

# Influence of reaction conditions on the channel shape of 3d-4f heterometallic metal–organic framework†‡

Xiang-Jian Kong,<sup>a</sup> Yan-Ping Ren,<sup>b</sup> La-Sheng Long,<sup>\*a</sup> Rong-Bin Huang,<sup>a</sup> Lan-Sun Zheng<sup>a</sup> and Mohamedally Kurmoo<sup>\*c</sup>

Received 25th March 2008, Accepted 16th July 2008

First published as an Advance Article on the web 5th August 2008

DOI: 10.1039/b804966a

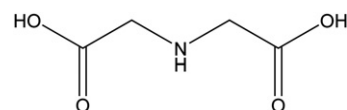
Three structural kinds of 3d-4f metal–organic-frameworks (MOFs),  $\{[\text{Ln}_4(\text{ox})_3(\text{Ni}(\text{IDA})_2)_3(\text{H}_2\text{O})_6]\}_n \cdot x n \text{H}_2\text{O}$  (Type I: Ln=La, Nd, Eu, Gd; IDA = iminodiacetate, ox = oxalate),  $\{[\text{Ln}_2(\text{ox})(\text{Ni}(\text{IDA})_2)_2(\text{H}_2\text{O})_2]\}_n \cdot 2n \text{H}_2\text{O}$  (Type II: Ln=La, Pr, Nd, Eu) and  $\{[\text{Dy}_2(\text{ox})_2(\text{Ni}(\text{IDA})_2(\text{H}_2\text{O})_2)]\}_n \cdot 2n \text{H}_2\text{O}$  (Type III), have been synthesized under hydrothermal condition. The crystal structures consist of Ln-oxalate tetramers for Type I, dimers for Type II and one-dimensional polymers for Type III bridged by the metalloligand  $[\text{Ni}(\text{IDA})_2]^{2-}$ . While Type I contains a mixture of “ $\text{Ln}_6\text{Ni}_4$ -parallelogram” (A-Type) and “ $\text{Ln}_6\text{Ni}_2$ -parallelogram” (B-Type) channels, Type II and Type III contain only A-type and B-type channels, respectively. A fairly high stability of the MOFs is indicated by thermogravimetric analyses and reversible dehydration and rehydration of guest water molecules, which is confirmed by single crystal-to-single crystal transformation of **1** and **5**.

The construction of heterometallic metal–organic frameworks, such as, 3d-4f and 3d-5f metal systems, are currently of interest because of their structural diversity and potential applications in magnetism, catalysis, separation, gas storage and molecular recognition.<sup>1–3</sup> However, owing to the variable and versatile coordination behavior of 4f metals<sup>4</sup> as well as the competitive reactions between 3d and 4f

metals chelating to the same ligand,<sup>5</sup> the construction of 3d-4f metal–organic frameworks is mainly focused on those containing one single ligand<sup>4–7</sup> and the utilization of mixed ligands to construct heterometallic metal–organic framework is rather limited.<sup>8</sup> In particular, how to control the shape and/or the size of cavity/channel of heterometallic MOFs remains a great challenge. Here, we report the syntheses and crystal structures of a novel family of 3d-4f heterometallic MOFs, namely,  $\{[\text{Ln}_4(\text{ox})_3(\text{Ni}(\text{IDA})_2)_3(\text{H}_2\text{O})_6]\}_n \cdot x n \text{H}_2\text{O}$  (Ln=La (**1**),  $x = 3$ , Nd (**2**),  $x = 2$ , Eu (**3**),  $x = 2$ , Gd (**4**),  $x = 2$ ; IDA = iminodiacetate (Scheme 1), ox = oxalate),  $\{[\text{Ln}_2(\text{ox})(\text{Ni}(\text{IDA})_2)_2(\text{H}_2\text{O})_2]\}_n \cdot 2n \text{H}_2\text{O}$  (Ln=La (**5**), Pr (**6**), Nd (**7**), Eu (**8**)) and  $\{[\text{Dy}_2(\text{ox})_2(\text{Ni}(\text{IDA})_2(\text{H}_2\text{O})_2)]\}_n \cdot 2n \text{H}_2\text{O}$  (**9**). The most interesting of these results is the occurrence of two types of channels in Type I MOFs (**1–4**) characterized by “ $\text{Ln}_6\text{Ni}_4$ -parallelogram” (A-type channel) and “ $\text{Ln}_6\text{Ni}_2$ -parallelogram” (B-type channel), while Type II MOFs (**5–8**) contain only A-type channel, and Type III MOF (**9**) contains only B-type channel, revealing that the shape and size of the channel of 3d-4f MOFs can be controlled by the reaction conditions.

