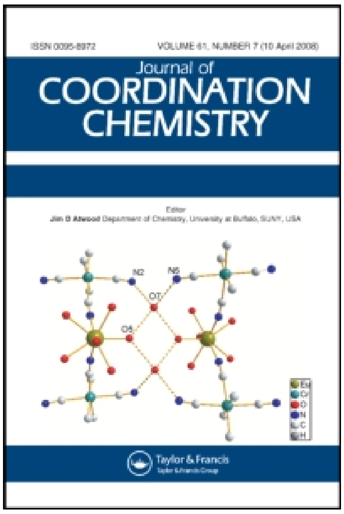

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, structures and magnetic properties of isonicotinate-bridged heterometallic Ln(III)-Cu(II) coordination polymers

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To cite this Article Liang, Fu-Pei , Huang, Miao-Ling , Jiang, Chun-Fang , Li, Yan and Hu, Rui-Xiang(2007) 'Syntheses, structures and magnetic properties of isonicotinate-bridged heterometallic Ln(III)-Cu(II) coordination polymers', Journal of Coordination Chemistry, 60: 21, 2343 — 2350

To link to this Article: DOI: 10.1080/00958970701266039

URL: http://dx.doi.org/10.1080/00958970701266039

Journal of Coordination Chemistry
Vol. 60, No. 21, 1 November 2007, 2343–2350

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Syntheses, structures and magnetic properties of isonicotinate-bridged heterometallic Ln(III)–Cu(II) coordination polymers

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(*Received 30 October 2006; in final form 12 December 2006*)

The heterometallic Ln(III)–Cu(II) coordination polymers $[CuLn_2(IN)_8(H_2O)_4]_n$ (IN = isonicotinate, Ln = Gd (**1**), Dy (**2**), Er(**3**)) have been synthesized by hydrothermal reactions and characterized by elemental analysis, IR and single crystal X-ray diffraction. The compounds are isomorphous and crystallize in monoclinic space group $P2_1/c$, adopting a one-dimensional chain structure with alternately arranged $[Ln_2(IN)_6(H_2O)_4]$ and $[Cu(IN)_2]$ building blocks bridged by isonicotinates. Temperature-dependent magnetic susceptibility for complex **1** was studied, and a very weak ferromagnetic interaction between metal ions was observed.

Keywords: Copper; Lanthanide; Isonicotinic acid; Heterometallic complex

1. Introduction

Heterometallic coordination polymers containing both lanthanide and transition metals are of great interest because of their potential applications in molecular recognition, catalytic, microporous, nonlinear optical, magnetic and fluorescent materials. Many heterometallic lanthanide–transition metal polymers exhibiting fascinating structural and topological features have been reported [1–6]. The ligands, synthetic method and conditions are the key factors determining the structures of the heterometallic complexes. Organic ligands with mixed *N*- and *O*-donor atoms are usually used in the assembly of various types of lanthanide–transition metal coordination polymers [7].

Isonicotinic acid is a good linear bridging ligand with oxygen and nitrogen donors on opposite sides, and it is also a good donor and/or acceptor of hydrogen bonds in assembly of supermolecular systems. Transition metal complexes and rare earth complexes containing isonicotinate ligand have been extensively studied [8–14], however, only a few examples of heterometallic lanthanide–transition metal compounds

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701266039

with this ligand have been reported. Considering that rare-earth cations are extremely oxophilic and prefer to interact with the carboxylate group and copper(II) prefers to bind the nitrogen of the pyridyl group, Andruh [15] utilized $[CuPrL(NO_3)_3]$ [$L^{2-} = N,N'$-propylenedi(3-methoxysacylideneiminato)] as a building block to construct a two-dimensional heterometallic coordination polymer $[CuPrL(NO_3)_2(IN)]_\infty$ with isonicotinate as bridging ligand. Yang [16] reported that reactions of isonicotinic acid with Ln_2O_3 and $CuCl_2 \cdot 2H_2O$ under strongly acidic and hydrothermal conditions afforded three-dimensional heterometallic Ln(III)–Cu(I) coordination polymers $[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}(IN)_{22}Cu_6Cl_4(H_2O)_8] \cdot 6H_2O$ (Ln = Y, Gd, Dy). By introducing 1,2-benzenedicarboxylic acid as a second ligand, they obtained 3D Er(III)–Cu(II) polymers $[Er_7(\mu_3\text{-}O)(\mu_3\text{-}OH)_6(bdc)_3(IN)_9][Cu_3X_4]$ (bdc = 1,2-benzenedicarboxylate, X = Cl or Br) [17]. Herein we wish to report the synthesis and characterization of one-dimensional chain heterometallic lanthanide–copper polymers bridged only by isonicotinate.

