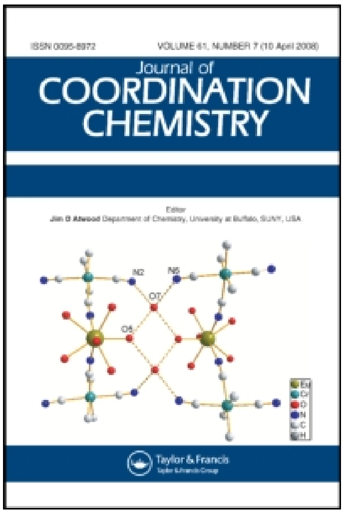

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structure of [Ln(4-Pyta)$_3$(H$_2$O)$_2$]<i>_n (Ln = Nd, Ce, Eu, Gd; 4-Pyta = 4-pyridylthioacetate)

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To cite this Article Li, Wen Ge , Pan, Zhao Rui , Li, Yi-Zhi and Zheng, He Gen(2008) 'Synthesis and crystal structure of [Ln(4-Pyta)$_3$(H$_2$O)$_2$]<i>_n (Ln = Nd, Ce, Eu, Gd; 4-Pyta = 4-pyridylthioacetate)', Journal of Coordination Chemistry, 61: 24, 3953 — 3959

To link to this Article: DOI: 10.1080/00958970802183844

URL: http://dx.doi.org/10.1080/00958970802183844

Journal of Coordination Chemistry
Vol. 61, No. 24, 20 December 2008, 3953–3959

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Synthesis and crystal structure of [Ln(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (Ln = Nd, Ce, Eu, Gd; 4-Pyta = 4-pyridylthioacetate)

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(*Received 1 December 2007; in final form 7 March 2008*)

Four new lanthanide complexes, [Nd(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**1**), [Ce(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**2**), [Eu(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**3**) and [Gd(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**4**), have been obtained from reaction of lanthanide(III) nitrate with 4-Pyta (4-pyridylthioacetate) in water. Their structures were characterized by elemental analysis, infrared spectroscopy and single-crystal X-ray diffraction. The crystals belong to triclinic, space group $P\bar{1}$ and all complexes exhibit one-dimensional chains that arrange to form a three-dimensional supramolecular architecture by hydrogen bonds between the chains.

Keywords: 4-Pyridylthioacetate; Lanthanide complex; Crystal structure; Hydrothermal synthesis

1. Introduction

Metal-organic coordination polymers with fascinating network topologies have attracted considerable attention in the last two decades due to their potential applications in ion exchange, separation, catalysis, molecular magnetism and electrical conductivity [1–5]. Versatile multidentate organic ligands, such as benzenedicarboxylic acid, benzenetricarboxylic acid, sulfoisophthalic acid, picolinic acid and hydroxypicolinic acid, coordinated with a wide range of metals to form chain, layer and network structures [6–15]. Previous studies of 4-pyridylthioacetate revealed the coordination of 4-Pyta with transition metal ions [16–18]. In this article we report the synthesis and characterization of four one-dimensional supramolecular lanthanide complexes, [Nd(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**1**), [Ce(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**2**), [Eu(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**3**), and [Gd(4-Pyta)$_3$(H$_2$O)$_2$]$_n$ (**4**), in which three-dimensional supramolecular architectures are constructed by intermolecular hydrogen bonds.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802183844

2. Experimental

2.1. *Materials and physical measurement*

All starting materials were from commercial sources of analytical grade without purification prior to use. IR spectra were recorded on a VECTOR-22 spectrometer with KBr discs in the range 400–4000 cm^{-1}. Elemental analyses were performed on a Perkin-Elmer 240 C. Single crystal data collection was carried out on a Bruker Smart Apex CCD diffractometer.

2.2. *Synthesis of* $[Nd(3\text{-}Pyta)_3(H_2O)_2]_n$ *(1)*

4-Pyridylthioacetic acid (0.085 g, 0.5 mmol) and NaOH (0.02 g, 0.5 mmol) in hot distilled water (20 mL) were stirred for 3 h. To the above solution was added a dilute aqueous solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.111 g, 0.25 mmol) and violet precipitate formed immediately. The slurry was further vigorously stirred under heating for 6 h and then filtered after cooling to room temperature. The violet block single crystals of $[Nd(4\text{-}Pyta)_3(H_2O)_2]_n$ were obtained by slow evaporation of the solvent within five days and washed with distilled water and then dried naturally (yield: 55% based on neodymium nitrate). Anal. Calcd for $C_{21}H_{22}N_3O_8S_3Nd$: C, 36.80%; H, 3.21%; N, 6.13%. Found: C, 36.60%; H, 3.11%; N, 6.01%. Main IR bands (cm^{-1}): 3411(w), 2970(w), 1581(vs), 1485(w), 1412(m), 1392(s).

