Inorg. Chem. **2003**, *42*, 428–435

Inorganic Chemistry
Article

Synthesis, Crystal Structures, and Magnetic Properties of Three Novel Ferrocenecarboxylato-Bridged Lanthanide Dimers

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Received May 25, 2002

Three novel ferrocenecarboxylato-bridged lanthanide dimers $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]\cdot 2MeOH\cdot 2H_2O$ (**1**) (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$), $[Nd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH\cdot H_2O$ (**2**), and $[Y_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH$ (**3**) have been synthesized and characterized by single-crystal X-ray crystallography. In each complex, two Ln(III) (Ln = Gd, Nd, or Y) ions are bridged by two ferrocenecarboxylate anions as asymmetrically bridging ligands, leading to dimeric cores, $[Ln_2(\mu_2\text{-}OOCFc)_2]$; each Ln(III) ion has an irregular polyhedral coordination environment with nine coordinated oxygen atoms derived from the ferrocenecarboxylate ligands and coordinated solvent molecules. In the solid-state structure of compound **1,** $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ groups are joined together by hydrogen bonds forming a two-dimensional network. Both compounds **2** and **3** show one-dimensional chain structures by hydrogen bonding; they are different from **1**. Magnetic measurements show unexpected ferromagnetic coupling between the gadolinium(III) ions; the best fittings to the experimental magnetic susceptibilities gave $J = 0.006$ cm^{-1} and $g = 2.0$ for **1**. The magnetic behavior for **2** was also studied in the temperature range of 1.8–300 K.

Introduction

It is well-known that carboxylate ligands play an important role in coordination chemistry. They usually adopt binding modes diverse as terminal monodentate, chelating to one metal center, bridging bidentate in a syn-syn, syn-anti, and anti-anti configuration to two metal centers, and bridging tridentate to two metal centers.[1] A large number of lanthanide complexes containing carboxylate ligands have been prepared, and almost all of them are in polymeric forms.[2]

Ferrocenecarboxylic acid and its sodium salt as very important carboxylate derivatives have attracted much interest in coordination chemistry. They have been exploited as multifunctional ligands due to their size and the strong inductive effect of the ferrocene unit from early on.[3] Studies revealed that ferrocenecarboxylate anions also act as terminal monodentate or bidentate ligands or O,O′-bridging ligands. Importantly, depending on the coordination mode of ferrocenecarboxylato ligand to one or more metal cations, a wide variety of interesting compounds containing ferrocene can be obtained since ferrocene-containing complexes may have some unusual properties, for example as components in homogeneous catalysts[4] and potential applications of material sciences such as molecular sensors[5] and molecular magnetic[6] and nonlinear optical materials.[7] Several groups have reported a number of transition metal complexes containing ferrocenecarboxylato ligands,[8] but little is known of lanthanide complexes containing ferrocenecarboxylate to date.

On the other hand, the complexes containing lanthanide metals are of great interest because of their unique physi-

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10.1021/ic025753w CCC: $25.00

cochemical properties.[9−11] In this context, people have reported the magnetic properties of some homobinuclear[12] and heterobinuclear lanthanide complexes,[13] but it is limited unlike those of binuclear transition metal complexes.[14] This may be due partly to the limited number of well-characterized compounds and partly to the difficulty in the precise interpretation of the experimental data in most cases.[15] In this contribution, we explore these types of novel binuclear complexes containing both ferrocene and lanthanide ions. We utilized sodium ferrocenecarboxylate to react with lanthanide ions to afford three novel homobinuclear complexes $[Gd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]\cdot 2MeOH\cdot 2H_2O$ (**1**) (Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)), $[Nd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH\cdot H_2O$ (**2**), and $[Y_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH$ (**3**), characterized their single-crystal structures, and further studied their magnetic properties in the temperature range of 1.8−300 K. The results show unexpected ferromagnetic interaction in the homobinuclear Gd complex.

Experimental Section

General Details. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Sodium ferrocenecarboxylate was prepared according to the literature method.[16]

C, H, and N analyses were carried out on a MOD 1106 analyzer. IR data were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer with KBr pellets in the 400−4000 cm^{-1} region. Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range 1.8−300 K with an applied field of 500 G. All data have been corrected for diamagnetism by using Pascal's constants.[17]

Preparation of $[Gd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]\cdot 2MeOH\cdot 2H_2O$ (1). NaOOCFc (0.0375 g; 0.15 mmol) in MeOH (5 mL) was added dropwise to a methanol solution (4 mL) of $Gd(NO_3)_3\cdot 5H_2O$ (0.0217 g; 0.05 mmol). The result pale yellow solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after several days. Crystals of **1** are unstable in the air. Yield: 68%. Anal. Calcd for $C_{70}H_{78}Fe_6O_{20}Gd_2$: C, 44.51; H, 4.16. Found: C, 45.12; H, 3.98. IR (cm^{-1}, KBr): 3405 m, 1522 s, 1474 s, 1393 m, 1360 s, 1185 m, 1105 m, 1024 m, 816 m, 800 m, 509 m, 490 m.