2. Experimental

2.1. *Materials and general methods*

All chemicals used in syntheses were analytic grade purchased from commercial sources and used as received. Elemental analyses for C, H and N were performed on a PE-2400 II analyzer. IR spectra were obtained in KBr pellets on a Nicolet 360 FT-IR spectrometer in the range 4000–400 cm^{-1}. Magnetic susceptibility data were collected as polycrystalline samples on a Quantum-Design MPMS-XL SQUID magnetometer in the temperature range from 2 to 300 K.

2.2. *Synthesis*

$[CuGd_2(IN)_8(H_2O)_4]_n$ (1). A mixture of Gd_2O_3 (0.0908 g, 0.25 mmol), CuO (0.0399 g, 0.5 mmol), HIN (0.2461 g, 2.0 mmol), and H_2O (14.0 mL) in a molar ratio of about 1 : 2 : 8 : 290 was sealed in a 25-mL Teflon-lined stainless steel reactor, heated in an oven at 140°C for 72 h, and then slowly cooled to room temperature. Blue block crystals of **1** were collected in 61% yield (based on copper). Anal. Calcd for $C_{48}H_{40}CuGd_2N_8O_{20}$ (%): C, 40.40; H, 2.83; N, 7.85. Found: C, 40.38; H, 2.75; N, 7.81. IR (KBr pellet): 3277(br, s), 1665(vs), 1608(vs), 1581(s), 1561(s), 1555(s), 1536(vs), 1421(vs), 1370(vs), 773(s), 693(vs).

$[CuDy_2(IN)_8(H_2O)_4]_n$ (2). The preparation is similar to that for **1**, except replacing Gd_2O_3 by Dy_2O_3, and heating the mixture at 140°C for 96 h. Blue block crystals of **2** were obtained in 62% yield (based on copper). Anal. Calcd for $C_{48}H_{40}CuDy_2N_8O_{20}$ (%): C, 40.11; H, 2.80; N, 7.80. Found: C, 40.05; H, 2.69; N, 7.78. IR (KBr pellet): 3277(br, s), 1666(vs), 1609(vs), 1581(s), 1561(s), 1555(s), 1536(vs), 1421(vs), 1369(vs), 773(s), 693(vs).

$[CuEr_2(IN)_8(H_2O)_4]_n$ (3). The preparation is similar to that for **1**, except replacing Gd_2O_3 by Er_2O_3, and heating the mixture at 140°C for 108 h. Green block crystals of **3** were obtained in 64% yield (based on copper). Anal. Calcd for $C_{48}H_{40}CuEr_2N_8O_{20}$

Table 1. Crystallographic data and refinement details for **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{24}H_{20}Cu_{0.50}GdN_4O_{10}$	$C_{24}H_{20}Cu_{0.50}DyN_4O_{10}$	$C_{24}H_{20}Cu_{0.50}ErN_4O_{10}$
Formula weight	713.46	718.71	723.47
Temperature (K)	293(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.4896(14)	9.456(1)	9.428(2)
b (Å)	14.993(2)	14.966(3)	14.950(3)
c (Å)	18.225(3)	18.166(4)	18.141(3)
β (°)	93.815(3)	93.74(1)	93.73(1)
V (Å^3)	2587.3(7)	2565.4(8)	2551.5(7)
Z	4	4	4
D_c (g cm^{-3})	1.832	1.861	1.883
μ (mm^{-1})	3.027	3.381	3.760
$F(000)$	1402	1410	1418
Crystal size (mm^3)	$0.50 \times 0.41 \times 0.32$	$0.54 \times 0.42 \times 0.28$	$0.54 \times 0.42 \times 0.28$
θ range (°)	2.24–27.00	1.76–25.25°	1.77–25.25°
Limiting indices	$-10 \le h \le 12$, $-19 \le k \le 15$, $-23 \le l \le 22$	$0 \le h \le 11$, $0 \le k \le 17$, $-21 \le l \le 21$	$0 \le h \le 11$, $0 \le k \le 17$, $-21 \le l \le 21$
Reflections collected	14760	5313	5289
Data/restraints/parameters	5613/0/374	4638/4/375	4610/4/375
Goodness-of-fit on F^2	1.094	1.029	0.990
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0168$, $wR_2 = 0.0429$	$R_1 = 0.0255$, $wR_2 = 0.0562$	$R_1 = 0.0252$, $wR_2 = 0.0566$
R indices (all data)	$R_1 = 0.0184$, $wR_2 = 0.0435$	$R_1 = 0.0334$, $wR_2 = 0.0577$	$R_1 = 0.0323$, $wR_2 = 0.0581$
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e A^{-3})	0.941 and −0.588	0.608 and −0.892	1.163 and −0.855