The nine metal–organic-frameworks described this work are formed of lanthanide cations connected by two different bridging units, the oxalate ion and a metalloligand consisting of *fac*- $\text{Ni}^{\text{II}}(\text{IDA})_2^{2-}$  which has four divergent carboxylate oxygen atoms (Fig. S1, ESI).† When the oxalate ion is generated in hydrothermal reactions, different crystal phases are obtained compared to when oxalate ion is added in the reaction mixture.

Complex **1**, a representative of Type I, consists of four La(III), three  $[\text{Ni}(\text{IDA})_2]^{2-}$ , three  $\text{ox}^{2-}$  and nine water molecules. Analyses of the diffraction data reveal two independent La(III) centers in the crystal structure of **1** (Fig. 1) which are both nine-coordinated but have different geometries. La1 adopts a tri-capped trigonal prism geometry and is coordinated by two  $[\text{Ni}(\text{IDA})_2]^{2-}$ , one as a bidentate and the other as monodentate ligand, two bidentate  $\text{ox}^{2-}$  and two water molecules. La2 adopts a capped square antiprism geometry and is coordinated by four metalloligands, with two bidentate and two monodentate, one bidentate  $\text{ox}^{2-}$  and one molecule of water. The range of the bond lengths for Ni–N, Ni–O and La–O are 2.033(3)–2.064(3), 2.005(3)–2.071(3) and 2.395(3)–2.677(3) Å, respectively, being normal even if slightly shorter than those reported for a nine-coordinated La–Ni-complex.<sup>9</sup> The key feature of this structure is the formation of  $\text{La}_4(\text{ox})_3$  tetramers connected by



Scheme 1 The structure of IDA ligand.

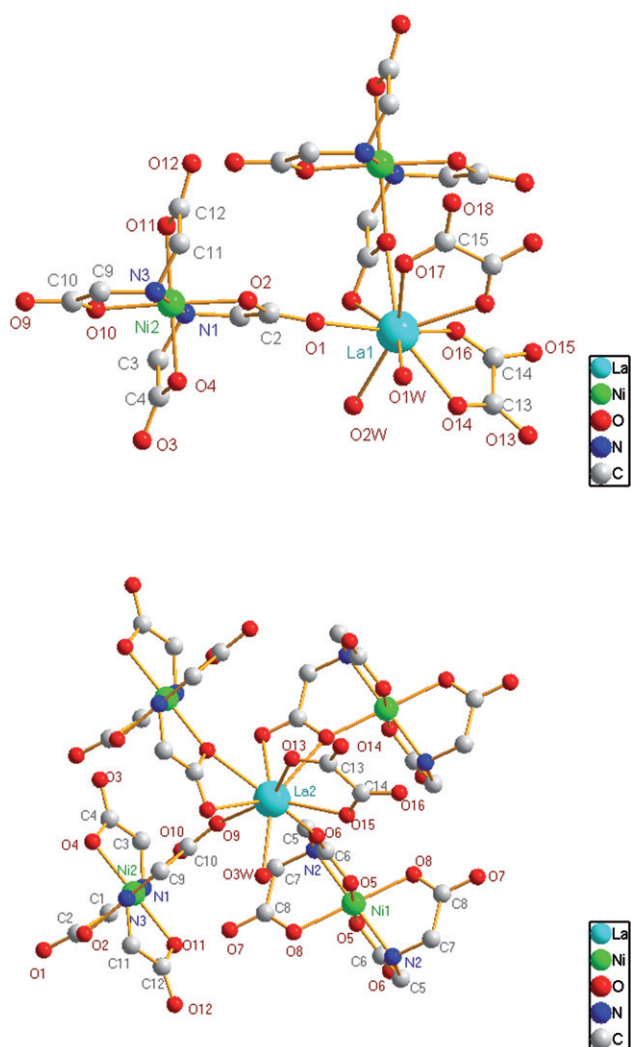
<sup>a</sup>State Key Laboratory of Physical Chemistry of solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China. E-mail: lslong@xmu.edu.cn