Preparation of $[Nd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH\cdot H_2O$ (2). The complex **2** was prepared in a manner analogous to that used to prepare **1**. Reaction of $Nd(NO_3)_3\cdot 6H_2O$ with NaOOCFc gave **2** as red single crystals. Crystals of **2** are unstable in the air. Yield: 72%. Anal. Calcd for $C_{68}H_{72}Fe_6O_{19}Nd_2$: C, 44.95; H, 3.99. Found: C, 44.74; H, 3.75. IR (cm^{-1}, KBr): 3411 m, 1524 s, 1468 s, 1359 m, 1184 m, 1105 m, 1024 m, 815 m, 794 m, 509 m, 489 m.

Preparation of $[Y_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH$ (3). The complex **3** was prepared according to the above methods also. Reaction of $Y(NO_3)_3\cdot 6H_2O$ with NaOOCFc produced red single crystals of **3**. Crystals of **3** are unstable in the air. Yield: 66.5%. Anal. Calcd for $C_{68}H_{70}Fe_6O_{18}Y_2$: C, 48.38; H, 4.18. Found: C, 48.11; H, 3.95. IR (cm^{-1}, KBr): 3396 m, 1522 s, 1472 s, 1394 s, 1360 s, 1105 m, 10244 m, 817 m, 802 m, 512 m, 492 m.

X-ray Crystallography. Crystal data and experimental details for compounds **1**−**3** are contained in Table 1. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Red prismatic single crystals of **1** (0.30 × 0.20 × 0.20 mm), of **2** (0.25 × 0.20 × 0.20 mm), and of **3** (0.28 × 0.25 × 0.20 mm) were selected and mounted on a glass fiber. All data were collected

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Table 1. Crystallographic Data

	1	**2**	**3**
formula	$C_{70}H_{78}O_{20}Fe_6Gd_2$	$C_{68}H_{72}O_{19}Fe_6Nd_2$	$C_{34}H_{35}O_9Fe_3Y$
fw	1888.92	1816.84	844.05
cryst system	triclinic	triclinic	triclinic
cryst size (mm)	0.30 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.28 × 0.25 × 0.20
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.019(2)	8.900(2)	8.812(2)
b (Å)	12.122(2)	14.621(3)	15.286(3)
c (Å)	15.297(3)	15.384(3)	15.542(3)
α (deg)	75.46(3)	117.83(3)	117.42(3)
β (deg)	87.25(3)	104.62(3)	91.03(3)
γ (deg)	65.25(3)	91.33(3)	104.92(2)
V (Å^3)	1792.4(6)	1689.5(6)	1772.9(6)
D_c (Mg m^{-3})	1.750	1.786	1.574
Z	1	1	2
μ (mm^{-1})	3.071	2.828	2.874
no. of reflcns	5462	6415	5701
data/restraints/params	5456/0/443	6415/0/434	5701/0/427
R^a	0.1035	0.0568	0.0926
$R_w{}^b$	0.2553	0.1407	0.02551
GOF on F^2	1.061	1.103	1.095
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−2.324 and 3.926	−1.662 and 1.204	−0.858 and 2.176

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**^{a}

Distances

Gd(1)−O(1)	2.390(10)	O(1)−C(1)	1.29(2)
Gd(1)−O(2)	2.504(12)	O(2)−C(1)	1.27(2)
Gd(1)−O(3)	2.438(13)	O(5)−C(23)	1.29 (2)
Gd(1)−O(4)	2.349(12)	O(6)−C(23)	1.29 (2)
Gd(1)−O(4)$^{\#1}$	2.941(13)	O(4)−C(12)	1.33(2)
Gd(1)−O(5)	2.559(11)	O(8)−C(12)$^{\#1}$	1.22(2)
Gd(1)−O(6)	2.394(11)	O(7)−C(34)	1.44(3)
Gd(1)−O(7)	2.439(11)	C(1)−C(2)	1.50(2)
Gd(1)−O(8)	2.417(12)	C(23)−C(24)	1.46(2)
Gd(1)−Gd(1)$^{\#1}$	4.409	C(12)−C(13)	1.41(3)

Angles

O(4)−Gd(1)−O(4)$^{\#1}$	67.5(5)	O(4)−Gd(1)−O(3)	90.3(4)
O(1)−Gd(1)−O(2)	54.0(4)	O(1)−Gd(1)−O(7)	137.8(4)
O(5)−Gd(1)−O(6)	53.4(4)	O(1)−Gd(1)−O(3)	131.5(4)
O(4)$^{\#1}$−Gd(1)−O(8)	47.0(4)	O(4)−Gd(1)−O(5)	150.7(3)
O(2)−Gd(1)−O(5)	118.3(4)	O(4)$^{\#1}$−Gd(1)−O(6)	124.4(5)
Gd(1)−O(4)−Gd(1)$^{\#1}$	112.5(5)	O(3)−Gd(1)−O(7)	79.4(4)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 2, -z + 1$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2^a

Distances

Nd(1)−O(1)	2.514(5)	O(1)−C(11)	1.263(8)
Nd(1)−O(2)	2.465(5)	O(2)−C(11)	1.278(9)
Nd(1)−O(3)	2.675(5)	O(5)−C(33)	1.273(9)
Nd(1)−O(3)$^{\#1}$	2.463(5)	O(6)−C(33)	1.251(8)
Nd(1)−O(4)	2.447(5)	O(4)−C(22)	1.267(9)
Nd(1)−O(5)	2.562(5)	O(3)−C(22)	1.295(8)
Nd(1)−O(6)	2.491(5)	C(10)−C(11)	1.459(9)
Nd(1)−O(7)	2.514(6)	C(32)−C(33)	1.474(9)
Nd(1)−O(8)	2.495(5)	C(21)−C(22)	1.458(9)
Nd(1)−Nd(1)$^{\#1}$	4.210		

