)	39(1)
N(2)	5674(3)	972(3)	4584(2)	58(1)
C(3)	7065(3)	2596(3)	4725(2)	40(1)
N(3)	7077(3)	2964(3)	5124(2)	58(1)
C(4)	8067(3)	2439(2)	3613(2)	35(1)
N(4)	8598(3)	2692(2)	3359(2)	49(1)
C(5)	7203(3)	1218(3)	3328(2)	37(1)
N(5)	7272(4)	855(2)	2935(2)	59(1)
C(6)	6232(3)	2424(3)	3511(2)	38(1)
N(6)	5750(3)	2667(3)	3207(2)	52(1)
O(1)	9420(2)	1644(2)	7311(2)	48(1)
O(2)	7879(3)	−268(2)	6862(2)	61(1)
O(3)	8518(2)	189(2)	5798(2)	46(1)
O(11)	9520(3)	1317(2)	6085(2)	52(1)
C(11)	9757(3)	1531(3)	5588(2)	49(1)
C(12)	10267(4)	1069(4)	5190(3)	65(2)
N(11)	9572(3)	2139(3)	5407(2)	54(1)
C(13)	9067(5)	2584(3)	5783(2)	69(2)
C(14)	9806(5)	2389(4)	4807(3)	80(2)
O(21)	8243(2)	755(2)	7724(2)	48(1)
C(21)	7692(6)	732(3)	8117(4)	80(3)
C(22)	6774(5)	765(4)	7877(5)	99(3)
N(21)	7848(8)	700(3)	8665(3)	124(4)
C(23)	8741(8)	703(5)	8845(5)	108(4)
C(24)	7138(9)	647(5)	9099(5)	163(6)
O(31)	7645(3)	1427(2)	6535(2)	56(1)
C(31)	6954(10)	1666(6)	6441(6)	45(3)
C(31′)	7119(17)	1950(2)	6646(11)	47(6)
C(32)	6308(6)	1291(5)	6056(5)	115(4)
N(31)	6754(9)	2266(5)	6687(4)	50(2)
N(31′)	6418(16)	1900(2)	6471(13)	80(8)
C(33)	5917(5)	2561(5)	6576(4)	102(3)
C(34)	7394(5)	2602(4)	7027(3)	78(2)
O(41)	9780(3)	12(2)	7003(2)	58(1)
C(41)	10169(3)	−540(3)	7053(3)	51(1)
C(42)	10466(5)	−911(4)	6507(3)	79(2)
N(41)	10337(3)	−793(3)	7569(2)	58(1)
C(43)	10038(7)	−422(6)	8106(3)	111(4)
C(44)	10802(5)	−1432(4)	7660(4)	81(2)
O(4)	7406(3)	−888(2)	5805(2)	54(1)
O(5)	9064(3)	330(2)	10396(2)	71(1)

Figure 3 shows the packing for the complex SmCr. The hydrogen bonding network involves O–H···N interactions between the aqua ligands in $[Sm(DMA)_4(H_2O)_3]^{3+}$ and the CN group of $[Cr(CN)_6]^{3-}$, and between the two crystal H_2O molecules and the aqua ligands as well as the CN group

