Inorg. Chem. **2006**, *45*, 6756–6760

Inorganic Chemistry

Article

2D Ln^{III}Ru$^{III}_2$ Compounds Constructed from *trans*-[Ru(acac)$_2$(CN)$_2$]$^-$. Syntheses, Structures, and Magnetic Properties

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Received April 6, 2006

A series of cyano-bridged Ln^{III}Ru$^{III}_2$ coordination polymers, Ph$_4$P{Ln(NO$_3$)$_2$[Ru(acac)$_2$(CN)$_2$]$_2$} [Ln = Tb (**1**), Dy (**2**), Er (**3**), Gd (**4**); Hacac = acetylacetone] have been synthesized by the reaction of Ln(NO$_3$)$_3$ with *trans*-Ph$_4$P[Ru(acac)$_2$(CN)$_2$] in methanol. X-ray crystallographic determination reveals that these compounds are isostructural and have a wavy (4,4) layer structure with the Ln^{3+} ions bridged by *trans*-[Ru(acac)$_2$(CN)$_2$]$^-$. Magnetic studies shows that the magnetic coupling between the Ln(III) and Ru(III) ions through the cyano bridges in **1**–**4** is negligibly weak.

Introduction

In recent years there has been a growing interest in the preparation and study of mixed d−f compounds[1] because of their potential application as luminescent materials,[2] as magnetic materials, such as single-molecule magnets (SMMs)[3] and single-chain magnets (SCMs),[4] and as useful materials in host−guest chemistry.[5] A popular approach to the preparation of d−f compounds has been to combine a 3d hexacyanometalate with a lanthanide ion in the presence or absence of an additional ligand.[6−11] Some of these compounds show interesting magnetic properties. For example, the 3D [SmFe(CN)$_6$]·4H$_2$O exhibits long-range ferromagnetic ordering and a large coercive field even for a long interaction path.[6] The

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10.1021/ic060580m CCC: $33.50

2D $[NdCo(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (bpym = 2,2′-bipyrimidine) shows an unusual field-dependent slow-relaxation behavior.[7a] The layered compounds $[Ln(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ (Ln = Gd, Sm)[7b,c] display variable long-range magnetic ordering. $Nd(DMF)_4(H_2O)_3M(CN)_6\cdot H_2O$ (DMF = *N*,*N*′-dimethylformamide, M = Fe and Co) shows interesting photoinduced magnetization.[8a,b] We are interested in preparing mixed d−f compounds using 4d or 5d metal ions since they have received less attention, and we anticipate that they may have topologies and magnetic behaviors that are different from those of 3d−4f compounds. As far as we know, examples of 4d−4f and 5d−4f cyano-bridged coordination polymers are limited to those using the diamagnetic $[Ru^{II}(CN)_6]^{4-}$ [9a−c] and $[RuL(CN)_4]^{2-}$ (L = 2,2′-bipyridine, 2,2′-bipyrimidine, 1,10-phenanthroline)[12] building blocks, as well as a few reports of Sm−W-, Gd/Sm−W-, and Gd−W-containing polymers based on the $[W(CN)_8]^{3-}$ building block.[13] Herein we report the syntheses, structures, and magnetic properties of four 2D $Ln^{III}Ru^{III}_2$ compounds, $Ph_4P\{Ln(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ [Ln = Tb (**1**), Dy (**2**), Er (**3**), Gd(**4**)], constructed with the paramagnetic *trans*-$[Ru^{III}(acac)_2(CN)_2]^-$ ion as the building block. These are the first examples 4d−4f compounds of paramagnetic ruthenium(III). We have previously demonstrated the use of *trans*-$[Ru(acac)_2(CN)_2]^-$ for the construction of new 3d−4d magnetic materials.[14]

Experimental Procedures

Measurements. Elemental analyses were carried out using an Elementar Vario EL CHN analyzer. The IR spectra were recorded as KBr disks on a Perkin-Elmer FTIR-1600 spectrophotometer in the 4000−400 cm^{-1} region. XRD patterns were recorded with a Rigaku D/Max-2000 diffractometer equipped with a Cu Kα radiation source ($\lambda = 0.15418$ nm). Magnetic measurements were performed on either a Maglab 2000 System or a MPMS XL-5 SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).[15]

Preparations. *trans*-$Ph_4P[Ru(acac)_2(CN)_2]$ was synthesized according to the literature.[14a] Other chemicals and reagents were commercially available and used as received.