(%): C, 39.84; H, 2.78; N, 7.74. Found: C, 39.79; H, 2.66; N, 7.69. IR (KBr pellet): 3281(br, s), 1668(vs), 1609(vs), 1581(s), 1562(s), 1555(s), 1537(vs), 1422(vs), 1369(vs), 773(s), 693(vs).

2.3. *X-ray crystallography*

Intensity data for **1** were collected at 293 K on a Bruker Smart CCD 1000 area detector, and those for **2** and **3** were obtained at 296 K on a Siemens P4 diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined by least-squares procedures on F_o^2 with SHELXL-97. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located geometrically and refined isotropically. Crystallographic data and structure refinement are given in table 1. Selected bond lengths and angles are listed in tables 2 and 3.

3. Results and discussion

3.1. *Synthesis and characterization*

The hydrothermal reaction of Ln_2O_3, CuO, isonicotinic acid, and H_2O in a molar ratio of 1 : 2 : 8 : 290 at 140°C resulted in formation of single crystals of $[CuLn_2(IN)_8(H_2O)_4]_n$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Gd(1)–O(5)	2.3281(14)	Gd(1)–O(4)#1	2.3284(15)
Gd(1)–O(3)	2.3392(15)	Gd(1)–O(6)#1	2.3486(15)
Gd(1)–O(9W)	2.3961(15)	Gd(1)–O(10W)	2.4399(15)
Gd(1)–O(2)	2.4628(14)	Gd(1)–O(1)	2.5322(14)
Cu(2)–O(7)	1.9782(13)	Cu(2)–O(7)#2	1.9782(13)
Cu(2)–N(3)	2.0123(15)	Cu(2)–N(3)#2	2.0123(15)
O(5)–Gd(1)–O(4)#1	77.02(7)	O(4)#1–Gd(1)–O(3)	121.27(6)
O(5)–Gd(1)–O(6)#1	121.06(6)	O(3)–Gd(1)–O(6)#1	75.64(6)
O(4)#1–Gd(1)–O(9W)	79.38(6)	O(2)–Gd(1)–O(1)	52.11(5)
O(9W)–Gd(1)–O(10W)	73.73(6)	O(5)–Gd(1)–O(2)	89.84(6)
O(3)–Gd(1)–O(2)	76.72(6)	O(9W)–Gd(1)–O(2)	99.44(6)
O(3)–Gd(1)–O(1)	75.28(5)	O(10W)–Gd(1)–O(1)	109.24(5)
O(7)–Cu(2)–O(7)#2	180.0	O(7)–Cu(2)–N(3)	90.71(6)
O(7)#2–Cu(2)–N(3)	89.29(6)	N(3)–Cu(2)–N(3)#2	180.0

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

Table 3. Selected bond lengths (Å) and angles (°) for **2** and **3**.