2.3. *Synthesis of* $[Ce(3\text{-}Pyta)_3(H_2O)_2]$ *(2)*

Complex **2** was synthesized as colorless block single crystals by the same procedure as described above, using $Ce(NO_3)_3 \cdot 6H_2O$ in place of $Nd(NO_3)_3 \cdot 6H_2O$. Yield: 52% based on cerium nitrate. Anal. Calcd for $C_{21}H_{22}N_3O_8S_3Ce$: C, 37.02%; H, 3.23%; N, 6.17%. Found: C, 37.21%; H, 3.04%; N, 6.09%. Main IR bands (cm^{-1}): 3411(w), 2972(w), 1580(vs), 1536(m), 1485(w), 1411(m), 1390(s).

2.4. *Synthesis of* $[Eu(3\text{-}Pyta)_3(H_2O)_2]$ *(3)*

Complex **3** was synthesized as colorless block single crystals by the same procedure as described above using $Eu(NO_3)_3 \cdot 6H_2O$ in place of $Nd(NO_3)_3 \cdot 6H_2O$. Yield: 49% based on europium nitrate. Anal. Calcd for $C_{21}H_{22}N_3O_8S_3Eu$: C, 36.38%; H, 3.18%; N, 6.06%. Found: C, 36.59%; H, 3.27%; N, 6.24%. Main IR bands (cm^{-1}): 3423(w), 2924(w), 1586(vs), 1485(w), 1415(m), 1385(s).

2.5. *Synthesis of* $[Gd(3\text{-}Pyta)_3(H_2O)_2]_n$ *(4)*

Complex **4** was synthesized as colorless block single crystals by the same procedure as described above using $Gd(NO_3)_3 \cdot 6H_2O$ in place of $Nd(NO_3)_3 \cdot 6H_2O$. Yield: 48% based on gadolinium nitrate. Anal. Calcd for $C_{21}H_{22}N_3O_8S_3Gd$: C, 36.11%; H, 3.15%; N, 6.01%. Found: C, 36.32%; H, 3.26%; N, 6.12%. Main IR bands (cm^{-1}): 3406(w), 2924(w), 1586(vs), 1415(w), 1413(m), 1384(s).

Table 1. Crystallographic data for $[Nd(4\text{-}Pyta)_3(H_2O)_2]_n$ (**1**), $[Ce(4\text{-}Pyta)_3(H_2O)_2]_n$ (**2**), $[Eu(4\text{-}Pyta)_3(H_2O)_2]_n$ (**3**) and $[Gd(4\text{-}Pyta)_3(H_2O)_2]_n$ (**4**).

Compound	**1**	**2**	**3**	**4**
Formula	$C_{21}H_{22}N_3NdO_8S_3$	$C_{21}H_{22}CeN_3O_8S_3$	$C_{21}H_{22}EuN_3O_8S_3$	$C_{21}H_{22}GdN_3O_8S_3$
Mr	684.84	680.72	692.56	697.85
Crystal size (mm^3)	0.34 × 0.20 × 0.16	0.36 × 0.20 × 0.18	0.32 × 0.18 × 0.16	0.30 × 0.19 × 0.18
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	9.109(3)	9.104(2)	9.1144(4)	9.1084(5)
b	11.881(3)	11.923(3)	11.8566(5)	11.8411(6)
c	12.196(3)	12.196(3)	12.2068(5)	12.1998(7)
α	79.855(5)	79.858(4)	79.7780(10)	79.7540(10)
β	74.159(5)	74.196(4)	74.1300(10)	74.1620(10)
γ	84.977(5)	84.990(5)	84.8300(10)	84.8070(10)
V (Å^3)	1248.9(6)	1252.8(5)	1247.51(9)	1244.43(12)
ρ_{Calcd} (g cm^{-3})	1.821	1.805	1.844	1.862
T (K)	293(2)	293(2)	293(2)	293(2)
θ range (°)	1.74–25.50	2.27–25.0	1.75–26.00	1.75–26.00
Goodness-of-fit on F^2	1.067	1.003	1.020	1.016
Z	2	2	2	2
λ (Mo-$K\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	2.381	2.118	2.817	2.968
R_1	0.0503	0.0308	0.0270	0.0285
wR_2	0.1146	0.0646	0.0672	0.0693