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for GdCr. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x/a	y/b	z/c	$U(eq)$
Gd(1)	8736(1)	736(1)	6762(1)	21(1)
Cr(1)	7110(1)	1910(1)	4023(1)	19(1)
C(1)	7897(5)	1325(5)	4517(3)	25(2)
N(1)	8322(7)	982(5)	4808(4)	47(2)
C(2)	6174(5)	1324(5)	4392(4)	26(2)
N(2)	5663(6)	977(6)	4582(4)	49(2)
C(3)	7073(6)	2603(6)	4725(4)	36(2)
N(3)	7078(6)	2957(5)	5129(3)	45(2)
C(4)	8062(6)	2447(5)	3619(3)	26(2)
N(4)	8616(6)	2701(5)	3361(4)	44(2)
C(5)	7212(6)	1203(5)	3331(4)	28(2)
N(5)	7278(8)	869(5)	2936(3)	51(3)
C(6)	6234(6)	2424(6)	3511(4)	32(2)
N(6)	5752(6)	2677(3)	3213(3)	43(2)
O(1)	9429(5)	1624(4)	7307(2)	42(2)
O(2)	7900(7)	−243(4)	6865(3)	55(3)
O(3)	8516(5)	190(4)	5805(2)	40(2)
O(11)	9515(4)	1314(4)	6098(2)	39(2)
C(11)	9762(5)	1508(5)	5596(3)	41(3)
C(12)	10296(7)	1058(7)	5215(5)	60(4)
N(11)	9562(6)	2163(5)	5406(3)	49(3)
C(13)	9087(7)	2596(7)	5791(5)	55(3)
C(14)	9823(8)	2379(8)	4815(4)	59(4)
O(21)	8258(5)	758(4)	7717(2)	39(2)
C(21)	7649(7)	740(6)	8088(5)	63(4)
C(22)	6772(8)	754(10)	7872(8)	95(6)
N(21)	7886(10)	681(6)	8691(5)	123(9)
C(23)	8746(12)	742(10)	8852(9)	102(8)
C(24)	7185(14)	597(12)	9095(8)	150(12)
O(31)	7668(5)	1413(5)	6542(3)	51(2)
C(31)	6957(7)	1657(6)	6441(5)	70(4)
C(32)	6320(11)	1294(13)	6067(8)	129(10)
N(31)	6747(6)	2298(6)	6685(4)	75(4)
C(33)	5906(9)	2531(12)	6593(7)	98(7)
C(34)	7393(9)	2616(8)	7022(6)	70(4)
O(41)	9759(5)	36(4)	6995(3)	48(2)
C(41)	10165(6)	−514(5)	7029(3)	45(3)
C(42)	10453(9)	−904(8)	6498(5)	62(4)
N(41)	10340(7)	−799(4)	7582(4)	50(3)
C(43)	10014(12)	−427(12)	8091(6)	112(8)
C(44)	10810(9)	−1425(7)	7654(7)	75(4)
O(4)	7412(5)	−875(4)	5812(3)	43(2)
O(5)	9035(5)	345(5)	10402(4)	58(2)

of $[Cr(CN)_6]^{3-}$ (O···H···O and O···H···N). Among the three coordinated H_2O molecules, O(1) and O(2) each forms a pair of hydrogen bonds with adjacent cyano groups (N(2)(#1), N(6)(#2)), and (N(2)(#1), N(3)(#3)), while O(3) forms hydrogen bonds with H_2O molecules (O(4),

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for ErCr. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Er(1)	4933	8025(1)	336	23(1)
Cr(1)	−87(7)	2786(1)	338(5)	22(1)
O(1)	6076(18)	6456(15)	1266(14)	30(4)
O(2)	3850(2)	6287(17)	−548(13)	40(5)
O(3)	7040(3)	8593(19)	1504(19)	52(5)
O(4)	2990(3)	8774(18)	−823(16)	48(6)
O(11)	4960(4)	10004(7)	440(2)	47(3)
N(11)	4910(4)	11923(12)	640(2)	98(16)
C(11)	5017(17)	10995(11)	−12(12)	68(7)
C(12)	5090(4)	11030(3)	−1084(16)	108(12)
C(13)	5030(10)	13150(2)	420(4)	270(4)
C(14)	5060(5)	11680(3)	1660(2)	128(17)
O(21)	3663(18)	7842(15)	1415(12)	40(5)
N(21)	2050(2)	6968(12)	2059(13)	56(5)
C(21)	2518(18)	8001(12)	1700(12)	47(4)
C(22)	1780(4)	9200(3)	1730(3)	96(13)
C(23)	780(5)	6730(6)	2330(6)	130(2)
C(24)	2940(5)	5950(2)	2110(3)	114(18)
O(31)	6230(2)	7920(18)	−724(16)	58(7)
N(31)	8231(18)	7740(2)	−1194(15)	90(7)
C(31)	7019(19)	7182(16)	−1066(13)	69(6)
C(32)	6750(6)	5913(19)	−1460(3)	115(19)
C(33)	8500(5)	8910(3)	−800(3)	114(18)
C(34)	9270(4)	7200(4)	−1590(3)	82(10)
C(1)	1120(2)	4070(2)	−80(2)	43(9)
N(1)	1830(3)	4760(3)	−280(3)	77(10)
C(2)	970(4)	1490(3)	−210(3)	73(12)
N(2)	1550(2)	777(15)	−555(14)	36(5)
C(3)	−1182(18)	1502(13)	889(13)	15(4)
N(3)	−1760(3)	760(2)	1170(2)	80(10)
C(4)	−1260(3)	4080(2)	780(2)	45(9)
N(4)	−1940(3)	4830(2)	960(2)	74(11)
C(5)	−1500(2)	2817(18)	−1051(11)	18(5)
N(5)	−2290(2)	2863(17)	−1819(12)	30(5)
C(6)	1360(3)	2780(3)	1681(16)	47(8)
N(6)	2120(4)	2800(4)	2445(18)	80(11)