$Ph_4P\{Tb(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ (1). A solution of $Tb(NO_3)_3\cdot 6H_2O$ (45 mg, 0.1 mmol) and $Ph_4P[Ru(acac)_2(CN)_2]$ (276 mg, 0.4 mmol) in methanol (25 mL) was heated to 50 °C for 30 min. Slow evaporation of the resulting solution at room temperature to ca. 1 mL over a period of two weeks produced dark purple crystals which were washed with ethanol and dichloromethane. Yield: 21%. Anal. Calcd for $TbRu_2N_6C_{48}O_{14}H_{48}P$: C, 43.34; H, 3.64; N, 6.32. Found: C, 43.56; H, 3.75; N, 6.26. IR (KBr, cm^{-1}): ν_{CN} 2115 s.

$Ph_4P\{Dy(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ (2). This was prepared in a manner similar to that of **1**. Yield: 16%. Anal. Calcd for $DyRu_2N_6C_{48}O_{14}H_{48}P$: C, 43.39; H, 3.64; N, 6.33. Found: C, 43.56; H, 3.55; N, 6.25. IR (KBr, cm^{-1}): ν_{CN} 2113 s.

$Ph_4P\{Er(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ (3). This was prepared in a manner similar to that of **1**. Yield: 30%. Anal. Calcd for $ErRu_2N_6C_{48}O_{14}H_{48}P$: C, 43.24; H, 3.63; N, 6.30. Found: C, 43.56; H, 4.66; N, 6.22. IR (KBr, cm^{-1}): ν_{CN} 2115 s.

$Ph_4P\{Gd(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ (4). This was prepared in a manner similar to that of **1**. Yield: 28%. Anal. Calcd for $GdRu_2N_6C_{48}O_{14}H_{48}P$: C, 43.75; H, 3.66; N, 6.35. Found: C, 43.37; H, 3.61; N, 6.31. IR (KBr, cm^{-1}): ν_{CN} 2113 s.

X-ray Crystallography. The data collections of **1**−**3** were performed on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 301 K. The structures were solved by the heavy-atom Patterson method[16] (PATTY) and were expanded using Fourier difference techniques (DIRDIF99).[17] The atomic coordinates and thermal parameters were refined by full-matrix least squares on *F*, with anisotropic displacement parameters for non-hydrogen atoms whenever possible. Hydrogen atoms were included but not refined. All calculations were performed using the CrystalStructure crystallographic software package.[18] The diffracted intensities were corrected for Lorentz and polarization effects.

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Table 1. Crystal Data for $Ph_4P\{Ln(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$ [Ln = Tb **1**, Dy **2**, Er **3**]

	1	**2**	**3**
chemical formula	$Ru_2TbN_6C_{48}O_{14}H_{48}P$	$Ru_2DyN_6C_{48}O_{14}H_{48}P$	$Ru_2ErN_6C_{48}O_{14}H_{48}P$
fw	1324.98	1328.55	1333.31
cryst syst	triclinic	triclinic	triclinic
cryst dimensions (mm)	0.08 × 0.20 × 0.32	0.11 × 0.28 × 0.30	0.03 × 0.12 × 0.28
lattice type	primitive	primitive	primitive
a (Å)	10.951(1)	10.933(2)	10.9180(10)
b (Å)	13.196(2)	13.196(3)	13.208(2)
c (Å)	19.194(2)	19.173(4)	19.155(2)
α (deg)	87.99(1)	88.03(1)	88.10(1)
β (deg)	73.90(1)	73.95(1)	73.98(1)
γ (deg)	81.92(1)	81.99(1)	82.08(1)
V (Å^3)	2638.4(5)	2632.3(9)	2629.6(5)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	2	2
D_{calcd} (g cm^{-3})	1.668	1.676	1.684
F_{000}	1316.00	1318.00	1322.00
μ(Mo Kα) (cm^{-1})	19.87	20.72	22.44
params	700	700	700
T (K)	301	301	301
$2\theta_{max}$ (deg)	55	55	55
measured reflns	16 499	16 175	16 313
obsd reflns	8531	10 077	8649
largest peak/hole (e Å^{-3})	1.55/−3.73	1.68/−4.22	1.95/−2.20
final *R* indices	$[I > 2.00\sigma(I)]$	$[I > 2.00\sigma(I)]$	$[I > 1.00\sigma(I)]$
residuals: R^a, R_w^b	0.045, 0.053	0.04, 0.05	0.051, 0.040
GOF	1.034	1.035	1.009