Angles

O(3)−Nd(1)−O(3)$^{\#1}$	70.2(2)	O(4)−Nd(1)−O(3)$^{\#1}$	120.7(2)
O(1)−Nd(1)−O(2)	52.4(2)	O(1)−Nd(1)−O(7)	76.5(2)
O(5)−Nd(1)−O(6)	51.1(2)	O(1)−Nd(1)−O(3)	123.5(2)
O(3)−Nd(1)−O(4)	50.9(2)	O(4)−Nd(1)−O(5)	77.3(2)
O(2)−Nd(1)−O(4)	80.2(2)	O(3)$^{\#1}$−Nd(1)−O(6)	155.1(2)
Nd(1)−O(3)−Nd(1)$^{\#1}$	110.0(2)	O(7)−Nd(1)−O(8)	76.2(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z + 1$.

at a temperature of 291(2) K using the $\omega-2\theta$ scan technique and corrected for Lorenz−polarization effects. A correction for secondary extinction was applied.

The three structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5462 observed reflections and 443 variable parameters for **1**, 6415 observed reflections and 434 variable parameters for **2**, and 5701 observed reflections and 427 variable parameters for **3**. All calculations were performed using the SHELX-97 crystallographic software package.[18] Selected bond lengths and bond angles are listed in Tables 2−4. Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 184319, 184320, and 184321 for compounds **1**−**3**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk. www: http://www.ccdc.cam.ac.uk). X-ray CIF files have also been deposited as Supporting Information.

Results and Discussion

Preparation of Complexes. The self-assembly reaction of $Ln(NO_3)_3$ (Ln = Gd, Nd, Y) with sodium ferrocenecarboxylate in the dark is an effective route for preparation of novel rare-earth complexes containing ferrocene. It is well-known that electron-withdrawing substituents on the Cp ring for ferrocenes may provide a greater photolability, and the ferrocenes can undergo photolysis in some solvents to cause both ring−metal and ring−carbonyl cleavages, giving free Fe^{2+} cation and some free radicals.[19] These active intermediates are sensitive to oxygen, water, heat, and light and make the secondary reactions complicated. For example, if the

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Table 4. Selected Bond Distances (Å) and Angles (deg) for **3**[a]

Distances			
Y(1)−O(1)	2.419(9)	O(1)−C(11)	1.314(14)
Y(1)−O(2)	2.634(9)	O(2)−C(11)	1.366(15)
Y(1)−O(3)	2.457(9)	O(5)−C(33)	1.250(14)
Y(1)−O(4)	2.396(9)	O(6)−C(33)	1.35(2)
Y(1)−O(2)$^{\#1}$	2.472(8)	O(3)−C(22)	1.327(15)
Y(1)−O(5)	2.509(9)	O(4)−C(22)	1.304(14)
Y(1)−O(6)	2.500(9)	C(11)−C(10)	1.48(2)
Y(1)−O(7)	2.462(9)	C(33)−C(32)	1.54(2)
Y(1)−O(8)	2.462(9)	C(22)−C(21)	1.44(2)
Y(1)−Y(1)$^{\#1}$	4.205		
Angles			
O(2)−Y(1)−O(2)$^{\#1}$	69.1(3)	O(4)−Y(1)−O(3)	55.0(3)
O(1)−Y(1)−O(2)$^{\#1}$	122.8(3)	O(1)−Y(1)−O(7)	148.9(3)
O(5)−Y(1)−O(6)	52.5(3)	O(1)−Y(1)−O(3)	124.2(3)
O(2)$^{\#1}$−Y(1)−O(5)	155.2(3)	O(4)−Y(1)−O(6)	131.3(3)
O(2)−Y(1)−O(1)	54.0(3)	O(2)$^{\#1}$−Y(1)−O(8)	75.4(3)
Y(1)−O(2)−Y(1)$^{\#1}$	110.9(3)	O(7)−Y(1)−O(8)	74.7(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z + 1$.

mixture of lanthanide ion and ferrocenecarboxylato ligand in methanol solution was placed under light, it could turn from pale yellow to dark-brown solution and then produce a brown precipitate, whose composition cannot be identified. We believe that the ferrocenecarboxylato ligand undergoes photolysis; thus, our target compounds, ferrocene-containing rare earth complexes, could not be obtained.

Most reported lanthanide(III) carboxylates usually show one-dimensional or two-dimensional polymeric structures;[2] there are only several dimeric complexes.[1b,2e,12b,e,f] We obtained three novel lanthanide dimers in our reaction system; this may be due to the structural characterization of ferrocenyl ligands. When six ferrocenecarboxylates coordinate to two Ln(III) ions, the bulky ferrocenyl groups hold the oxygen atoms of carboxylate groups to coordinate to more Ln(III) ions simultaneously. From this point of view, the ferrocenecarboxylate is a useful ligand for the generation of dimeric lanthanide(III) complexes.

All three complexes are unstable, slowly losing their shape in the air. They are not soluble in common organic solvents, such as MeOH, EtOH, MeCN, and THF, but just soluble in highly polar solvents DMSO or DMF. Single crystals suitable for X-ray crystallography for these compounds were collected by slow evaporation of their methanol solutions in the dark.