Dy–O(2)#1	2.300(3)	Dy–O(7)	2.298(3)
Dy–O(8)#1	2.313(3)	Dy–O(1)	2.324(3)
Dy–O(10)	2.366(3)	Dy–O(9)	2.409(3)
Dy–O(6)	2.433(3)	Dy–O(5)	2.513(3)
Cu–O(3)	1.976(3)	Cu–O(3)#2	1.976(3)
Cu–N(1)	2.004(3)	Cu–N(1)#2	2.004(3)
O(7)–Dy–O(2)#1	76.94(12)	O(7)–Dy–O(8)#1	121.52(12)
O(2)#1–Dy–O(1)	121.25(11)	O(8)#1–Dy–O(1)	75.69(12)
O(7)–Dy–O(10)	79.29(11)	O(6)–Dy–O(5)	52.71(9)
O(10)–Dy–O(9)	73.66(11)	O(2)#1–Dy–O(6)	89.43(11)
O(8)#1–Dy–O(6)	76.52(11)	O(10)–Dy–O(6)	99.76(11)
O(8)#1–Dy–O(5)	75.13(10)	O(9)–Dy–O(5)	109.42(10)
O(3)–Cu–O(3)#2	180.000(1)	O(3)–Cu–N(1)	89.27(12)
O(3)#2–Cu–N(1)	90.73(12)	N(1)–Cu–N(1)#2	180.00(17)
Er–O(2)#1	2.283(3)	Er–O(7)	2.276(3)
Er–O(8)#1	2.291(3)	Er–O(1)	2.299(3)
Er–O(10)	2.337(3)	Er–O(9)	2.391(3)
Er–O(6)	2.409(3)	Er–O(5)	2.490(3)
Cu–O(3)	1.983(3)	Cu–O(3)#2	1.983(3)
Cu–N(1)	2.005(3)	Cu–N(1)#2	2.005(3)
O(7)–Er–O(2)#1	77.34(12)	O(7)–Er–O(8)#1	121.84(12)
O(2)#1–Er–O(1)	121.63(11)	O(8)#1–Er–O(1)	75.55(12)
O(7)–Er–O(10)	79.41(12)	O(6)–Er–O(5)	52.95(9)
O(10)–Er–O(9)	73.38(11)	O(2)#1–Er–O(6)	88.90(11)
O(8)#1–Er–O(6)	76.43(11)	O(10)–Er–O(6)	99.60(11)
O(8)#1–Er–O(5)	74.94(10)	O(9)–Er–O(5)	109.34(10)
O(3)–Cu–O(3)#2	180.0	O(3)–Cu–N(1)	89.10(12)
O(3)#2–Cu–N(1)	90.90(12)	N(1)–Cu–N(1)#2	180.000(1)

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

complexes (Ln = Gd (**1**), Dy (**2**), Er(**3**)) in high purity and yield. It was found that the reaction took more time with decrease of the ionic radius of the lanthanide ions from Gd(III) to Er(III). The present polymers are different to those previously reported by Yang [16] obtained *via* the hydrothermal reactions with $CuCl_2 \cdot 2H_2O$ rather than CuO and under higher acidic and temperature conditions, indicating the effects of the starting materials and the conditions to the final products of the hydrothermal reaction. All three complexes display similar IR spectra, and all show the presence of isonicotinate and H_2O. Several strong peaks around 1561–1536 cm^{-1} due to $\upsilon_{as}(COO)$ and one broad strong absorption at 1421 cm^{-1} ascribed to $\upsilon_s(COO)$ are observed, suggesting the existence of different carboxylate coordination modes. The characteristic vibrational frequencies ($\nu_{(C=C+C=N)}$) of the isonicotinate pyridyl ring appear at 1608 and 1555 cm^{-1}, showing red-shift compared with those of free isonicotinic acid at 1616 and 1564 cm^{-1}. The OH vibrational absorption of H_2O is a strong and broad peak at about 3277 cm^{-1}.

3.2. *Crystal structure*

X-ray crystal diffraction studies reveal that **1**–**3** are isostructural. As representative, only the structure of **1** is described in detail herein. As shown in figure 1, the complex displays a one-dimensional chain (1-D) structure. The chain consists of two building blocks, $[Gd_2(IN)_6(H_2O)_4]$ and $[Cu(IN)_2]$, which are linked to each other by isonicotinate ligands through Cu–N bonds. As shown in figure 2, the Gd(III) in $[Gd_2(IN)_6(H_2O)_4]$ is coordinated by eight oxygen atoms in a distorted square antiprism with four from bridging carboxylate oxygens of four IN ligands, two from chelating carboxylate oxygens of a IN ligand and two from coordinated water. Two Gd(III) ions are connected by four bridging carboxylate groups of four IN ligands with a Gd $\cdots$ Gd distance of 4.504 Å. The Gd–O bonds show typical lengths ranging from 2.3281(14) to 2.5322(14) Å. The Cu(II) in $[Cu(IN)_2]$ is coordinated by two nitrogen and two oxygen atoms from four different IN ligands in an exactly square planar geometry with the Cu–O and Cu–N distances of 1.9782(13) Å and 2.0123(15) Å, respectively. Two weak Cu–N bonds with a distance of 2.644(3) Å on both sides of the square planar copper center are observed, in which the coordination N atoms come from pyridyl groups of two IN ligands bridging two Gd(III) ions via carboxylates in two adjacent molecular chains.