O(5)#4)). One cyano group (C(2)N(2)) forms two hydrogen bonds, while all others form only one hydrogen bond. The hydrogen bonding distance O···H···N is in the range 2.688–2.911 Å (SmCr) and 2.723–2.927 Å (GdCr), while the distance O···H···O is shorter and falls in the range 2.785–2.790 Å (SmCr), 2.735–2.791 Å (GdCr) (as shown in Table VIII).

Figure 4 shows the packing ErCr, which is similar to that of the previous two complexes. This complex exhibits only hydrogen bonding between

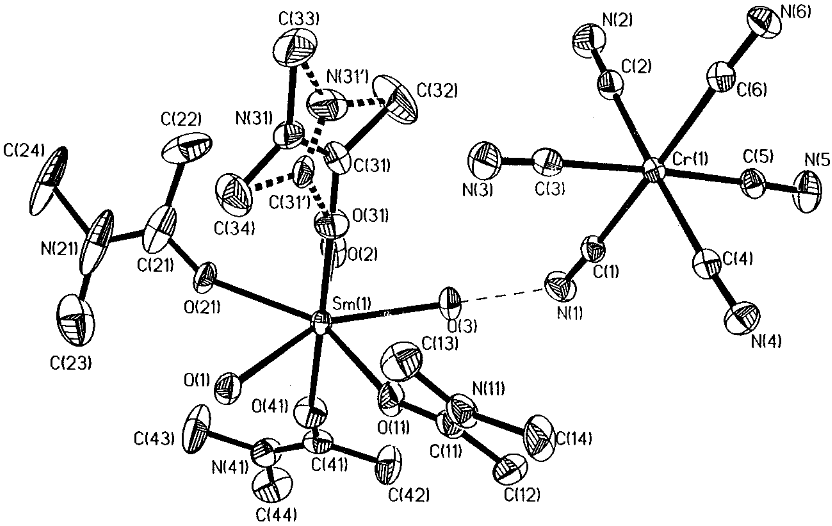

FIGURE 1 Crystal structure of the complex SmCr; the complex GdCr shows a very similar structure.

