Hydrogen-Bonded Ion-Pair Complexes [Ln(DMA)$_4$(H$_2$O)$_3$][Cr(CN)$_6$] ·2H$_2$O (Ln = Sm, Gd; DMA = N,N-Dimethylacetamide): Crystal Structures and Magnetic Properties

[a,b]B. YAN, [a,c]S. X. WANG, and [a,b]Z. D. CHEN*

[a]*State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering,*
Peking University, Beijing, 100871, China
e-mail: zdchen@pku.edu.cn

[b]*Peking University—Hong Kong University Joint Laboratory of Rare Earth Material and Bioinorganic Chemistry,*
Beijing, 100871, China

[c]*Department of Chemistry, Jining Teachers College, Jining, 272125, China*

Two novel ion-pair complexes: [Ln(DMA)$_4$(H$_2$O)$_3$][Cr(CN)$_6$]·2H$_2$O (Ln = Sm, Gd; DMA = dimethylacetamide) have been synthesized. X-Ray crystal diffraction analyses reveal that these two complexes form hydrogen-bonded structure through CN group and H$_2$O molecules. Variable temperature susceptibility for the GdCr complex indicates the weak antiferromagnetic interactions between cation and anion pairs through a hydrogen-bonded network.

In recent years, a great number of research works have been reported on the molecular-based magnets [1—7], which have great advantages over the traditional alloy magnets, such as small volume, low density, variable structure, and good recombination, processing, and shaping. However, it is rather difficult to design and synthesize target molecular-based magnets. In order to keep the magnetic domain parallel range in the whole lattice, the first step is a molecular magnetic engineering, *i.e.* to prepare molecules with one-dimensional chain-like and two-dimensional layer-like structures and with the spin multiplicity as high as possible. The second step of the designed synthesis is crystal magnetic engineering, *i.e.* to assemble macroscopic three-dimensional crystals by means of ferromagnetic coupling. So far there are some ways to achieve the crystal magnetic engineering: one way is to obtain the molecule from the chemical reaction, without reassembling [8]; another way is to assemble the magnetic molecules by means of hydrogen bond or organic ligands [9, 10].

In the present work, using dimethylacetamide (DMA) as the hybrid ligand, two novel ion-pair complexes with the hydrogen bond network were synthesized: [Sm(DMA)$_4$(H$_2$O)$_3$][Cr(CN)$_6$]·2H$_2$O (SmCr) and [Gd(DMA)$_4$(H$_2$O)$_3$][Cr(CN)$_6$]·2H$_2$O (GdCr). The detailed crystal structures and magnetic properties for the two complexes were reported.

Complexes SmCr and GdCr crystallize in orthorhombic space group Pbca. Fig. 1 shows the crystal structure of the title complex SmCr. Crystal structures are isostructural. Unit cell X-ray diffraction crystal structure analysis reveals that unit cell of the two complex units consists of the ion pairs [Sm(DMA)$_4$(H$_2$O)$_3$]$^{3+}$ (or [Gd(DMA)$_4$(H$_2$O)$_3$]$^{3+}$) and [Cr(CN)$_6$]$^{3-}$. In the anion [Cr(CN)$_6$]$^{3-}$, Cr atom has six CN coordinations and belongs to a distorted octahedron configuration (Fig. 1). The distance of Cr—C is in the range of 2.067(5)—2.097(5) Å (SmCr) (2.048(9)—2.093(10) Å (GdCr)), and the bond angle of C—Cr—C is near 90° or 180°. In the cation [Sm(DMA)$_4$(H$_2$O)$_3$]$^{3+}$ (or [Gd(DMA)$_4$(H$_2$O)$_3$]$^{3+}$), Sm (or Gd) atom has seven coordinated oxygen atoms from four DMA molecules (O(11), O(21), O(31), and O(41)) and three H$_2$O molecules (O(1), O(2), and O(3)) (Table 2). The coordination polyhedron can be described as a distorted pentagonal bipyramid (Fig. 2). The two apices are the two-coordinated oxygen atoms of DMA molecules, O(31) and O(41). The symmetry mirror plane is a pentagon composed of O(1), O(11), O(3), O(2), and O(21). Sm (or Gd) atom, three H$_2$O and two DMA groups lie in the mirror plane. The bond lengths between the apices oxygen atoms and central Sm (or Gd) atom are 2.285(4) Å for Sm(1)—O(31) and 2.290(4) Å for Sm(1)—O(41) (2.242(8) Å for Gd(1)—O(31) and