$W^{-1} = 1/[\sigma^2(F_0)^2 + (XP)^2 + YP]$, $P = (F_o^2 + 2F_c^2)/3$, $X = 0.0217$, $Y = 0$ (**1**); $X = 0.070$, $Y = 1.9900$ (**2**); $X = 0.0415$, $Y = 0$ (**3**); $X = 0.0401$, $Y = 0$ (**4**).

3. X-ray crystallography

The single crystal was mounted on a glass fiber for data collection. Single crystal X-ray diffraction measurements were carried out with a Bruker Smart Apex CCD diffractometer equipped with a Mo-Kα radiation ($\lambda = 0.71073$ Å) by using an ω–φ scan mode at 293(2) K. The raw data were reduced and corrected for Lorentz and polarization effects using the SAINT program and for absorption using SADABS. All non-hydrogen atoms were located by direct methods and refined anisotropically. The hydrogen atoms were located from difference Fourier syntheses and allowed to ride on the parent atoms [19]. The relevant crystallographic data are presented in table 1 while selected bond lengths and angles are given in table 2.

4. Results and discussion

The structures of **1**–**4** are similar, only **1** is discussed in detail here. The molecular structure of **1** is shown in figure 1. Each Nd(III), surrounded by nine oxygens, is in a distorted coordination environment. Each structural unit consists of one Nd(III) ion, three 4-pyridylthioacetates and two crystal water molecules forming the nine-coordinate distorted polyhedron, in which Nd(III) coordinates to seven O atoms from four 4-pyta ligands and two O atoms from two coordinated H_2O molecules. O(3), O(4), O(5) and O(6) come from two carboxyl groups of 4-pyridylthioacetate, O(1), O2b and O6a from other three carboxyl groups of 4-pyridylthioacetate, and O(7) and O(8) from two coordinated H_2O molecules. The bond distances of Nd(III)–O range from

Table 2. Bond distance (Å) and angle (°) around Ln (Ln = Ce, Nd, Eu, Gd) in [Ln(4-pyta)$_3$(H$_2$O)$_2$].