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

Because no single crystals suitable for single-crystal X-ray diffraction were obtained, **4** was characterized by XRD. For comparison, both the XRD patterns of **1** and **4** were collected using ground single crystals. They are similar to each other and also to the theoretical positions calculated from the single-crystal data of **1** except for some orientation effects (Figure S4, Supporting Information).

Results and Discussion

Structures. The reaction of $Ph_4P[Ru(acac)_2(CN)_2]$ with $Ln(NO_3)_3$ in methanol readily produces $Ph_4P\{Ln(NO_3)_2[Ru(acac)_2(CN)_2]_2\}$[Ln = Tb (**1**), Dy (**2**), Er (**3**), Gd(**4**)]. All compounds show a single strong cyanide peak at around 2115 cm^{-1}.

The structures of compounds **1**−**3** have been determined by single-crystal X-ray crystallography. Summaries of crystal data collection and refinement parameters are given in Table 1. Selected bond lengths and angles for compounds **1**−**3** are given in Tables 2−4. Compounds **1**−**3** are isostructural, so only the structure of **1** is described in detail.

The perspective view of **1** is depicted in Figure 1. Each Tb^{3+} ion is eight coordinated and is surrounded by four oxygen atoms of two nitrate ions and four nitrogen atoms of the cyano groups of four $[Ru(acac)_2(CN)_2]^-$ ions. The Tb−O(nitrate) and Tb−N bond lengths range from 2.423(5) to 2.489(6) Å and 2.420(8) to 2.451(6) Å, respectively. The Tb atoms are connected by the linear $[NC\text{-}Ru(acac)_2\text{-}CN]^-$ ions to produce a wavy (4,4) 2D layer structure. The Tb(III) and the $[Ru(acac)_2(CN)_2]^-$ units form 24-member $Tb_4Ru_4(CN)_8$ squares with the Tb atoms occupying the vertexes and the Ru atoms residing in the middle of the four sides of the squares (Figure 2). The side view of the 2D layer is shown in Figure 3. The C≡N distances in each $[Ru(acac)_2(CN)_2]^-$ unit are similar to those in $Ph_4P[Ru(acac)_2(CN)_2]$.[14a] The bridging Ru−C≡N units are close to linear (171.3(7)−176.3(6)°). The Tb−N≡C units are bent with angles ranging from 152.8(9) to 165.2(7)°. The closest intra-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Tb(1)−N(1)	2.451(6)	Tb(1)−N(2)	2.430(8)
Tb(1)−N(3)	2.422(7)	Tb(1)−N(4)	2.420(8)
Tb(1)−O(9)	2.441(6)	Tb(1)−O(10)	2.489(6)
Tb(1)−O(12)	2.423(5)	Tb(1)−O(13)	2.475(6)
C(1^{i})-N(1)	1.143(11)	C(2)−N(2)	1.15(1)
C(3)−N(3)	1.16(1)	C(4)−N(4)	1.16(1)
C(1)−Ru(1)−C(2)	176.0(3)	C(3)−Ru(2)−C(3^{ii})	180.0
C(4)−Ru(3)−C(4^{iii})	180.0	Tb(1)−N(1)−C(1^{i})	161.6(6)
Tb(1)−N(2)−C(2)	164.5(6)	Tb(1)−N(3)−C(3)	165.2(7)
Tb(1)−N(4)−C(4)	152.8(9)	Ru(1)−C(1)−N(1^{iv})	172.3(7)
Ru(1)−C(2)−N(2)	171.3(7)	Ru(2)−C(3)−N(3)	176.3(6)
Ru(3)−C(4)−N(4)	171.7(9)		