---

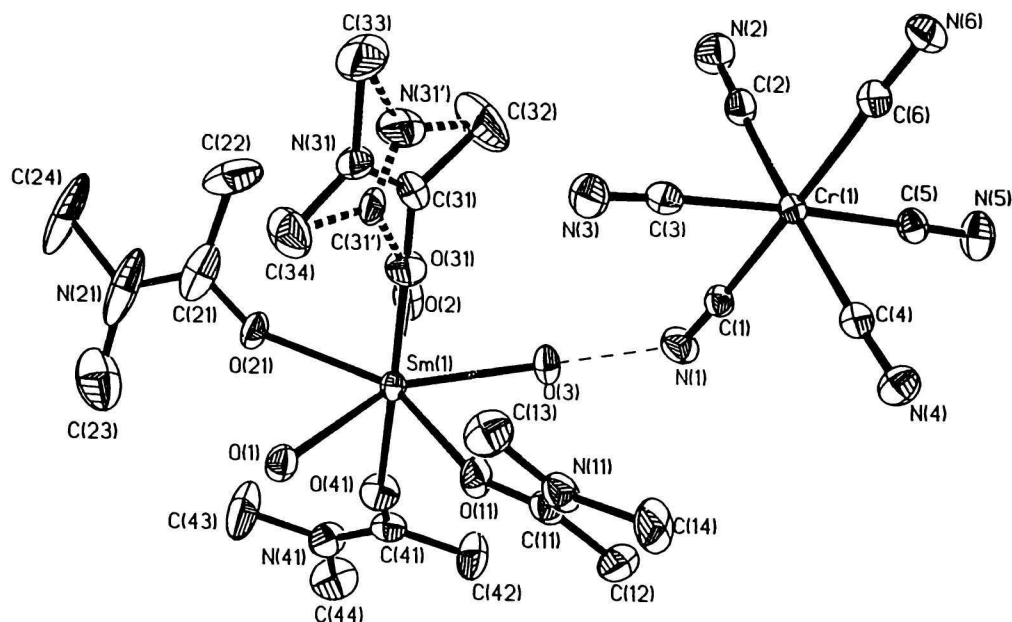*The author to whom the correspondence should be addressed.

Fig. 1. Crystal structure of the complex SmCr (that of GdCr is very similar).

Table 1. Crystallographic and Experimental Data for Title Complexes

Complexes	SmCr	GdCr
Formula	$C_{22}H_{46}CrSmN_{10}O_9$	$C_{22}H_{46}CrGdN_{10}O_9$
Molecular mass	797.04	803.94
Temperature	293(2) K	293(2) K
Wavelength	0.71073 $\mathring{A}$	0.71073 $\mathring{A}$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca
Unit cell dimensions	$a = 16.2892(15)$ $\mathring{A}$	$a = 16.285(3)$ $\mathring{A}$
	$b = 19.6680(18)$ $\mathring{A}$	$b = 19.596(4)$ $\mathring{A}$
	$c = 22.520(2)$ $\mathring{A}$	$c = 22.527(5)$ $\mathring{A}$
Volume	7215.0(11) $\mathring{A}^3$	7189(3) $\mathring{A}^3$
Z	8	8
Calculated density	1.468 Mg m^{-3}	1.486 Mg m^{-3}
Absorption coefficient	1.968 mm^{-1}	2.187 mm^{-1}
$F(000)$	3248	3264
Crystal size	0.30 mm × 0.20 mm × 0.15 mm	0.35 mm × 0.30 mm × 0.30 mm
Θ range for data collection	1.86 to 25.03°	2.08 to 24.97°
Reflections collected	28672	5939
Reflections unique	6382	5939
$R(int)$	0.0369	0.0000
Absorption correction	Sadabs	Psi
Max. and min. transmission	0.96 and 0.73	0.996 and 0.579
Refinement method	Full-matrix	Least-squares on F^2
Data/restraints/parameters	6382/0/406	5939/20/389
Goodness-of-fit on F^2	1.023	1.213
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0332$, $wR2 = 0.0956$	$R1 = 0.0733$, $wR2 = 0.1827$
Largest diff. peak and hole	0.710 and -0.727 e $\mathring{A}^{-3}$	1.856 and -2.108 e $\mathring{A}^{-3}$