TABLE V Bond lengths (Å) and angles (°) for SmCr

Sm(1)–O(41)	2.285(4)	O(41)–Sm(1)–O(11)	93.10(15)	O(21)–Sm(1)–O(3)	142.00(13)
Sm(1)–O(11)	2.292(3)	O(41)–Sm(1)–O(31)	177.33(16)	O(2)–Sm(1)–O(3)	69.10(12)
Sm(1)–O(31)	2.292(4)	O(11)–Sm(1)–O(31)	89.44(15)	O(1)–Sm(1)–O(3)	146.89(12)
Sm(1)–O(21)	2.314(3)	O(41)–Sm(1)–O(21)	92.48(15)	C(1)–Cr(1)–C(5)	89.8(2)
Sm(1)–O(2)	2.430(4)	O(11)–Sm(1)–O(21)	143.84(13)	C(1)–Cr(1)–C(2)	86.1(2)
Sm(1)–O(1)	2.444(3)	O(31)–Sm(1)–O(21)	85.94(15)	C(5)–Cr(1)–C(2)	89.4(2)
Sm(1)–O(3)	2.445(3)	O(41)–Sm(1)–O(2)	84.17(16)	C(1)–Cr(1)–C(3)	88.18(19)
Cr(1)–C(1)	2.067(5)	O(11)–Sm(1)–O(2)	142.10(13)	C(5)–Cr(1)–C(3)	177.3(2)
Cr(1)–C(5)	2.072(5)	O(31)–Sm(1)–O(2)	93.32(16)	C(2)–Cr(1)–C(3)	92.2(2)
Cr(1)–C(2)	2.083(5)	O(21)–Sm(1)–O(2)	74.04(13)	C(1)–Cr(1)–C(6)	175.1(2)
Cr(1)–C(3)	2.086(5)	O(41)–Sm(1)–O(1)	89.64(15)	C(5)–Cr(1)–C(6)	87.6(2)
Cr(1)–C(6)	2.091(5)	O(11)–Sm(1)–O(1)	73.59(12)	C(2)–Cr(1)–C(6)	89.7(2)
Cr(1)–C(4)	2.097(5)	O(31)–Sm(1)–O(1)	91.87(14)	C(3)–Cr(1)–C(6)	94.6(2)
		O(21)–Sm(1)–O(1)	70.74(12)	C(1)–Cr(1)–C(4)	92.53(19)
		O(2)–Sm(1)–O(1)	143.90(12)	C(5)–Cr(1)–C(4)	86.49(19)
		O(41)–Sm(1)–O(3)	92.65(14)	C(2)–Cr(1)–C(4)	175.70(19)
		O(11)–Sm(1)–O(3)	73.30(12)	C(3)–Cr(1)–C(4)	91.82(19)
		O(31)–Sm(1)–O(3)	87.29(14)	C(6)–Cr(1)–C(4)	91.43(19)

the aqua ligands and the cyano groups of $[Cr(CN)_6]^{3-}$. Among the four coordinated H_2O molecules, both O(1) and O(3) each form two hydrogen bonds with adjacent cyano groups N(4)(#1), N(5)(#2), and N(3)(#3), N(5)(#2), while O(2) and O(4) form only one hydrogen bond to N(1) and

TABLE VI Bond lengths (Å) and angles (°) for GdCr

Gd(1)–O(41)	2.222(7)	O(41)–Gd(1)–O(31)	177.7(3)	O(21)–Gd(1)–O(3)	142.3(3)
Gd(1)–O(31)	2.242(8)	O(41)–Gd(1)–O(11)	92.5(3)	O(2)–Gd(1)–O(3)	69.2(2)
Gd(1)–O(11)	2.265(6)	O(31)–Gd(1)–O(11)	89.6(3)	O(1)–Gd(1)–O(3)	146.9(2)
Gd(1)–O(21)	2.288(5)	O(41)–Gd(1)–O(21)	92.6(3)	C(1)–Cr(1)–C(2)	86.1(4)
Gd(1)–O(2)	2.363(8)	O(31)–Gd(1)–O(21)	86.2(3)	C(1)–Cr(1)–C(4)	93.2(3)
Gd(1)–O(1)	2.409(7)	O(11)–Gd(1)–O(21)	143.4(3)	C(2)–Cr(1)–C(4)	176.5(4)
Gd(1)–O(3)	2.434(6)	O(41)–Gd(1)–O(2)	84.7(3)	C(1)–Cr(1)–C(3)	88.3(4)
Cr(1)–C(1)	2.048(9)	O(31)–Gd(1)–O(2)	93.2(3)	C(2)–Cr(1)–C(3)	92.0(4)
Cr(1)–C(2)	2.082(9)	O(11)–Gd(1)–O(2)	142.4(2)	C(4)–Cr(1)–C(3)	91.3(4)
Cr(1)–C(4)	2.083(9)	O(21)–Gd(1)–O(2)	74.2(2)	C(1)–Cr(1)–C(5)	89.1(4)
Cr(1)–C(3)	2.086(10)	O(41)–Gd(1)–O(1)	88.5(3)	C(2)–Cr(1)–C(5)	89.4(4)
Cr(1)–C(5)	2.091(10)	O(31)–Gd(1)–O(1)	92.8(3)	C(4)–Cr(1)–C(5)	87.2(3)
Cr(1)–C(6)	2.093(10)	O(11)–Gd(1)–O(1)	73.3(2)	C(3)–Cr(1)–C(5)	177.0(4)
		O(21)–Gd(1)–O(1)	70.6(2)	C(1)–Cr(1)–C(6)	174.4(4)
		O(2)–Gd(1)–O(1)	143.7(2)	C(2)–Cr(1)–C(6)	89.2(4)
		O(41)–Gd(1)–O(3)	92.7(3)	C(4)–Cr(1)–C(6)	91.3(4)
		O(31)–Gd(1)–O(3)	87.2(3)	C(3)–Cr(1)–C(6)	94.8(4)
		O(11)–Gd(1)–O(3)	73.6(2)	C(5)–Cr(1)–C(6)	87.9(4)