<sup>b</sup>Key Laboratory of Analytical Sciences, Ministry of Education and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China

<sup>c</sup>Laboratoire de Chimie de Coordination Organique, CNRS-UMR7140, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France. E-mail: kurmoo@chimie.u-strasbg.fr; Fax: +86-592-2183047

† Electronic supplementary information (ESI) available: Preparation data for compounds **1–9**. CCDC reference numbers 647829–647839. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b804966a

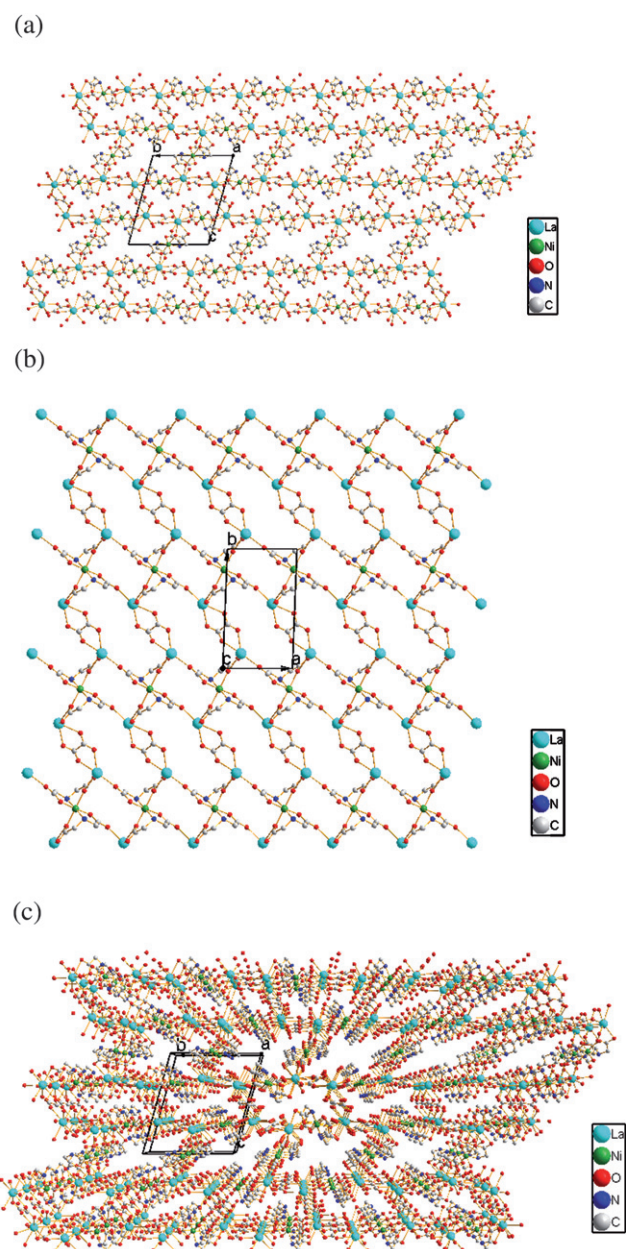
‡ Single-crystal X-ray structure determination: Data were collected on a Bruker SMART Apex CCD diffractometer at 123 K for **1**, **3**, **6**, **7**, **8** and **9** and at 298 K for **1a**, **2**, **4**, **5** and **5a**. Absorption corrections were applied using the multiscan program SADABS.<sup>12</sup> The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically by the least-squares method on  $F^2$  using the SHELXTL program.<sup>13</sup> The hydrogen atoms of the organic ligand were generated geometrically (C–H, 0.96 Å, N–H, 0.90 Å). Crystal data, as well as details of the data collection and refinement for the complexes are summarized in Table 1. CCDC 647829–647839 (complexes **1** to **9**, respectively). The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif.



**Fig. 1** Ball and stick plot showing the coordination environment of two independent La(III) centers in **1** (hydrogen atoms are omitted for clarity).