2.222(7) $\mathring{A}$ for Gd(1)—O(41)), respectively (Table 3). The distances between Sm (or Gd) atom and coordinated H_2O molecules, Sm—O (and Gd—O), are within 2.429(4)—2.445(3) $\mathring{A}$ (and 2.363(8)—2.434(6) $\mathring{A}$); while it is 2.285(4)—2.314(3) $\mathring{A}$ (and 2.222(7)—2.288(5) $\mathring{A}$) for the distance between Sm (or Gd) and coordinated O atoms of DMA. The angles be-

tween the apices O atoms, O(31), O(41), and the symmetry mirror plane are in the range 85.98(15)—93.37(16)°, 84.15(16)—93.10(15)° for SmCr complex (and 86.2(3)—93.2(3)°, 84.7(3)—92.7(3)° for GdCr complex). It is worth pointing out a little distinction between SmCr and GdCr complexes: one of the DMA molecules coordinated to Sm atom has two kinds of

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$ $\text{\AA}^2$) for SmCr and GdCr Complexes

Atoms	x	y	z	U(eq)	Atoms	x	y	z	U(eq)
Gd(1)	8736(1)	736(1)	6762(1)	21(1)	Sm(1)	8736(1)	736(1)	6760(1)	29(1)
Cr(1)	7110(1)	1910(1)	4023(1)	19(1)	Cr(1)	7105(1)	1907(1)	4021(1)	28(1)
C(1)	7897(5)	1325(5)	4517(3)	25(2)	C(1)	7904(3)	1323(3)	4519(2)	35(1)
N(1)	8322(7)	982(5)	4808(4)	47(2)	N(1)	8308(3)	980(3)	4807(2)	53(1)
C(2)	6174(5)	1324(5)	4392(4)	26(2)	C(2)	6174(3)	1315(3)	4388(2)	39(1)
N(2)	5663(6)	977(6)	4582(4)	49(2)	N(2)	5674(3)	972(3)	4584(2)	58(1)
C(3)	7073(6)	2603(6)	4725(4)	36(2)	C(3)	7065(3)	2596(3)	4725(2)	40(1)
N(3)	7078(6)	2957(5)	5129(3)	45(2)	N(3)	7077(3)	2964(3)	5124(2)	58(1)
C(4)	8062(6)	2447(5)	3619(3)	26(2)	C(4)	8067(3)	2439(2)	3613(2)	35(1)
N(4)	8616(6)	2701(5)	3361(4)	44(2)	N(4)	8598(3)	2692(2)	3359(2)	49(1)
C(5)	7212(6)	1203(5)	3331(4)	28(2)	C(5)	7203(3)	1218(3)	3328(2)	37(1)
N(5)	7278(8)	869(5)	2936(4)	51(3)	N(5)	7272(4)	855(2)	2935(2)	59(1)
C(6)	6234(6)	2424(6)	3511(4)	32(2)	C(6)	6232(3)	2424(3)	3511(2)	38(1)
N(6)	5752(6)	2677(6)	3213(3)	43(2)	N(6)	5750(3)	2667(3)	3207(2)	52(1)
O(1)	9429(5)	1624(4)	7307(2)	42(2)	O(1)	9420(2)	1644(2)	7311(2)	48(1)
O(2)	7900(7)	−243(4)	6865(3)	55(3)	O(2)	7879(3)	−268(2)	6862(2)	61(1)
O(3)	8516(5)	190(4)	5805(2)	40(2)	O(3)	8518(2)	189(2)	5798(2)	46(1)
O(11)	9515(4)	1314(4)	6098(2)	39(2)	O(11)	9520(3)	1317(2)	6085(2)	52(1)