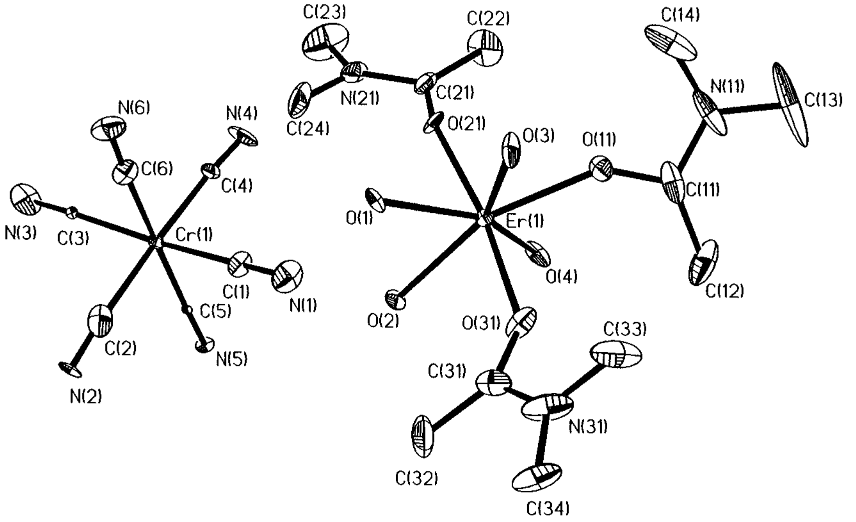

FIGURE 2 Crystal structure of the complex ErCr.

N(2)(#4). One cyano group (C(5)N(5)) forms two hydrogen bonds, while the others form only one. The O···H···N distance is in the range of 2.716 Å and 2.830 Å (Table VIII).

TABLE VII Bond lengths (Å) and angles (°) for ErCr

Er(1)–O(31)	2.204(19)	O(31)–Er(1)–O(21)	171.5(4)	O(1)–Er(1)–O(2)	75.3(3)
Er(1)–O(21)	2.209(13)	O(31)–Er(1)–O(11)	95.7(10)	O(4)–Er(1)–O(2)	76.6(7)
Er(1)–O(11)	2.234(9)	O(21)–Er(1)–O(11)	92.7(10)	O(3)–Er(1)–O(2)	139.8(8)
Er(1)–O(1)	2.299(18)	O(31)–Er(1)–O(1)	93.3(7)	C(6)–Cr(1)–C(1)	87.3(13)
Er(1)–O(4)	2.30(2)	O(21)–Er(1)–O(1)	79.6(6)	C(6)–Cr(1)–C(4)	91.8(12)
Er(1)–O(3)	2.35(2)	O(11)–Er(1)–O(1)	137.2(9)	C(1)–Cr(1)–C(4)	89.9(5)
Er(1)–O(2)	2.405(17)	O(31)–Er(1)–O(4)	93.6(9)	C(6)–Cr(1)–C(2)	92.5(15)
Cr(1)–C(6)	2.027(13)	O(21)–Er(1)–O(4)	90.4(8)	C(1)–Cr(1)–C(2)	90.5(15)
Cr(1)–C(1)	2.046(11)	O(11)–Er(1)–O(4)	71.0(10)	C(4)–Cr(1)–C(2)	175.7(14)
Cr(1)–C(4)	2.050(11)	O(1)–Er(1)–O(4)	149.8(7)	C(6)–Cr(1)–C(5)	177.9(17)
Cr(1)–C(2)	2.057(12)	O(31)–Er(1)–O(3)	85.8(9)	C(1)–Cr(1)–C(5)	90.8(10)
Cr(1)–C(5)	2.061(10)	O(21)–Er(1)–O(3)	95.7(9)	C(4)–Cr(1)–C(5)	89.1(10)
Cr(1)–C(3)	2.069(9)	O(11)–Er(1)–O(3)	71.9(10)	C(2)–Cr(1)–C(5)	86.6(13)
		O(1)–Er(1)–O(3)	67.3(7)	C(6)–Cr(1)–C(3)	87.4(12)
		O(4)–Er(1)–O(3)	142.6(4)	C(1)–Cr(1)–C(3)	174.6(10)
		O(31)–Er(1)–O(2)	82.3(8)	C(4)–Cr(1)–C(3)	89.7(11)
		O(21)–Er(1)–O(2)	91.3(7)	C(2)–Cr(1)–C(3)	90.2(8)
		O(11)–Er(1)–O(2)	147.4(10)	C(5)–Cr(1)–C(3)	94.5(9)