$[\text{Ni}(\text{IDA})_2]^{2-}$  metalloligands. From another point of view, one may regard this structure as two adjacent La(III) centers alternately connected by an  $\text{ox}^{2-}$  ligand and a  $[\text{Ni}(\text{IDA})_2]^{2-}$  to generate a 1D chain of  $\{[\text{La}_2(\text{H}_2\text{O})_3(\text{ox})\text{Ni}(\text{IDA})]\}_n^{2n+}$  that is further extended into a 1D ladder of  $\{[\text{La}_4(\text{ox})_3\text{Ni}_2(\text{IDA})_2]\}_n^{2n+}$  (along the *b*-axis) through  $\text{ox}^{2-}$  coordinating to the La(III) cations. The 2D (*bc*-face) structure in **1** can be viewed as the connection of two adjacent 1D ladders through coordination of the  $[\text{Ni}(\text{IDA})_2]^{2-}$  to the La(III) centers. This linking mode generates a structure containing two types of parallelogram channels, *i.e.*, a  $9.12 \times 12.81 \text{ \AA}$  “ $\text{La}_6\text{Ni}_4$ ” (namely, A-type) and a  $6.48 \times 12.81 \text{ \AA}$  “ $\text{La}_6\text{Ni}_2$ ” (namely, B-type). The adjacent chains of  $\{[\text{La}_2(\text{H}_2\text{O})_3(\text{ox})\text{Ni}(\text{IDA})]\}_n^{2n+}$  are connected to each other through uncoordinated carboxylate oxygen atoms of the  $[\text{Ni}(\text{IDA})_2]^{2-}$  along the the *a*-axis forming layers in the *ab*-plane, as shown in Fig. 2b. Adjacent layers are further linked alternately by oxalate and  $[\text{Ni}(\text{IDA})_2]^{2-}$  units, generating the 3D structure (namely, Type I MOF) with two kinds of channels as shown in Fig. 2c. The guest water molecules are located only in the A-type channel and hydrogen-bonded to its host.

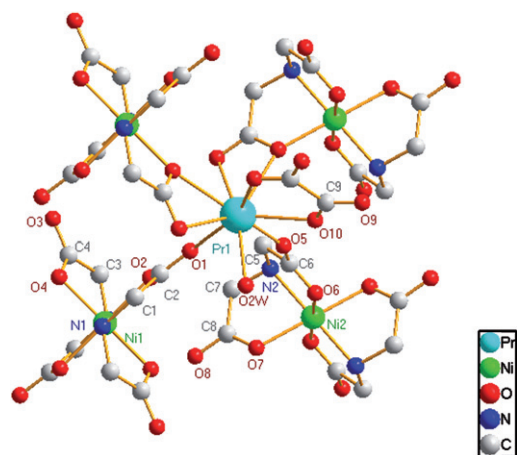
Complexes **2**, **3** and **4** are isomorphs of **1**, except for the number of guest water molecules which may be a consequence of the larger ionic



**Fig. 2** Ball and stick plot showing the 2D structure in **1** viewed along (a) the *bc* face, (b) the *ab* face, (c) the 3D structure of **1** (guest water molecules and hydrogen atoms are omitted for clarity).

radius of La (122 pm) than those of Nd (104 pm), Eu (98 pm) and Gd (97 pm). The bond lengths for Ni–N, Ni–O and Ln–O are 2.034(4)–2.067(4), 2.002(4)–2.072(3) and 2.325(3)–2.618(35)  $\text{\AA}$  in **2**, 2.040(5)–2.064(4), 2.014(4)–2.072(3), 2.300(4)–2.604(4)  $\text{\AA}$  in **3** and 2.034(4)–2.058(4), 2.004(4)–2.076(4) and 2.295(6)–2.581(4)  $\text{\AA}$  in **4**, respectively. The bond lengths of Ni–N, Ni–O and Ln–O in **2**, **3** and **4** are very close to those in **1**.