C(11)	9762(5)	1508(5)	5596(3)	41(3)	C(11)	9757(3)	1531(3)	5588(2)	49(1)
C(12)	10296(7)	1058(7)	5215(5)	60(4)	C(12)	10267(4)	1069(4)	5190(3)	65(2)
N(11)	9562(6)	2163(5)	5406(3)	49(3)	N(11)	9572(3)	2139(3)	5407(2)	54(1)
C(13)	9087(7)	2596(7)	5791(5)	55(3)	C(13)	9067(5)	2584(3)	5783(3)	69(2)
C(14)	9823(8)	2379(8)	4815(4)	59(4)	C(14)	9806(5)	2389(4)	4807(3)	80(2)
O(21)	8258(5)	758(4)	7717(2)	39(2)	O(21)	8243(2)	755(2)	7724(2)	48(1)
C(21)	7649(7)	740(6)	8088(5)	63(4)	C(21)	7692(6)	732(3)	8117(4)	80(3)
C(22)	6772(8)	754(10)	7872(8)	95(6)	C(22)	6774(5)	765(4)	7877(5)	99(3)
N(21)	7886(10)	681(6)	8691(5)	123(9)	N(21)	7848(8)	700(3)	8665(3)	124(4)
C(23)	8746(12)	742(10)	8852(9)	102(8)	C(23)	8741(8)	703(5)	8845(5)	108(4)
C(24)	7185(14)	597(12)	9095(8)	150(12)	C(24)	7138(9)	647(5)	9099(5)	163(6)
O(31)	7668(5)	1413(5)	6542(3)	51(2)	O(31)	7645(3)	1427(2)	6535(2)	56(1)
C(31)	6957(7)	1657(6)	6441(5)	70(4)	C(31)	6954(10)	1666(6)	6441(6)	45(3)
C(32)	6320(11)	1294(13)	6067(8)	129(10)	C(31')	7119(17)	1950(2)	6646(11)	47(6)
N(31)	6747(6)	2298(6)	6685(4)	75(4)	C(32)	6308(6)	1291(5)	6056(5)	115(4)
C(33)	5906(9)	2531(12)	6593(7)	98(7)	N(31)	6754(9)	2266(5)	6687(4)	50(2)
C(34)	7393(9)	2616(8)	7022(6)	70(4)	N(31')	6418(16)	1900(2)	6471(13)	80(8)
O(41)	9759(5)	36(4)	6995(4)	48(2)	C(33)	5917(5)	2561(5)	6576(4)	102(3)
C(41)	10165(6)	−514(5)	7029(3)	45(3)	C(34)	7394(5)	2602(4)	7027(3)	78(2)
C(42)	10453(9)	−904(8)	6498(5)	62(4)	O(41)	9780(3)	12(2)	7003(2)	58(1)
N(41)	10340(7)	−799(4)	7582(4)	50(3)	C(41)	10169(3)	−540(3)	7053(3)	51(1)
C(43)	10014(12)	−427(12)	8091(6)	112(8)	C(42)	10466(5)	−911(4)	6507(3)	79(2)
C(44)	10810(9)	−1425(7)	7654(7)	75(4)	N(41)	10337(3)	−793(3)	7569(2)	58(1)
O(4)	7412(5)	−875(4)	5812(3)	43(2)	C(43)	10038(7)	−422(6)	8106(3)	111(4)
O(5)	9035(5)	345(5)	10402(4)	58(2)	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)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

stereo configuration, besides the coordinated oxygen atoms of acetamide group of DMA, the other atoms rotate 180° around the O(31)—Sm axis, while it does not exist in GdCr complex.