Four types of IN ligands are present in **1**; the first is bidentate bridging connecting two Gd(III) ions via carboxylate, the second is bidentate chelating binding to a Gd(III) ion via carboxylate, the third is monodentate coordinating to a Cu(II) via a oxygen of carboxylate, and the final is tridentate bridging, linking two Gd(III) and a Cu(II) via two carboxyl oxygen atoms and a pyridyl nitrogen atom. The uncoordinated oxygen atoms of IN with the third mode and the chelating carboxylate oxygen atoms of IN with the second mode form hydrogen bonds with coordinated water molecules [O(10W)–H $\cdots$ $O(8)^{i}$ 2.775(2) Å and O(9W)–H $\cdots$ $O(1)^{ii}$ 2.783(2) Å; symmetry mode: i: $x-1$, y, z; ii: $-x$, $-y+1$, $-z$], which links the 1-D chains of the complex into a two-dimensional layer (figure 3). The uncoordinated nitrogen atoms of IN with the second

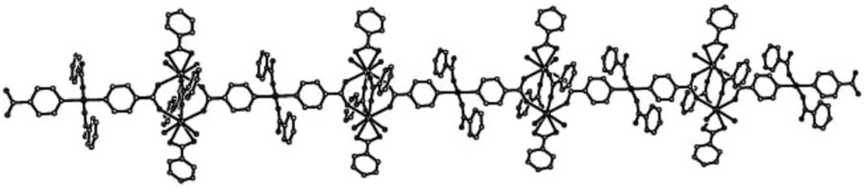

Figure 1. Illustration of 1-D chain of **1**.

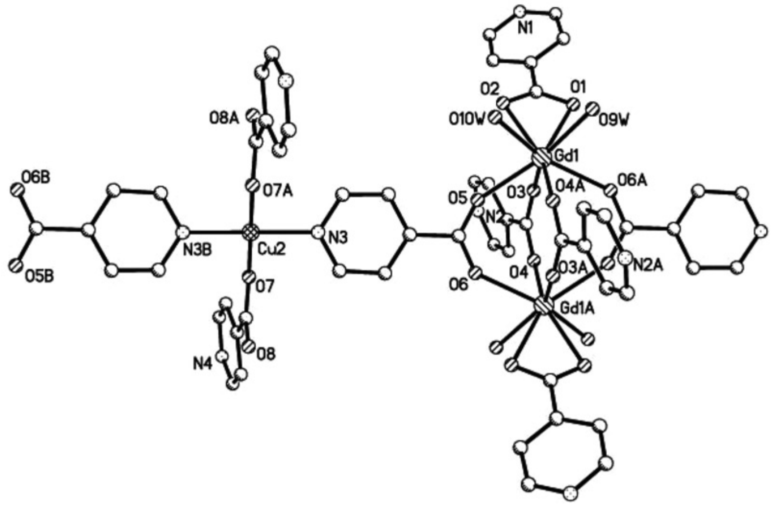

Figure 2. Coordination environments of Gd(III) and Cu(II) centers in **1**.