[a] Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 − *x*, −*y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, 1 − *z*; (iv) *x* − 1, *y*, *z*.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Dy(1)−N(1)	2.434(5)	Dy(1)−N(2)	2.417(6)
Dy(1)−N(3)	2.407(5)	Dy(1)−N(4)	2.423(6)
Dy(1)−O(9)	2.431(5)	Dy(1)−O(10)	2.475(4)
Dy(1)−O(12)	2.409(4)	Dy(1)−O(13)	2.467(4)
Dy(1)−O(13)	2.467(4)	Dy(1)−O(13)	2.467(4)
C(1)−N(1^{i})	1.145(7)	C(2)−N(2)	1.145(8)
C(3)−N(3)	1.156(8)	C(4)−N(4)	1.15(1)
C(1)−Ru(1)−C(2)	175.8(2)	C(3)−Ru(2)−C(3^{ii})	180.00
C(4)−Ru(3)−C(4^{iii})	180.00	Dy(1)−N(1)−C(1^{i})	162.1(5)
Dy(1)−N(2)−C(2)	165.2(5)	Dy(1)−N(3)−C(3)	166.0(6)
Dy(1)−N(4)−C(4)	153.6(6)	Ru(1)−C(1)−N(1^{i})	172.5(5)
Ru(1)−C(2)−N(2)	171.2(5)	Ru(2)−C(3)−N(3)	176.8(5)
Ru(3)−C(4)−N(4)	171.6(6)		

[a] Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 − *x*, −*y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, 1 − *z*; (iv) *x* − 1, *y*, *z*.

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(18) (a) *CrystalStructure 3.5.1: Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC: The Woodlands, TX, 2000−2003. (b) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*, issue 10; Chemical Crystallography Laboratory: Oxford, U.K., 1996.

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

Er(1)−N(1)	2.408(5)	Er(1)−N(2)	2.388(6)
Er(1)−N(3)	2.390(6)	Er(1)−N(4)	2.376(6)
Er(1)−O(9)	2.408(5)	Er(1)−O(10)	2.449(5)
Er(1)−O(12)	2.384(4)	Er(1)−O(13)	2.442(5)
C(1^{i})-N(1)	1.152(9)	C(2)−N(2)	1.145(9)
C(3)−N(3)	1.155(9)	C(4)−N(4)	1.13(1)

C(1)−Ru(1)−C(2)	176.0(3)	C(3)−Ru(2)−C(3^{ii})	180.0
C(4)−Ru(3)−C(4^{iii})	180.0	Er(1)−N(1)−C(1^{iii})	162.7(4)
Er(1)−N(2)−C(2)	168.0(5)	Er(1)−N(3)−C(3)	165.8(6)
Er(1)−N(4)−C(4)	156.0(6)	Ru(1)−C(1)−N(1^{iv})	172.1(5)
Ru(1)−C(2)−N(2)	169.3(6)	Ru(2)−C(3)−N(3)	175.7(5)
Ru(3)−C(4)−N(4)	170.3(7)		

[a] Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, y, z$.

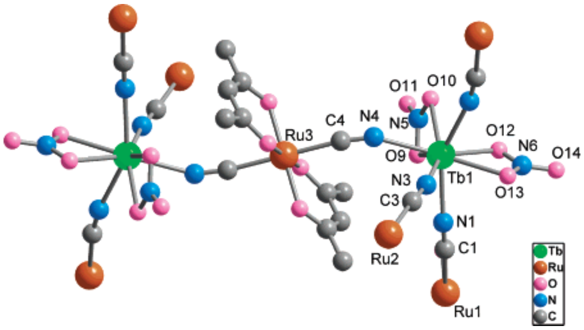

Figure 1. Perspective view of **1**. The Ph_4P^+ ions have been omitted for clarity.

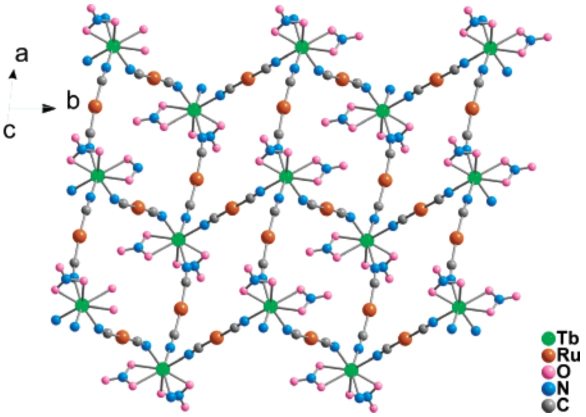

Figure 2. Two-dimensional network of **1**. The two acac molecules at each Ru center have been omitted for clarity.