1		**2**		**3**		**4**	
Nd1–O2	2.336(5)	Ce1–O6	2.376(3)	Eu1–O6	2.298(2)	Gd1–O5	2.281(3)
Nd1–O6	2.412(4)	Ce1–O2	2.436(2)	Eu1–O2	2.367(2)	Gd1–O4	2.358(2)
Nd1–O7	2.434(5)	Ce1–O8	2.529(3)	Eu1–O8	2.456(2)	Gd1–O8	2.439(2)
Nd1–O1	2.481(4)	Ce1–O5	2.534(2)	Eu1–O10	2.464(2)	Gd1–O6	2.448(2)
Nd1–O4	2.545(5)	Ce1–O3	2.540(3)	Eu1–O3	2.488(2)	Gd1–O1	2.487(2)
Nd1–O3	2.557(6)	Ce1–O7	2.567(3)	Eu1–O4	2.515(2)	Gd1–O2	2.500(3)
Nd1–O5	2.570(4)	Ce1–O4	2.589(3)	Eu1–O7	2.528(2)	Gd1–O7	2.516(3)
Nd1–O8	2.574(5)	Ce1–O1	2.608(3)	Eu1–O1	2.531(2)	Gd1–O3	2.519(2)
Nd1–O6	2.631(4)	Ce1–O2	2.673(2)	Eu1–O2	2.637(2)	Gd1–O4	2.629(2)
O2–Nd1–O6	154.6(2)	O6–Ce1–O2	154.66(10)	O6–Eu1–O2	152.51(9)	O5–Gd1–O4	152.26(10)
O2–Nd1–O7	81.57(19)	O6–Ce1–O8	81.31(9)	O6–Eu1–O8	79.62(8)	O5–Gd1–O8	79.42(9)
O6–Nd1–O7	79.92(16)	O2–Ce1–O8	79.32(8)	O2–Eu1–O8	80.13(8)	O4–Gd1–O8	80.15(8)
O2–Nd1–O1	104.96(15)	O6–Ce1–O5	107.33(9)	O6–Eu1–O10	103.98(8)	O5–Gd1–O6	103.54(9)
O6–Nd1–O1	78.86(14)	O2–Ce1–O5	77.35(8)	O2–Eu1–O10	79.74(7)	O4–Gd1–O6	80.16(8)
O7–Nd1–O1	139.48(16)	O8–Ce1–O5	137.81(9)	O8–Eu1–O10	138.64(8)	O8–Gd1–O6	138.68(8)
O2–Nd1–O4	76.62(19)	O6–Ce1–O3	76.72(9)	O6–Eu1–O3	76.49(8)	O5–Gd1–O1	76.51(9)
O6–Nd1–O4	127.58(15)	O2–Ce1–O3	127.56(8)	O2–Eu1–O3	129.48(7)	O4–Gd1–O1	129.69(8)
O7–Nd1–O4	145.10(17)	O8–Ce1–O3	146.61(8)	O8–Eu1–O3	144.91(8)	O8–Gd1–O1	144.77(8)
O1–Nd1–O4	73.32(15)	O5–Ce1–O3	73.59(8)	O10–Eu1–O3	72.82(8)	O6–Gd1–O1	72.68(8)
O2–Nd1–O3	126.30(19)	O6–Ce1–O7	76.04(9)	O6–Eu1–O4	127.72(8)	O5–Gd1–O2	127.86(9)
O6–Nd1–O3	78.95(15)	O2–Ce1–O7	82.15(8)	O2–Eu1–O4	79.57(7)	O4–Gd1–O2	79.67(8)
O7–Nd1–O3	136.53(15)	O8–Ce1–O7	70.39(8)	O8–Eu1–O4	138.18(8)	O8–Gd1–O2	138.36(9)
O1–Nd1–O3	71.36(15)	O5–Ce1–O7	71.97(8)	O10–Eu1–O4	71.70(8)	O6–Gd1–O2	71.82(9)
O4–Nd1–O3	50.44(14)	O3–Ce1–O7	126.49(8)	O3–Eu1–O4	51.98(7)	O1–Gd1–O2	52.07(8)
O2–Nd1–O5	78.75(16)	O6–Ce1–O4	126.07(10)	O6–Eu1–O7	73.79(8)	O5–Gd1–O7	73.70(9)
O6–Nd1–O5	113.30(14)	O2–Ce1–O4	79.20(8)	O2–Eu1–O7	82.02(8)	O4–Gd1–O7	81.90(8)
O7–Nd1–O5	76.56(16)	O8–Ce1–O4	137.54(8)	O8–Eu1–O7	70.46(7)	O8–Gd1–O7	70.52(8)
O1–Nd1–O5	143.84(15)	O5–Ce1–O4	70.54(9)	O10–Eu1–O7	71.23(8)	O6–Gd1–O7	70.99(8)
O4–Nd1–O5	72.71(15)	O3–Ce1–O4	50.31(8)	O3–Eu1–O7	125.20(7)	O1–Gd1–O7	125.09(8)
O3–Nd1–O5	77.66(15)	O7–Ce1–O4	140.87(8)	O4–Eu1–O7	140.89(8)	O2–Gd1–O7	140.69(9)
O2–Nd1–O8	75.04(18)	O6–Ce1–O1	78.01(8)	O6–Eu1–O1	79.15(8)	O5–Gd1–O3	79.10(9)
O6–Nd1–O8	82.75(16)	O2–Ce1–O1	113.61(8)	O2–Eu1–O1	114.38(7)	O4–Gd1–O3	114.55(8)
O7–Nd1–O8	71.87(16)	O8–Ce1–O1	78.60(8)	O8–Eu1–O1	78.04(8)	O8–Gd1–O3	77.99(8)
O1–Nd1–O8	71.51(15)	O5–Ce1–O1	143.28(9)	O10–Eu1–O1	143.31(8)	O6–Gd1–O3	143.33(8)
O4–Nd1–O8	126.44(15)	O3–Ce1–O1	72.49(8)	O3–Eu1–O1	72.52(7)	O1–Gd1–O3	72.51(8)
O3–Nd1–O8	141.04(16)	O7–Ce1–O1	141.95(8)	O4–Eu1–O1	77.71(8)	O2–Gd1–O3	77.93(9)
O5–Nd1–O8	141.29(16)	O4–Ce1–O1	77.18(8)	O7–Eu1–O1	141.39(8)	O7–Gd1–O3	141.36(9)
O2–Nd1–O6	123.31(15)	O6–Ce1–O2	122.60(8)	O6–Eu1–O2	123.98(8)	O5–Gd1–O4	124.17(9)
O6–Nd1–O6	64.01(16)	O2–Ce1–O2	64.51(9)	O2–Eu1–O2	64.33(8)	O4–Gd1–O4	64.24(9)
O7–Nd1–O6	67.36(15)	O8–Ce1–O2	69.33(8)	O8–Eu1–O2	69.37(7)	O8–Gd1–O4	69.50(8)
O1–Nd1–O6	129.69(13)	O5–Ce1–O2	127.76(8)	O10–Eu1–O2	130.20(7)	O6–Gd1–O4	130.49(8)
O4–Nd1–O6	102.92(15)	O3–Ce1–O2	102.18(8)	O3–Eu1–O2	103.93(7)	O1–Gd1–O4	104.02(8)
O3–Nd1–O6	69.26(15)	O7–Ce1–O2	131.29(8)	O4–Eu1–O2	68.92(7)	O2–Gd1–O4	68.95(8)
O5–Nd1–O6	49.30(13)	O4–Ce1–O2	68.41(8)	O7–Eu1–O2	130.86(7)	O7–Gd1–O4	130.89(8)
O8–Nd1–O6	130.62	O1–Ce1–O2	49.10(7)	O1–Eu1–O2	50.05(7)	O3–Gd1–O4	50.30(7)