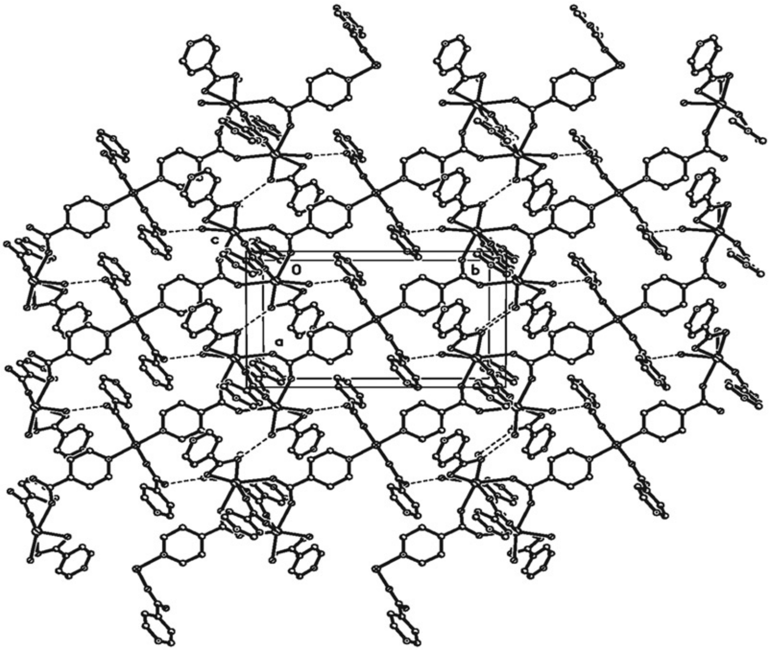

Figure 3. Two-dimensional structure of 1 built by H-bonds (along *c*-axis).

and the third mode form hydrogen bonds with coordinated water molecules [O(10W)–H $\cdots$ N(1)$^{\text{iii}}$ 2.880(3) Å and O(9W)–H $\cdots$ N(4)$^{\text{iv}}$ 2.804(3) Å; symmetry mode: iii: $x+1/2$, $-y+3/2$, $z-1/2$; iv: $x-3/2$, $-y+3/2$, $z-1/2$], which extends the layers into a three-dimensional structure.

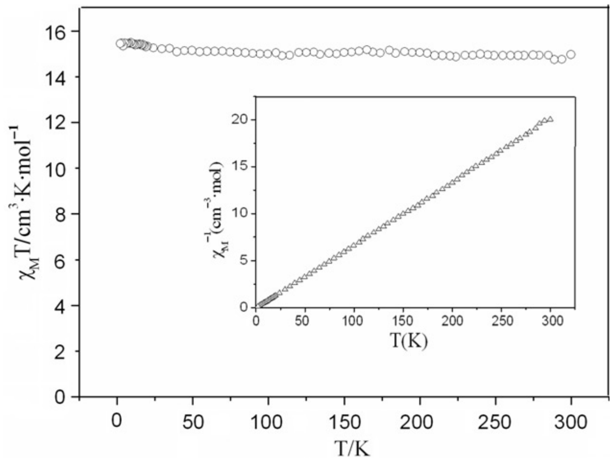

Figure 4. Experimental $\chi_M T$ *vs.* T curves for **1**.

3.3. *Magnetic properties of 1*

The molar magnetic susceptibility of **1** was measured between 2 and 300 K, under an applied field of 2000 Oe. The experimental results for the temperature dependence of the product $\chi_M T$ are shown in figure 4. $\chi_M T$ is $14.96\,\mathrm{cm^3\,K\,mol^{-1}}$ at 300 K. As the temperature is lowered, the $\chi_M T$ value increases very slowly and reaches $15.44\,\mathrm{cm^3\,K\,mol^{-1}}$ at 2 K. In the $1/\chi_M$ *versus* T plot (insert of figure 4), the observed susceptibility data are well-fitted to the Curie–Weiss law ($\chi_M = C/(T - \Theta)$), with Weiss constant $\Theta = 0.7027$ K and $C = 14.9009\,\mathrm{K\,cm^3\,mol^{-1}}$. The magnetic behavior of **1** with a very slow $\chi_M T$ variation and a small Θ value is quite similar to that exhibited by Gd–Cu polymer with pyridine-2,5-dicarboxylic acid as ligand [18]. The low positive value of Θ indicates a very weak ferromagnetic interaction between metal centres in the complex. It can be inferred from the structure of **1** that this magnetic interaction happens mainly between two carboxylate bridged Gd(III) ions, while that between Gd(III) and Cu(II) ions connected by a long isonicotinate bridge can be ignored.

Supplementary material

Crystallographic data for the structures given in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 613300-613302. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgement

This work is supported by the National Natural Science Foundation of China (No. 20461001) and the Education Department of Guangxi Province.

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