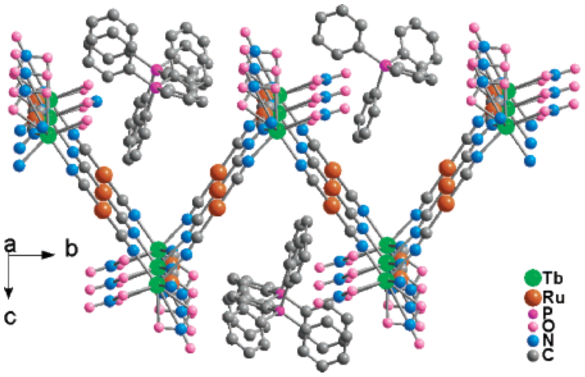

Figure 3. Side view of the two-dimensional network of **1** that shows the zigzag structure with embedded Ph_4P^+ ions. The two acac at each Ru center were omitted for clarity.

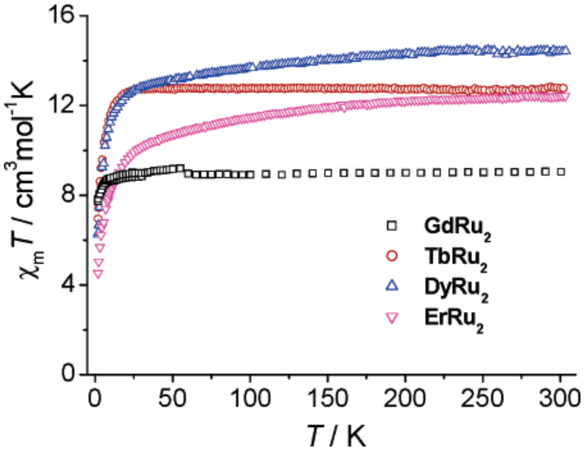

Figure 4. Temperature dependence of $\chi_m T$ for compounds **1**−**4**.

molecular Tb···Ru, Tb···Tb, and Ru···Ru distances are 5.414, 10.827, and 6.598 Å respectively. The 2D layers stack “face-to-face” with interlayer separations of Tb···Tb = 12.113 Å and Ru···Ru = 11.609 Å (Figure S1).

In compound **2**, the closest intramolecular Dy···Ru, Dy···Dy, and Ru···Ru distances are 5.412, 10.824, and 6.598 Å, respectively, while the interlayer separations are Dy···Dy = 12.119 Å and Ru···Ru = 11.617 Å.

In compound **3**, the closest intramolecular Er···Ru, Er···Er, and Ru···Ru distances are 5.411, 10.821, and 6.604 Å, respectively, while the interlayer separations are Er···Er = 12.928 Å and Ru···Ru = 11.637 Å.

The topology of these compounds has an anionic network consisting of 24-member $Ru_4Ln_4(CN)_8$ puckered squares, while the other known 2D cyano-bridged d−f mixed compounds are neutral networks. Alternating fused rows of $Fe_2Nd_2(CN)_4$ and $Fe_4Nd_4(CN)_8$ rings are found in [NdFe(bpym)($H_2O)_4(CN)_6$]·3H_2O;[7a] distorted 18-member $Cr_3Ln_3(CN)_6$ rectangles are observed in [Ln(DMF)$_2$($H_2O)_3$Cr(CN)$_6$]·H_2O (Ln = Gd, Sm),[7b,c] and 12-member $Ru_2Ln_2(CN)_4$ and $Sm_2W_2(CN)_4$ squares occur in [{Ru(bpy)(CN)$_4$}$_3${Ln($H_2O)_4$}$_2$]·$x$$H_2O$ (Ln = Nd, Gd)[12c] and Sm($H_2O)_5$[W(CN)$_8$],[13a] respectively.