Crystal Structure of $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]\cdot 2MeOH\cdot 2H_2O$ (1). The structure analysis by X-ray diffraction demonstrates that **1** contains two Gd(III) centers bridged by two ferrocenecarboxylate anions, leading to a dimeric $[Gd_2(\mu_2\text{-}OOCFc)_2]$ core. This molecule crystallizes in the space group $P\bar{1}$. The perspective view of **1** together with the atomic numbering scheme is illustrated in Figure 1.

Each Gd ion is nine-coordinate bonding to two bridging oxygen atoms and five oxygen atoms of four ferrocenecarboxylate units and two oxygen atoms from one coordinate water and one methanol. The Gd−O distances range from 2.349(12) to 2.941(13) Å. The average Gd−O distance at Gd1 is 2.492(12) Å, which is close to that of the reported acetate dimer $[Gd(O_2CCH_3)_2(phen)]_2$.[12b] It should be noted that six ferrocenecarboxylate ligands can be described as two groups (I and II). Group I contains two ferrocenecarboxylate ligands acting as tridentate fashion. O4 (or O4A) bridges two metals (Gd1 and Gd1A), and O8 (or O8A) only coordinates to one metal atom Gd1 (or Gd1A). The other four ferrocenecarboxylate ligands belong to group II, in which two oxygen atoms from each ferrocenecarboxylate ligand chelate the Gd1 (or Gd1A) atom forming four-membered rings. Hence, we noted that the distance between the bridging oxygen atom O4A and Gd1 is 2.941(13) Å, which is the longest distance around the Gd1 ion. The angles Gd1−O4−Gd1A and O4−Gd1−O4A are 112.5(5) and 67.5(5)°, respectively. The four-membered ring Gd1−O4−Gd1A−O4A is obviously perfectly planar. The distance of Gd1−Gd1A is 4.409 Å, which can be comparable to the value 3.9841(2) Å of reported complex $[(GdL1)]_2\cdot 2CHCl_3$ (H_3L1 = tris(((2-hydroxybenzyl)amino)ethyl)amine).[12a]

The carboxylate groups, with bite angles ranging from 117.8(16) to 120.4(13)°, are nearly coplanar with the C_5H_4 rings (angles varying from 1.6 to 7.7°). The C−C distances (1.414(8) Å, average), Fe−C_{ring} distances (2.036(2) Å, average), and C−C−C angles (108.0(5)°, average) of the ferrocenyl units are all similar to those reported in the literature.[20] In each ferrocenyl moiety, the cyclopentadienyl rings are planar and nearly parallel with a dihedral angle of 3.9° at Fe1, 3.4° at Fe2, or 3.3° at Fe3. Gd1···Fe1, Gd1···Fe2A, and Gd1···Fe3 distances are 5.577, 5.665, and 5.612 Å, respectively.

Interestingly, in the solid-state structure of **1**, $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ groups are joined together by hydrogen bonds forming a two-dimensional network. Figure 2 shows the hydrogen-bonding systems of the compound. As can be seen, the crystallization water molecule links O3 of the coordinated water from the $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group and O5 of ferrocenecarboxylate from the neighboring $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group forming two hydrogen bonds at the same time. Viewed from the *a* axis, each $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ links an adjacent $[Gd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ unit leading to an infinite chain through intermolecular O···H−O hydrogen bonds. We also noted that the crystallization methanol molecule joins O3 of the coordinated water from one chain and O2 of ferrocenecarboxylate from another chain forming two hydrogen bonds as those of the crystallization water. Thus, these O···H−O hydrogen bonds serve to link the chains into a 2-D sheet (Figure 2).

Crystal Structure of $[Nd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH\cdot H_2O$ (2). X-ray diffraction analysis of compound **2** shows that it crystallizes in the space group $P\bar{1}$ as compound **1**. Compound **2** contains a dimeric group $[Nd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(H_2O)_4]$, one crystallization water, and two crystallization methanol molecules.

As is depicted in Figure 3, each Nd(III) ion is at a nine-coordinated geometry in which seven oxygen atoms come

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[20] (a) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr.* **1979**, *B35*, 2888. (b) Allen, T. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 146.

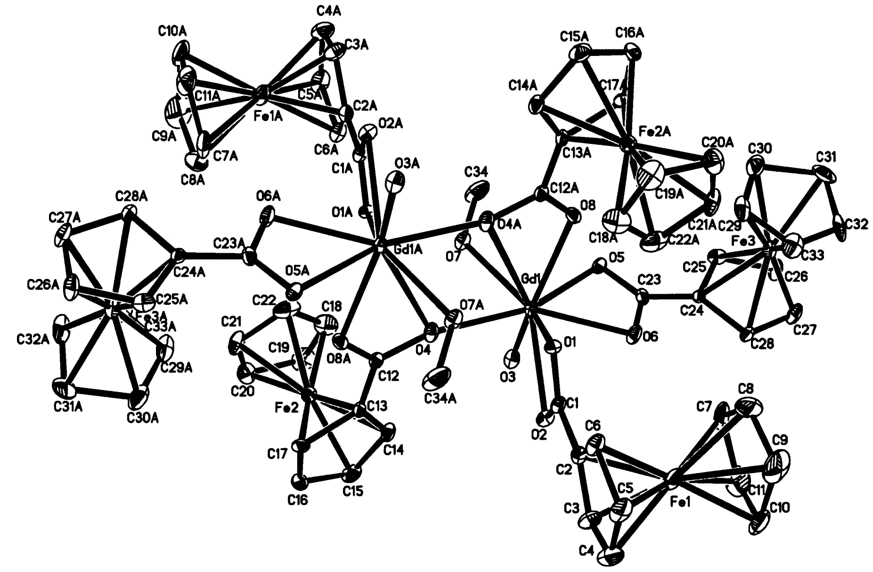

Figure 1. Perspective view of **1** with atom-labeling scheme. The hydrogen atoms are omitted for clarity.