2.336(5) Å to 2.631(4) Å, and all the Nd(III)–O bond distances are normal. All adjacent bond angles are in the range 49.30(13)° to 154.2(6)°. Two atomic bridges (–OCO–) connect two neighboring Nd(III) atoms to form one-dimensional architecture (figure 2). 4-pyta has two coordination modes, two O atoms in carboxyl coordinated to two different Nd atoms and other is one O atom from carboxyl coordinated to Nd and the other O atom coordinated with two Nd atoms. Analysis of crystal packing reveals the existence of three types of hydrogen bonds between one-dimensional chains, namely O7–H7A···N1 (symmetry code: x, $1+y$, z), O7–H7B···O3

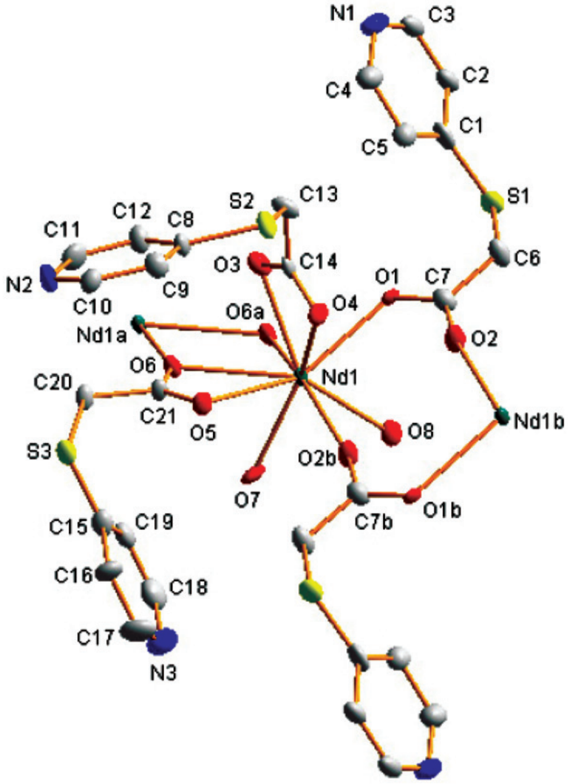

Figure 1. An ORTEP drawing of **1** showing 30% ellipsoid probability (hydrogen atoms are omitted for clarity). Symmetry code: a = $-x$, $2-y$, $1-z$; b = $1-x$, $2-y$, $1-z$.