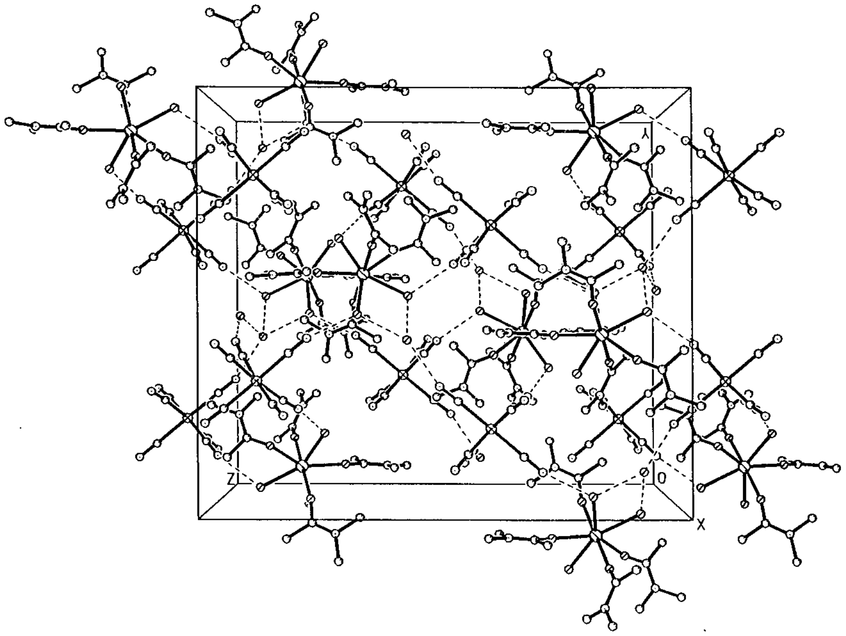

FIGURE 3 Packing view of the unit cell for the complex SmCr; the complex GdCr shows a very similar unit cell.

TABLE VIII Possible hydrogen bonds for the title complexes

SmCr				*GdCr*				*ErCr*		
O1				O1				O1		
Sml	2.444			Gdl	2.409			N4(#1)	2.784	
N6(#1)	2.807	119.6		N6(#1)	2.809	120.0		N5(#2)	2.830	94.8
O2				O2				O2		
Sml	2.429			Gdl	2.363			Erl	2.405	
N5(#2)	2.688	119.2		N5(#2)	2.723	120.9		N1	2.716	132.9
O4	2.785	115.7	123.7	O4	2.791	116.2	121.5			
O3				O3				O3		
Sml	2.445			Gdl	2.434			N3(#3)	2.800	
N1	2.741	119.3		N1	2.749	119.5		N5(#2)	2.792	129.5
O4	2.787	115.1	110.8	O4	2.787	115.1	110.8			
O4				O4				O4		
N3(#3)	2.856			N3(#3)	2.880			Erl	2.300	
O5(#4)	2.790	112.8		O5(#4)	2.735	111.7		N2(#4)	2.742	124.3
O5				O5						
N2(#5)	2.911			N2(#5)	2.927					
symmetry operations: #1 = $0.5+x,\ 0.5-y,\ 1-z$ #2 = $1.5-x,\ -y,\ 0.5+z$ #3 = $1.5-x,\ -0.5+y,\ z$ #4 = $1.5-x,\ -y,\ -0.5+z$ #5 = $0.5+x,\ y,\ 1.5-z$				symmetry operations: #1 = $0.5+x,\ 0.5-y,\ 1-z$ #2 = $1.5-x,\ -y,\ 0.5+z$ #3 = $1.5-x,\ -0.5+y,\ z$ #4 = $1.5-x,\ -y,\ -0.5+z$ #5 = $0.5+x,\ y,\ 1.5-z$				symmetry operations: #1 = $1+x,\ y,\ z$ #2 = $1+x,\ 1-y,\ 0.5+z$ #3 = $1+x,\ 1+y,\ z$ #4 = $x,\ 1+y,\ z$		