Complex **5**, a representative of Type II MOF, consists of two Pr(III) cations, two  $[\text{Ni}(\text{IDA})_2]^{2-}$  metalloligands, one  $\text{ox}^{2-}$  ligand and four water molecules. In the reactions, parts of the iminodiacetate ligand decompose into oxalate ligands, as has been noted in the literature.<sup>21</sup> Crystal structure analyses reveal that there is one independent Pr(III) cation in the asymmetric unit which is



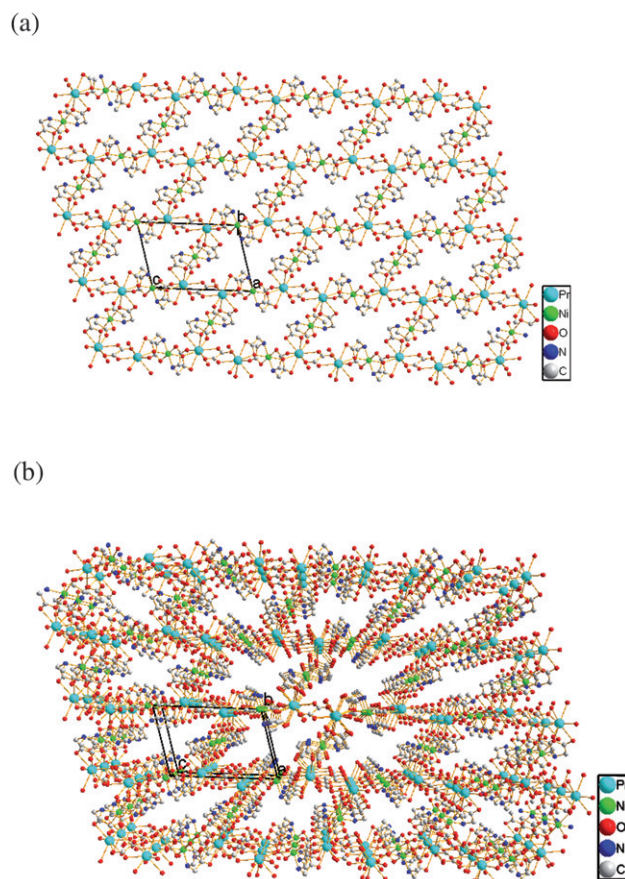
**Fig. 3** Ball and stick plot showing the coordination environment of Pr(III) center in **5** (hydrogen atoms are omitted for clarity).

nine-coordinated by two metalloligands in bidentate mode, two metalloligands in monodentate mode, one  $\text{ox}^{2-}$  ligand in chelate mode and one water molecule to adopt a capped square antiprism geometry as shown in Fig. 3. Its 3D structure can be described as follows: 1) two adjacent  $[\text{Pr}_2(\text{ox})]^{4+}$  units coordinated by a  $[\text{Ni}(\text{IDA})_2]^{2-}$  through its carboxylate in a bidentate fashion to form a 1D chain (along the  $c$ -axis) consisting of  $\{[\text{Pr}_2(\text{ox})\text{Ni}(\text{IDA})_2]_n\}^{2n+}$ ; 2) every 1D chain connects along the  $b$ -axis through the  $[\text{Ni}(\text{IDA})_2]^{2-}$  alternately coordinated to the Pr(III) cations in an adjacent 1D chain, generating a 2D ( $bc$ -face) layered structure  $\{[\text{Pr}_2\text{Ni}_2(\text{IDA})_4(\text{ox})(\text{H}_2\text{O})_2]_m\}$ ; when viewed along the  $b$ -axis, the 2D ( $ac$ -face) structure is identical to that of the  $ab$ -face of the Type I structure; 3) two adjacent 2D ( $ac$ -face) layers further extend into a 3D structure through the  $[\text{Ni}(\text{IDA})_2]^{2-}$  units as shown in Fig. 4b. This linking mode results in the framework of **5** having only A-type channels, significantly different from those of **1**. Water molecules are located in the A-type “ $\text{Pr}_6\text{Ni}_4$ -metal-parallelogram” channel ( $8.83 \times 12.64 \text{ \AA}$ ) and hydrogen bonded to the carboxylate group of the metalloligand. The bond lengths of Ni–N, Ni–O and Pr–O in **5** are 2.020(3)–2.035(2), 2.011(3)–2.049(3) and 2.313(3)–2.647(4)  $\text{\AA}$ , respectively.