Magnetic Properties. The temperature dependence of $\chi_m T$ for compounds **1**−**4** ($LnRu_2$) is shown in Figure 4. The $\chi_m T$ values at 300 K are 12.76, 14.41, 12.43, and 9.05 cm^3 mol^{-1} K for [$TbRu_2$], [$DyRu_2$], [$ErRu_2$], and [$GdRu_2$], respectively. These values are comparable with the expected uncoupled values of 12.56, 14.88, 12.25, and 8.63 cm^3 mol^{-1} K for one Ln^{III} free ion and two low-spin d^5 Ru^{III} centers in an octahedral environment with $S = 1/2$. The molar magnetic susceptibility data of compounds **1**−**4** can be fitted using the Curie−Weiss law [$\chi_m = C/(T-\theta)$] (Figure S5, for **1** and **4**, in the temperature range of 2−300 K, and for **2** and **3**, in the temperature range of 80−300 K), giving C = 12.74, 14.90, 12.98, and 9.03 cm^3 mol^{-1} K and θ = −0.19, −8.9, −12.9, and −0.36 K for [$TbRu_2$], [$DyRu_2$], [$ErRu_2$], and [$GdRu_2$], respectively. The C values are also consistent with noninteracting Ln−Ru_2 systems (C_{calcd} = 12.56, 14.88, 12.25, and 8.63 cm^3 mol^{-1} K for [$TbRu_2$], [$DyRu_2$], [$ErRu_2$], and [$GdRu_2$], respectively). The very small Weiss constant of −0.36 K for the $GdRu_2$ compound suggests very weak or negligible antiferromagnetic coupling between the Gd(III) and Ru(III) ions. The relatively large negative θ values for

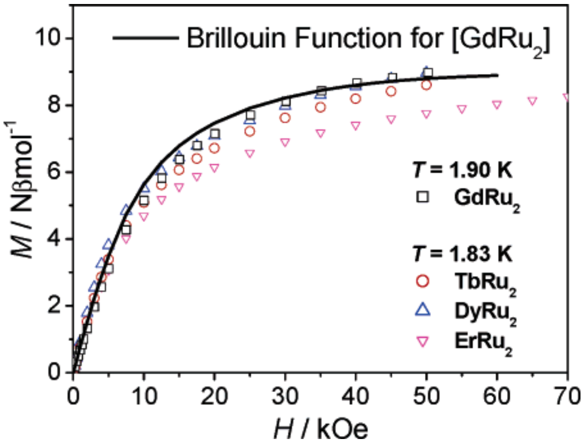

Figure 5. Field dependence of magnetization for compounds **1**−**4**, and the solid line presents the Brillouin curve calculated for uncoupled Gd^{3+} and Ru^{3+}.

[$DyRu_2$] and [$ErRu_2$] do not necessarily imply the presence of strong antiferromagnetic interactions because they may be the result of strong spin−orbital coupling in Dy(III) or Er(III). The field dependence of magnetization at about 1.8 K for **1**−**4** is shown in Figure 5, together with the Brillouin curve for the spin-only [$GdRu_2$]. All these *M(H)* curves are consistent with the paramagnetic state of the ions. The magnetization of [$GdRu_2$] is consistent with the Brillouin function, and at 50 kOe, it reaches 8.98 $N\beta$ mol^{-1}, very close to the expected saturation value of 9 for the sum of two Ru(III) and one Gd(III) magnetic moments.

Conclusions

Four new cyano-bridged 4d−4f compounds, **1**−**4**, were synthesized and structurally and magnetically investigated. They are isostructural and have an anionic wavy (4,4) 2D layer structure with Ln occupying the vertexes and Ru residing in the middle of the sides of the $Ru_4Ln_4(CN)_8$ squares. The magnetic coupling between the Ln(III) and Ru(III) ions through cyano-bridges in the title compounds are found to be negligible, although the 4d orbitals of Ru(III) are more diffuse than the 3d orbitals of Fe(III).[10a]

Acknowledgment. This work was supported by a grant from the NSFC/RGC Joint Research Scheme (CityU107/03, 20318001) and NSFC (20490210, and 20221101).

Supporting Information Available: Additional figures giving a view of **1** along *a* axis, ORTEP diagrams of **2** and **3**, powder XRD patterns, magnetic susceptibility plots, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060580M