Fig. 3 shows the packing view of a unit cell for the complex SmCr. Not only the hydrogen bonding network O···H···N forms between the coordinated H$_2$O molecules in [Sm(DMA)$_4$(H$_2$O)$_3$]$^{3+}$ and the CN group of [Cr(CN)$_6$]$^{3-}$, but also the two crystallized H$_2$O molecules form the hydrogen bond with coordinated H$_2$O molecules and the CN group of [Cr(CN)$_6$]$^{3-}$ (*—O···H···O and O···H···N). Among the three coordinated H$_2$O molecules, both O(1) and O(2) form

two hydrogen bonds with adjacent CN, (N(2)(#1), N(6)(#2)) and (N(2)(#1), N(3)(#3)); while O(3) forms two hydrogen bonds with the two O atoms in the crystal H$_2$O molecules (O(4), O(5)(# 4)). One CN (C(2)N(2)) forms two hydrogen bonds, while the other CN groups form one hydrogen bond. The distance of these hydrogen bonds, —O—H···N is in the range 2.688—2.911 $\text{\AA}$ (SmCr) and 2.723—2.927 $\text{\AA}$ (GdCr), while the distance of O···H···O is shorter, 2.785—2.790 $\text{\AA}$ (SmCr), 2.735—2.791 $\text{\AA}$ (GdCr) (see Table 4).

The variable temperature susceptibility (1.8 K—300 K) for the GdCr complex was measured by a MagLab-2000 magnetometer under the applied mag-
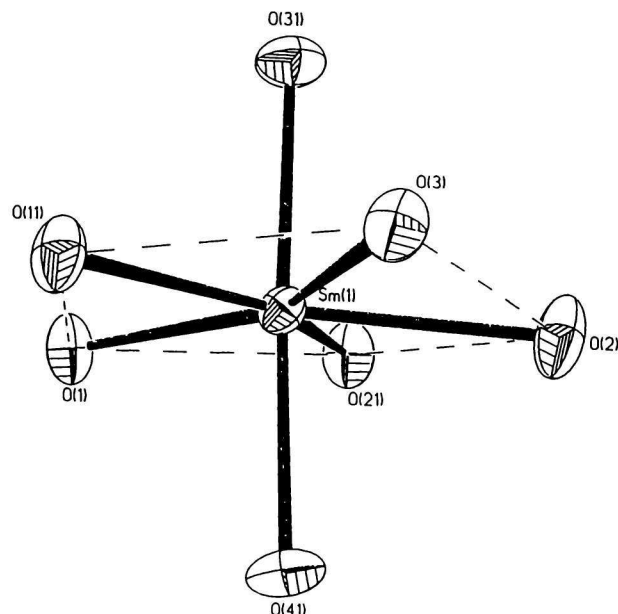
Fig. 2. Coordination polyhedron for Sm atom (Gd atom shows a very similar geometry).