Magnetic Properties

Variable temperature susceptibilities (1.8 K – 300 K) for the three complexes were measured by a MagLab-2000 magnetometer under the applied magnetic field of 10000 Oe (Figs. 5, 6, and 7). In the $\chi_m^{-1}$and χ_mT vs. T plots, χ_m is the magnetic susceptibility per mol of complex unit molecule and T is the absolute temperature. Plots of inverse magnetic susceptibility vs. temperature for the complexes are nearly straight lines, corresponding to the Curie–Weiss law. The Curie–Weiss constants, C (the spin only value) and θ, of these complexes have been obtained based on the expression $\chi_m = (C/(T-\theta))$, and are $5.41\,cm^3\,K\,mol^{-1}$ and -3.22 K (SmCr): $28.40\,cm^3\,K\,mol^{-1}$ and -9.35 K (GdCr); $4.55\,cm^3\,K\,mol^{-1}$ and -18.08 K (ErCr), respectively. The negative Curie–Weiss constants for the three complexes suggest an antiferromagnetic interaction between lanthanide ions Ln^{III} (Sm^{III} ($S=2$), Gd^{III} ($S=7/2$) and Er^{III} ($S=3/2$)) and Cr^{III} ($S=3/2$) through the hydrogen-bonding in the system.

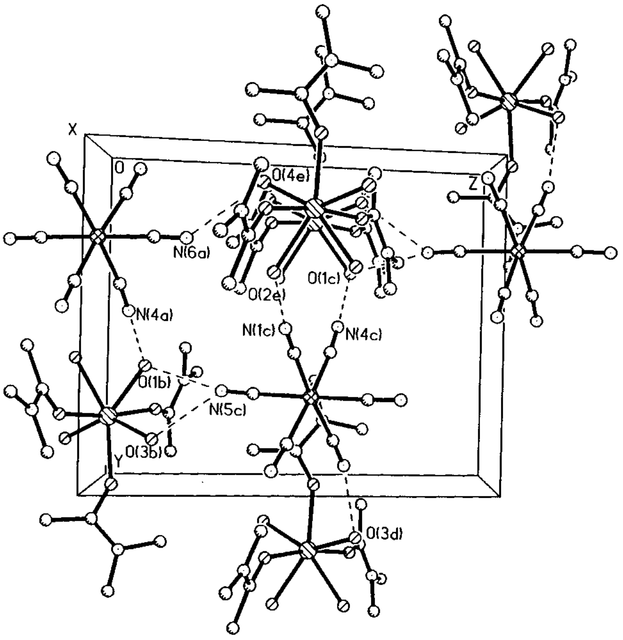

FIGURE 4 Packing view of the unit cell for the complex ErCr.