Consequently, both structures of Type I MOF and Type II MOF contain identical “layer- $[\text{Ni}(\text{IDA})_2]^{2-}$ -layer” sections, which contain the “A-type channels”. In the structure of Type II, this motif makes up the entire unit cell, and it repeats along the  $b$ -direction with a periodicity of *ca.* 8.5  $\text{\AA}$ . In the structure of Type I, the sections are linked through oxalate anions: essentially, the unit cell of the Type I structure is “pillared” by oxalate anions. The periodicity along the  $c$ -direction in the Type I structure is *ca.* 14.7  $\text{\AA}$ , *i.e.* inserting the oxalate anions expands the structure by about 6  $\text{\AA}$  and introduces the “B-type channels”.

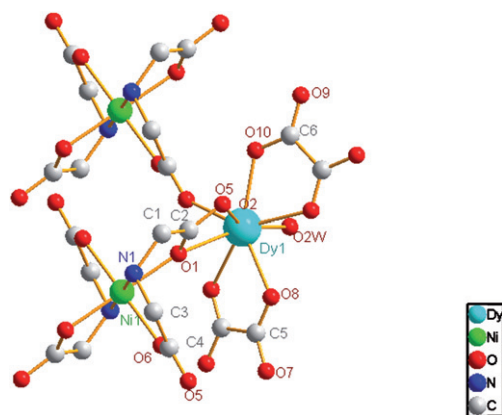
The crystal structures of **6**, **7** and **8** are isomorphous to that of framework **5**. The range of bond lengths for Ni–N, Ni–O and Ln–O are 2.041(2)–2.051(2), 2.025(2)–2.058(2) and 2.377(2)–2.681(2)  $\text{\AA}$  for **6**, 2.041(3)–2.062(3), 2.030(2)–2.071(2) and 2.320(3)–2.662(3) for **7** and 2.039(4)–2.065(4), 2.034(3)–2.083(3) and 2.279(4)–2.655(4) for **8**, respectively. The bond lengths for Ni–N, Ni–O and Ln–O in **6**, **7** and **8** are very close to those for **5**.

Complex **9**, the only one of its kind (namely, Type III MOF), consists of two Dy(III) cations, one  $[\text{Ni}(\text{IDA})_2]^{2-}$  metalloligand, two  $\text{ox}^{2-}$  ligands and four water molecules. Crystal structure analyses



**Fig. 4** Ball and stick plot showing (a) 2D structure in **5** along  $bc$  face, and (b) the 3D structure of **5** (guest water molecules and hydrogen atoms are omitted for clarity).

reveal that the central Dy(III) cation is eight-coordinated, respectively, by two  $[\text{Ni}(\text{IDA})_2]^{2-}$  (with one in bidentate mode and the other in monodentate mode), two  $\text{ox}^{2-}$  and one water molecules in a di-capped trigonal prism coordination geometry as shown in Fig. 5. The 2D structure in **9** can be viewed as the 1D chain in **5** connected to adjacent ones through  $\text{ox}^{2-}$  alternately coordinated to Dy(III) cations from the 1D chain of  $\{[\text{Dy}_2(\text{ox})\text{Ni}(\text{IDA})_2]_n\}^{2n+}$ , while the 3D structure of **5** can be viewed as the extension of the 2D layers through the