netic field of 800 kA m^{-1} (see Fig. 4). In the form of χ_m^{-1} and $\chi_m T$ *vs.* T plots, χ_m is the magnetic susceptibility per mole and T is the absolute temperature. For lanthanides the spin-orbit coupling is definitely important, but Gd^{III} ion has $4f^7$ configuration and the magnetic contribution can be regarded as spin only, Gd^{III} is considered to follow the Curie law. The plot of inverse magnetic susceptibility *vs.* temperature for the complex is nearly a straight line, corresponding to the Curie—Weiss law. The measured signal of the plot is a superposition of two curves of Gd^{III} ion and Cr^{III} ion, and the whole χ value can be considered as the composition of χ of Gd^{III} ion and χ of Cr^{III} ion. The Curie and Weiss constants, C (the only spin value) and θ of these complexes have been obtained based on the Curie—Weiss law $\chi_m = (C/(T - \Theta))$, and the detailed data are 28.40 cm^3 K mol^{-1} and -9.35 K, respectively. The negative Weiss constant for GdCr complex suggests an antiferromagnetic interaction between Gd^{III} ($S = 7/2$) and Cr^{III} ($S = 3/2$) through the hydrogen-bonding effect in the complex systems.
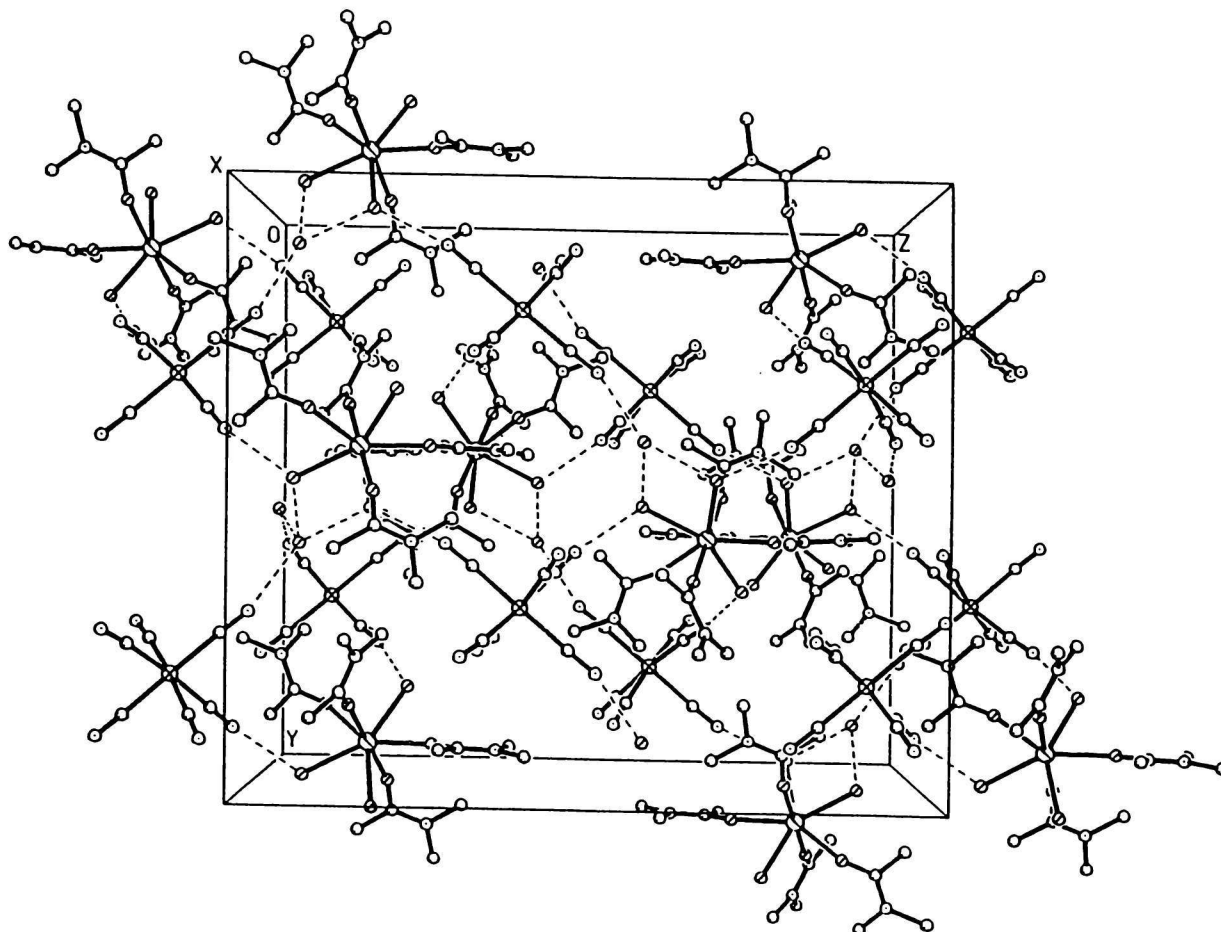