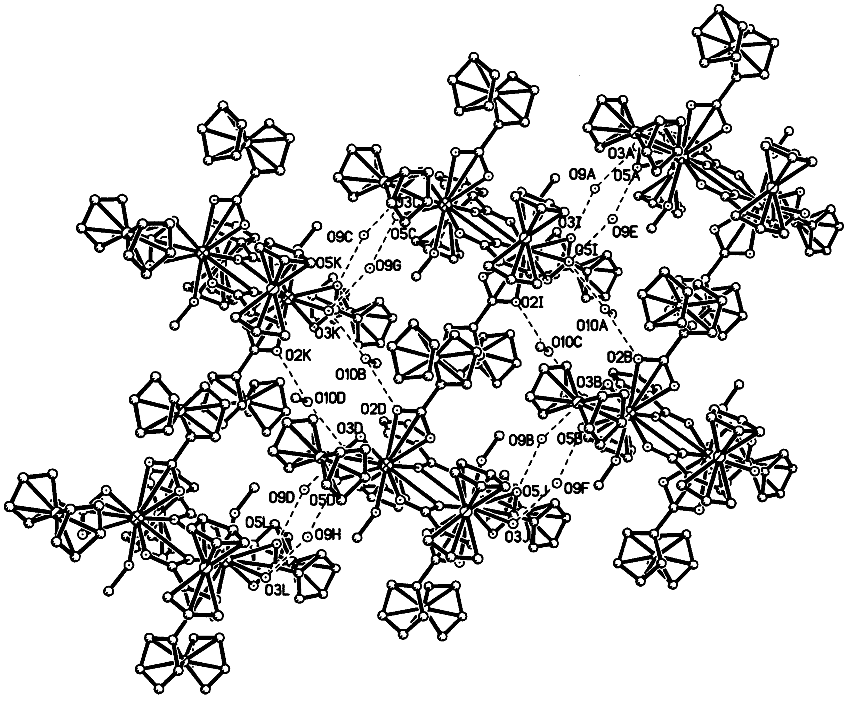

Figure 2. Hydrogen bond systems of **1** on the *bc* plane indicating a two-dimensional sheet.

from ferrocenecarboxylate ligands and two oxygen atoms from two coordinated water. As that of compound **1**, two oxygen atoms O3 and O3A from two ferrocenecarboxylate units bridge Nd1 and Nd1A to afford a dimeric core. The distances of Nd−O are ranging from 2.447(5) to 2.675(5) Å, and the average value is 2.514(5) Å. As is shown in Table 3, all of the C−O or Nd−O bond lengths are not equal. The bond angles around each Nd(III) ion vary from 50.9(2) to 155.1(2)°. Therefore, the nine oxygen atoms form an irregular polyhedron. The angles of Nd1−O3−Nd1A and O3A−Nd1−O3 are 110.0(2) and 70.0(2)°, respectively, which can be comparable to that of compound **1**. Obviously, four-membered ring Nd1−O3−Nd1A−O3A is perfectly planar. The Nd1−Nd1A distance is 4.210 Å, which is slightly longer than that of dimers $[Nd_2(phen)_2(ONO_2)_2(CH_3COO)_4]$ (3.974-(1) Å)[12e] and $[\{Nd[C_{10}H_6(OH)(COO)]_3(H_2O)(C_2H_6O)\}_2]\cdot 2H_2O\cdot 2C_2H_6O$ (4.087 Å).[2d]

The cyclopentadienyl rings in each ferrocenyl fragments are planar and nearly parallel with a dihedral angle of 1.7° at Fe1, 2.7° at Fe2, and 2.0° at Fe3. $Fe-C_{ring}$ distances range from 2.004(10) to 2.061(9) Å (average 2.038 Å), intracyclopentadienyl C−C bond lengths lie in the range 1.35-(2)−1.444(12) Å (average 1.418 Å), and C−C−C angles (average 108.0(5)°) are all similar to those reported in the literature.[20] The distances of Nd1···Fe1, Nd1···Fe2, and Nd1···Fe3 are 5.618, 5.679, and 5.686 Å, respectively.