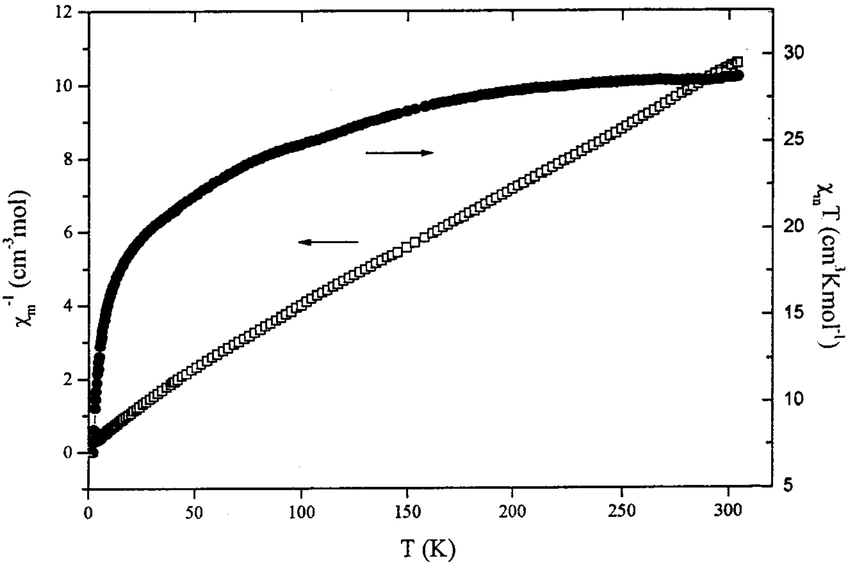

FIGURE 5 Variable-temperature susceptibility of the complex SmCr (1.8 – 300 K).

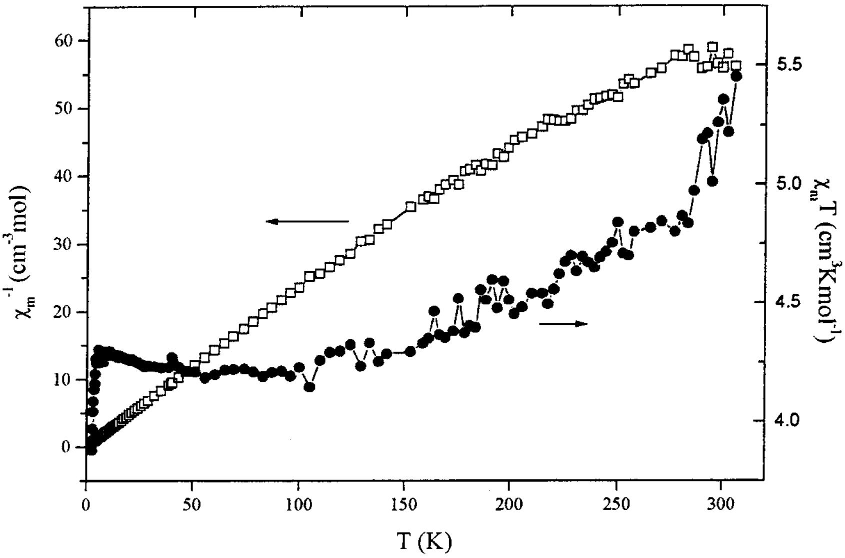

FIGURE 6 Variable-temperature susceptibility of the complex GdCr (1.8 – 300 K).

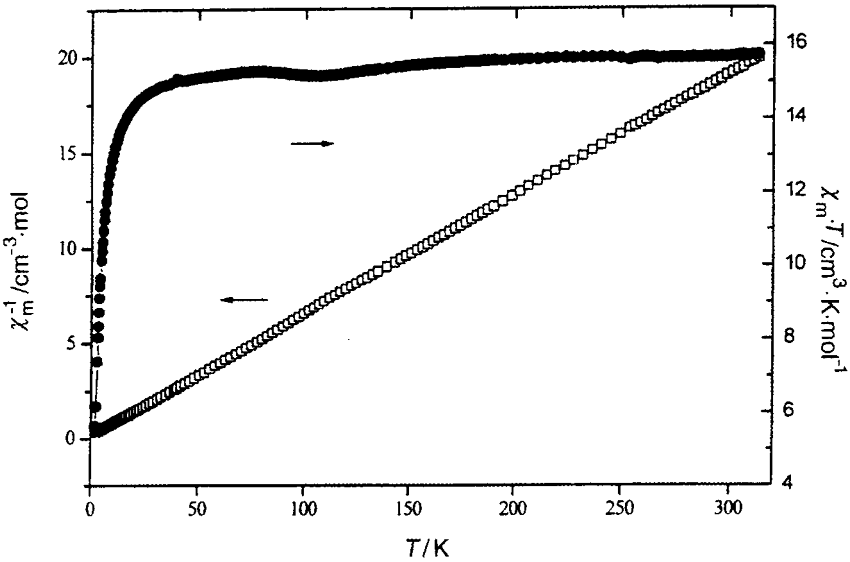

FIGURE 7 Variable-temperature susceptibility of the complex ErCr (1.8 – 300 K).

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