Fig. 3. Packing view of the unit cell for the complex SmCr (the GdCr complex shows a very similar unit cell).
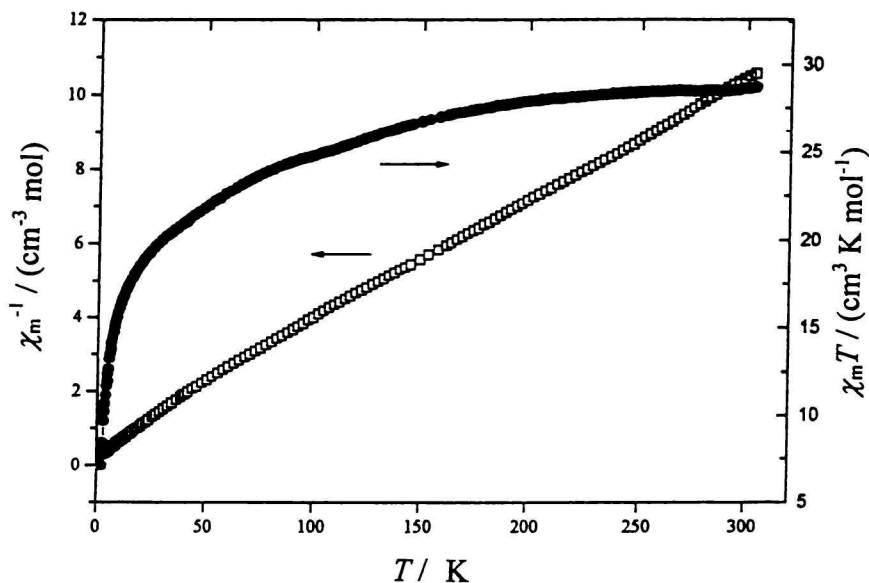
Fig. 4. Variable temperature molar susceptibility of the GdCr complex (1.8—300 K).

Table 3. Selected Bond Lengths for [Ln(DMA)$_4$(H$_2$O)$_3$]-[Cr(CN)$_6$]·2H$_2$O

	SmCr Bond lengths/Å	GdCr Bond lengths/Å
Ln(1)—O(41)	2.285(4)	2.222(7)
Ln(1)—O(11)	2.292(3)	2.265(6)
Ln(1)—O(31)	2.290(4)	2.242(8)
Ln(1)—O(21)	2.314(3)	2.288(5)
Ln(1)—O(2)	2.429(4)	2.363(8)
Ln(1)—O(1)	2.444(3)	2.409(7)
Ln(1)—O(3)	2.445(3)	2.434(6)
Cr(1)—C(1)	2.067(5)	2.048(9)
Cr(1)—C(5)	2.072(5)	2.091(10)
Cr(1)—C(2)	2.083(5)	2.082(9)
Cr(1)—C(3)	2.087(5)	2.086(10)
Cr(1)—C(6)	2.091(5)	2.093(10)
Cr(1)—C(4)	2.097(5)	2.083(9)

Symmetry transformations used to generate equivalent atoms; #1 $-x + 5/2$, $-y + 1$, $z + 1/2$; #2 $-x + 5/2$, $-y + 1$, $z - 1/2$.

Table 4. Possible Hydrogen Bonds for the Title Complexes

	SmCr d/Å	SmCr Θ/°	GdCr d/Å	GdCr Θ/°
O(1)···Ln(1)	2.444		2.409	
O(1)···N(6)(#1)	2.807		2.809	
O(1)—Ln(1)—N(6)(#1)		119.6		120.0
O(2)···Ln(1)	2.429		2.363	
O(2)···N(5)(#2)	2.688		2.723	
O(2)···Ln(1)···N(5)(#2)		119.2		120.9
O(2)···O(4)	2.785		2.791	
O(2)···Ln(1)—O(4)		115.7		116.2
O(2)···N(5)(#2)···O(4)		123.7		121.5
O(3)—Ln(1)	2.445		2.434	
O(3)—N(1)	2.741		2.749	
O(3)—Ln(1)—N(1)		119.3		119.5
O(3)···O(4)	2.787		2.787	
O(3)···Ln(1)···O(4)		115.1		115.1
O(3)···N(5)(#2)···O(4)		110.8		110.8
O(4)···N(3)(#3)	2.856		2.880	
O(4)···O(5)(#4)	2.790		2.735	
O(4)···N(3)(#3)···O(5)(#4)		112.8		111.7
O(5)···N(2)(#5)	2.911		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, $1.5 - z$.