In the solid-state structure of **2**, an infinite $[Nd_2(\mu_2\text{-}OOCFc)_2(OOCFc)_4(H_2O)_4]_n$ chain is formed by intermolecu-

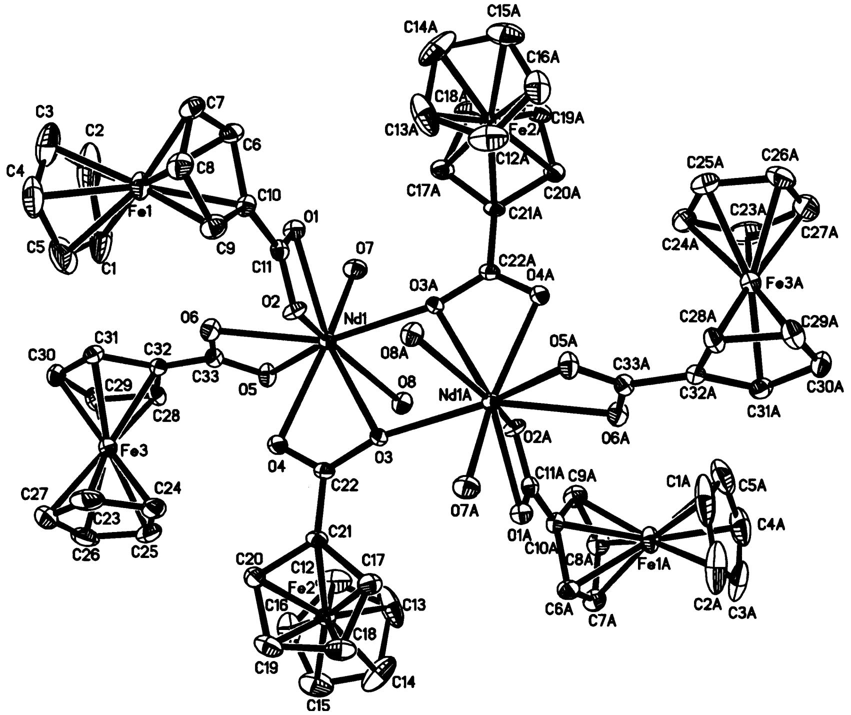

Figure 3. Perspective view of **2** with atom-labeling scheme. The hydrogen atoms are omitted for clarity.

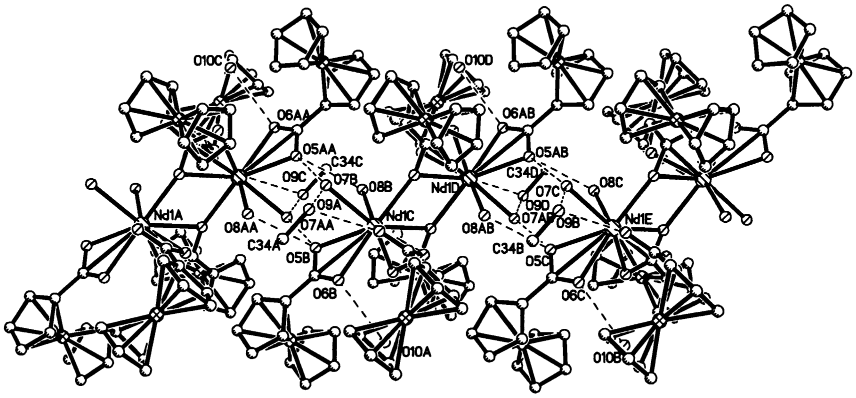

Figure 4. 1-D infinite chain structure of **2**.

lar hydrogen bonds (O···H−O). As can be seen from Figure 4, there are three kinds of hydrogen bonds. One is between the O7H (or O8H) unit of the coordinated water from one $[Nd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group and O5 of a ferrocenyl unit from the neighboring $[Nd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group. The second is arising from the interaction of O9H of one crystallization methanol molecule with O7 of the coordinated water and O4 of a ferrocenecarboxylate unit. The third originates from O10H of the crystallization water with O6 from a $[Nd_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group.

Crystal Structure of $[Y_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(H_2O)_4]\cdot 2MeOH$ (3). Complex **3** has a dimeric structure to similar to that of **2**, with a center of inversion between the metal atoms, bridged by two ferrocenecarboxylate ligands. The difference is that there is no crystallization water in **3**.

Each Y(III) is nine-coordinated too. The Y−O distances range from 2.396(9) to 2.634(9) Å (average value 2.479(5) Å), and the Y1−O2 distance is the longest due to the existing μ_2-bridge. The distances between oxygen atoms of two coordinated waters and Y1 are equal (O7−Y1 = O8−Y1 = 2.462(9) Å), which is shorter than the average distance between the ferrocenecarboxylato oxygen atoms and Y1 (2.484(9) Å). The angles of Y1−O2A−Y1A and O2−Y1−O2A are 110.9(3) and 69.1(3)°, respectively, which are close to those of compounds **1** and **2**. Four-membered ring Y1−O2−Y1A−O2A is perfectly planar too. The Y1−Y1A distance is 4.205 Å, which is similar to that of dimers $[Y_2(n\text{-}C_5H_{11}COO)_3(H_2O)_2]$ (4.086 Å)[2e] and $[Y_2(\mu_2\text{-}CH_3COO)_2(CH_3COO)_4(H_2O)_4]\cdot 4H_2O$ (4.163(2) Å).[1b]

The bond lengths and angles within the ferrocenyl group are unexceptional and close to those reported in the literature.[20] The distances of Y1···Fe1, Y1···Fe2, and Y1···Fe3 are 5.673, 5.703, and 5.870 Å, respectively.