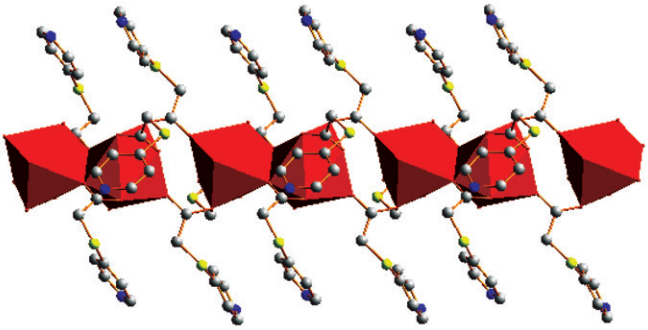

Figure 2. 1-D chain of **1** (irrelevent hydrogen atoms are omitted for clarity).

(symmetry code: $-x$, $2-y$, $1-z$), O8–H8A $\cdots$ O4 (symmetry code: $1-x$, $2-y$, $1-z$), forming a 2-D layer structure [figure 3(a)]. A 3-D network is formed by linking 2-D layers through an intermolecular hydrogen bond, O8–H8B $\cdots$ N2 (symmetry code: x, y, $1+z$) [figure 3(b)]. Thermogravimetric analyses of **1–4** are shown in figure 4, the initial weight loss temperature of **1** and **2** is about 120 °C, and for **3** and **4** about 140°C.

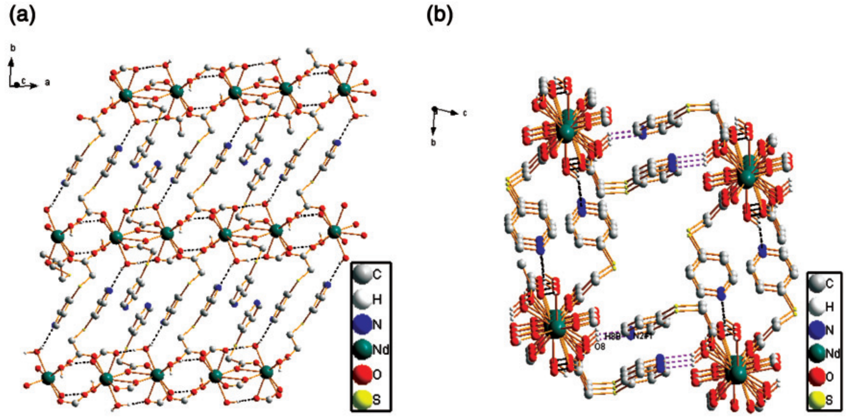

Figure 3. (a) 2-D and (b) 3-D networks in **1** (irrelevent hydrogen atoms are omitted for clarity).

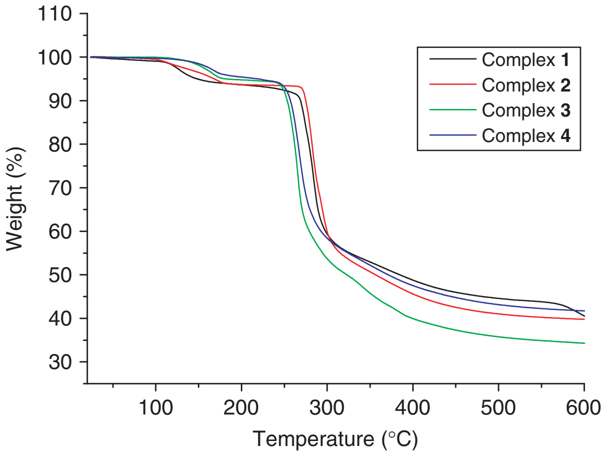

Figure 4. TGA curves of **1–4**.

Except for the initial weight loss temperature, thermogravimetric analysis curves of **1–4** are similar, with two main continuous weight losses. Complex **1** will be used as an example. The first step is from 120°C to 160°C with 5.4% weight loss, corresponding to loss of two coordinated water molecules (calculated 5.26%). The second step occurring from 160 to 500°C is the stage at which **1** loses its organic component.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 666987 for **1**, 666990 for **2**, 666989 for **3** and 666988 for **4**. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Natural Science Foundation (No. 20571039) and the Ministry of Education of China (No. 20050284031).

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