EXPERIMENTAL

For C$_{22}$H$_{46}$CrSmN$_{10}$O$_9$ (SmCr) w_i(calc.): 33.12 % C, 5.77 % H, 17.57 % N; w_i(found): 33.44 % C, 5.61 % H, 17.88 % N. For C$_{22}$H$_{46}$CrGdN$_{10}$O$_9$ (GdCr) w_i(calc.): 32.84 % C, 5.72 % H, 17.41 % N; w_i(found): 33.41 % C, 5.49 % H, 17.75 % N. IR spectra exhibit complicated pattern of bands in the range 400—4000 cm^{-1}. For SmCr $\tilde{\nu}$/cm^{-1}: 2113 (m), 2113 (s) and 1672 (m), 1651 (s); for GdCr $\tilde{\nu}$/cm^{-1}: 2129 (m), 2114 (s) and 1670 (m), 1654 (s), which are ascribed to ν(C—N) and ν(C—OO), respectively.

Elemental analyses (C, H, N) were carried out by the Cario EL Elemental Analyzer. Measurements of infrared spectroscopy on KBr pellets were performed on a Nicolet 7199B spectrophotometer in the $\tilde{\nu}$ range of 400—4000 cm^{-1}. Variable temperature magnetic susceptibilities (1.8—300 K) were carried out with a MagLab-2000 magnetometer, all data were corrected for diamagnetism of all the constituent atoms with Pascal's constants.

Diffraction experiments for a light yellow single crystal for SmCr or GdCr complexes were performed with graphite-monochromated Mo$K\alpha$ radiation on an Enraf—Nonius CAD4 four-circle diffractometer by the ω—2θ scan technique. The structures were solved by direct methods. All nonhydrogen atoms were re-

fined anisotropically by the full-matrix least-squares methods. The hydrogen atoms were added geometrically and were not refined. All calculations were performed on a 586PC computer using SHELXS-97 and SHELXL-97 [12, 13]. A summary of crystallographic data and additional data collection parameters is given in Table 1.

To a dimethylacetamide solution (2 cm^3) of Ln(NO$_3$)$_3 \cdot$6H$_2$O (0.222 g (Sm), 0.226 g (Gd); 0.5 mmol), K$_3$[Cr(CN)$_6$] (0.164 g; 0.5 mmol) in a minimum amount of water was slowly added under stirring. The resulting solution was filtered and the filtrate was allowed to stand at room temperature in dark. After two days, well-shaped light yellow crystals were obtained.

REFERENCES

1. Gatteschi, D., Kahn, O., Miller, J. S., and Palacio, F., *Molecular Magnetic Materials*, p. 198. Kluwer Academic, Dordrecht, the Netherlands, 1991.
2. Sato, O., Iyoda, T., and Hashimoto, K., *Science 271*, 49 (1996).
3. Gadet, C., Mallah, T., Castro, I., and Verdaguer, M., *J. Am. Chem. Soc. 114*, 9213 (1992).
4. Mallah, T., Thiebaut, S., Verdaguer, M., and Veillet, P., *Science 262*, 1554 (1993).
5. Entley, W. R. and Girolami, G. S., *Inorg. Chem. 33*, 5165 (1994).
6. Entley, W. R. and Girolami, G. S., *Science 268*, 397 (1995).
7. Sato, O., Iyoda, T., Fujishima, A., and Hashimoto, K., *Science 272*, 704 (1996).
8. Sun, X. R., Wang, Z. M., Chen, Z. D., Bian, J., Yan, C. H., and Xu, G. X., *Prog. Nat. Sci. 378*, 701 (1999).
9. Gao, E. Q., Tang, J. K., Leng, X. B., Liao, D. Z., Jiang, Z. H., and Yan, S. P., *Chem. J. Chin. Univ. 21*, 663 (2000).
10. Langenberg, K. V., Batten, S. R., and Berry, K. J., *Inorg. Chem. 36*, 5006 (1997).
11. Bigelow, J. H. and Bailar, J. C., *Inorg. Synth. 2*, 203 (1946).
12. Sheldrick, G. M., *Acta Crystallogr., Sect. A 46*, 467 (1990).
13. Sheldrick, G. M., SHELXL-97, a program for the refinement of crystal structures, University of Göttingen, Germany, 1997.