As can be seen from Figure 5, in the solid-state structure of **3** there are two kinds of hydrogen bonds. One is between the O7H unit of the coordinated water from one $[Y_2(\mu_2\text{-OOCFc})_2(OOCFc)_4(MeOH)_2(H_2O)_2]$ group and O6 of the

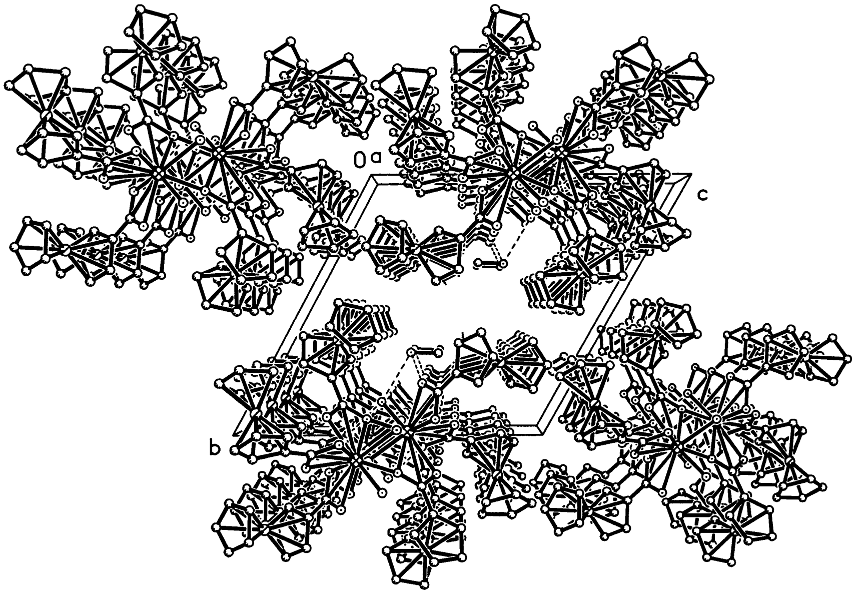

Figure 5. Crystal packing along the *a* axis of **3**.

ferrocenecarboxylate unit from the neighboring [$Y_2(\mu_2$-$OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2$] group. Another is arising from the O9H of the crystallization methanol with O7 of the coordinated water. Viewed from the *a* axis, each [Y_2-(μ_2-$OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2$] group links adjacent [$Y_2(\mu_2$-$OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2$] group by intermolecular O···H−O hydrogen bonds leading to an infinite 1-D chain [$Y_2(\mu_2$-$OOCFc)_2(OOCFc)_4(MeOH)_2(H_2O)_2]_n$.

IR Spectroscopy. Compounds **1**−**3** give rise to very similar infrared spectra in the range 400−4000 cm^{-1}. The bands attributable to H_2O occur at the same positions (3405 and 1636 cm^{-1} for **1**; 3411 and 1631 cm^{-1} for **2**; 3396 and 1632 cm^{-1} for **3**). The characteristic IR bands of the ferrocenyl group at 3097 and 489 cm^{-1} due to ν(C−H) and ν(Fe−Cp) vibrations, respectively, are close to the previous reported compounds.[8e,20] In the middle energy range, the strong absorption bands around 1522 and 1470 cm^{-1} can be assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively, which is consistent with the previous complexes.[1b,21] The vibrational bands around 1359 and 1024 cm^{-1} can be attributed to $\delta(CH_3)$ and $\rho(CH_3)$, respectively.[1b]

Magnetic Properties of [$Gd_2(\mu_2$-$OOCFc)_2(OOCFc)_4$-$(MeOH)_2(H_2O)_2$]·2MeOH·2H_2O (1). A variable-temperature magnetic study on **1** was carried out over the temperature range 1.8−300 K. The variations of the inverse of the magnetic susceptibility, χ_m^{-1}, and $\chi_m T$ of **1** are shown in Figure 6. The thermal evolution of χ_M^{-1} obeys Curie−Weiss law, $\chi_M = C/(T - \Theta)$, over the whole temperature range with Weiss constant, Θ, of 0.012 K. The Curie constant, C_M, of 15.763 cm^3 K mol^{-1} is consistent with the theoretical value for a binuclear complex of Gd (15.86 cm^3 K mol^{-1}).[12g] It can be seen from Figure 6, at 300 K, that $\chi_M T$ is equal to 15.766 cm^3 K mol^{-1}, which is close to the value for two isolated Gd^{3+} ions ($^8S_{7/2}$); as the temperature is lowered, $\chi_M T$ remains almost constant to 18.5 K and then increases rapidly below 18.5 K to 16.146 cm^3 K mol^{-1} at 1.8 K. Such behavior can be referred to the presence of a weak ferromagnetic exchange behavior. The data have been quantitative analyzed on the basis of the equation[12b] deduced from the isotropic spin Hamiltonian, $H = -JS_{Gd}S_{Gd'}$, with the quantum numbers $S_{Gd} = S_{Gd'} = 7/2$. The least-squares fit is given as a solid line in Figure 6. The best-fit parameters are $J = 0.006$ cm^{-1} and $g = 2.0$. The discrepancy factor $\sigma = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}]^{1/2}$ in the least-square fits is 6.1×10^{-4}. Such unexpected ferromagnetic behavior was only found in homobinuclear gadolinium complex [$GdL2_3(H_2O)]_2$ (HL2 = salicylic acid) ($J = 0.05$ cm^{-1}, $g = 2.0$) reported by Costes and co-workers in 2002.[12f] Obviously, the small *J* value reveals that the ferromagnetic Gd···Gd interactions in **1** are weaker than that in the compound [$GdL2_3(H_2O)]_2$. It is found that the interaction between gadolinium ions is generally antiferromagnetic, such as in Schiff base dimer [Gd_2L3-(NO_3)·3H_2O] (H_3L3 = tris(4-(2-hydroxy-3-methoxyphenyl)-3-azabutenyl)amine))[12c] ($J = -0.104$ cm^{-1}) and [$Gd_2(thd)_6$] (thd = 2,2,6,6-tetramethylheptanedionato)[12d] ($J = -$ 0.082(1) cm^{-1}). Because the factors governing the nature and magnitude of the Gd···Gd interactions are complicated, we

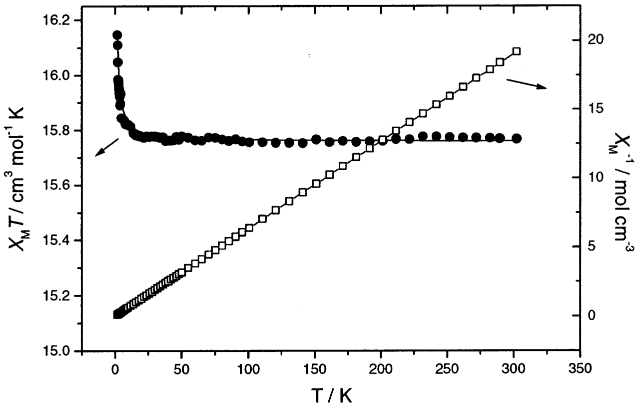

Figure 6. Plots of χ_M^{-1} and $\chi_M T$ vs *T* for **1**. The solid line is the theoretical curve obtained with $g = 2.0$ and $J = 0.006$ cm^{-1}.

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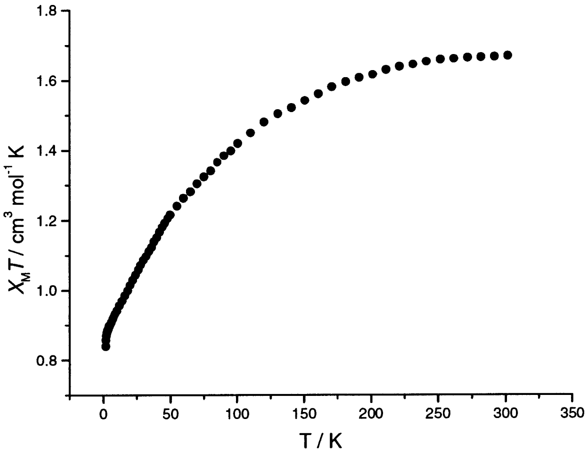

Figure 7. Plot of $\chi_M T$ vs T for **2**.

cannot explain why the two gadolinium ions in **1** do present ferromagnetic Gd···Gd interactions which are different from those of the reported Gd complexes. To further understand the magnetic interaction mechanism, we will design more homo-Gd complexes and study their magnetic properties.

Magnetic Properties of [$Nd_2(\mu_2$-OOCFc$)_2$(OOCFc$)_4$($H_2O)_4$]·2MeOH·H_2O (2). The variable-temperature magnetic susceptibility measurements were performed in the temperature range of 1.8−300 K. The $\chi_M T$ vs T curve is shown in Figure 7. The effective magnetic moment of the Nd^{3+} ion is determined to be 3.65 μ_B at room temperature, which is close to the theoretical value of 3.62 μ_B for the free Nd^{3+} ion. As can be seen from the Figure 7, at ca. 300 K, $\chi_M T$ is equal to 1.666 cm^3 K mol^{-1} and decreases continuously to a value of 0.838 cm^3 K mol^{-1} at 1.8 K. The thermal variation of $\chi_M T$ mainly depends on the populations of the Stark levels and on the possible antiferromagnetic interactions between the two Nd(III) ions. It is noted that the 4f^n configuration of a Ln(III) ion is split into $^{2S+1}L_J$ states by the interelectronic repulsion and the spin−orbit coupling. Further splitting into Stark components is caused by the crystal-field perturbation: the number of components depends on the symmetry site of the ion.[22] At room temperature, all the Stark levels arising from the 10-fold degenerate $^4I_{9/2}$ ground states are populated but, as the temperature decreases, a progressive depopulation of these levels occurs. Finally, the nature of the interactions between the two Nd(III) ions with an orbital momentum cannot be unambiguously deduced only from the shape of the $\chi_M T$ vs T curve.[23]

Because Y(III) ion has no unpaired electrons, complex **3** is expected to be diamagnetic.

Conclusion

By means of the "avoiding light method" we have successfully prepared three crystal products from the reaction of sodium ferrocenecarboxylate with Ln($NO_3)_3$ in methanol solution and clearly characterized the crystal structures of the three novel organometallic dimers. The elemental analyses and the IR data are consistent with the X-ray analysis results. On the basis of the magnetic studies, the unexpected ferromagnetic coupling between the gadolinium(III) ions can be observed.

Acknowledgment. The authors thank the National Natural Science Foundation of China, the Outstanding Young Teacher Foundation of the Ministry of Education, and the Innovation Foundation of Henan Province for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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