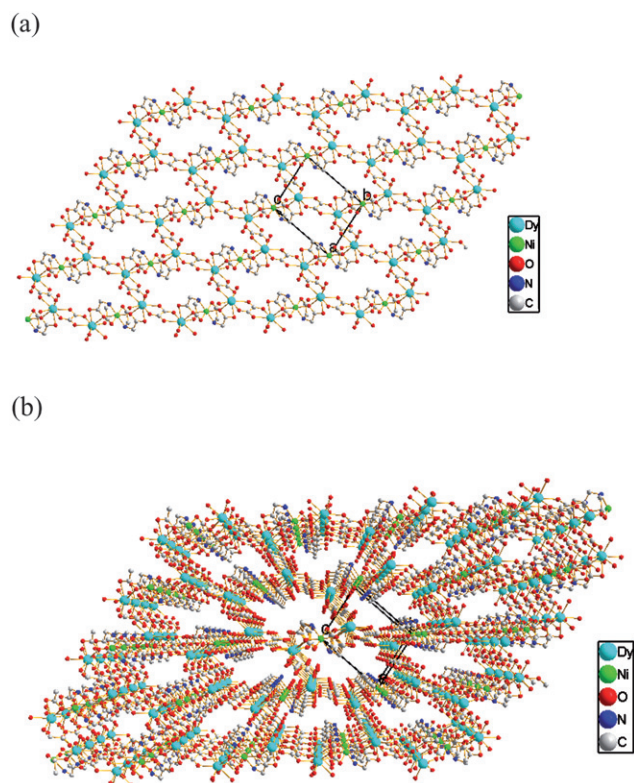


**Fig. 5** Ball and stick plot showing the coordination environment of Dy(III) center in **9**.

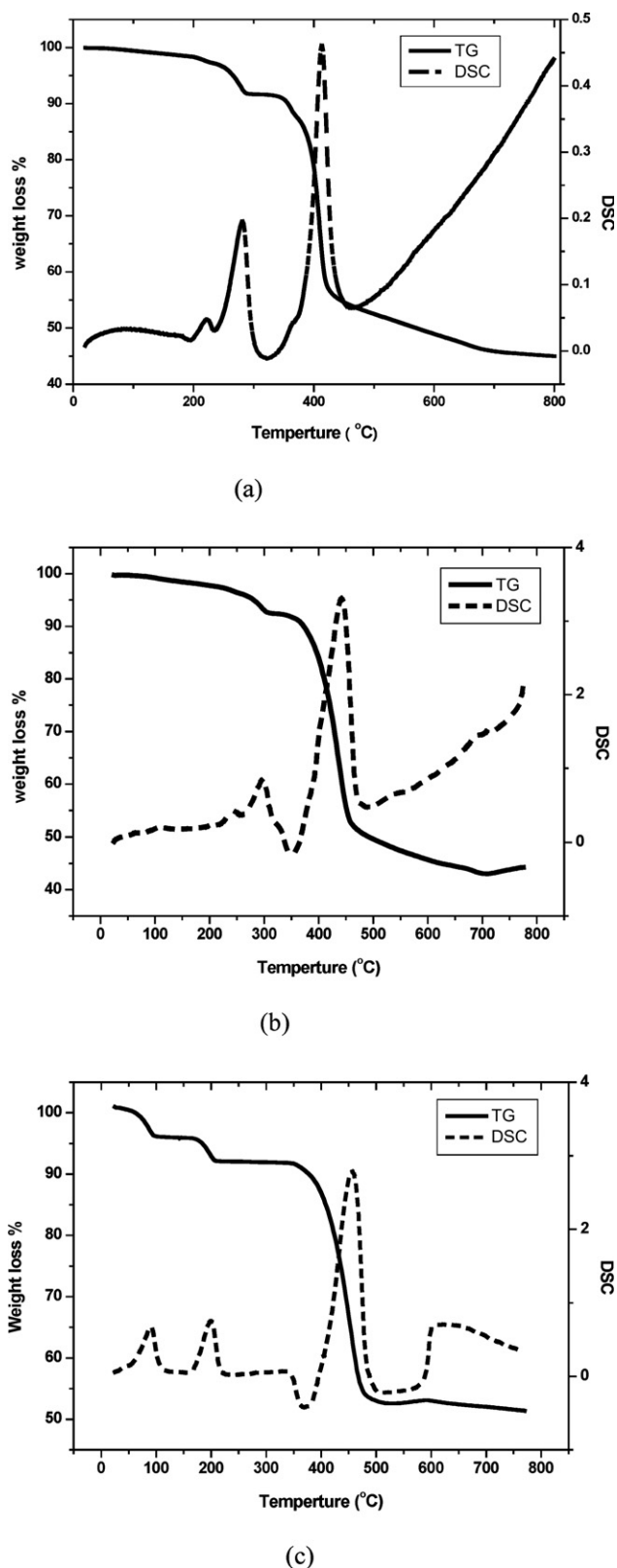
coordination of the uncoordinated carboxylate group of the  $[\text{Ni}(\text{IDA})_2]^{2-}$  metalloligand from one 2D layer coordinated to the Dy(III) cation of adjacent 2D layers as shown in Fig. 6. This linking mode results in the 2D layer containing only B-type 'Dy<sub>6</sub>Ni<sub>2</sub>-parallelogram' channels ( $6.10 \times 13.73 \text{ \AA}$ ), much different from those in **1** and **5**.

Interestingly, comparison of the channel dimensions with those of **1** ( $6.48 \times 12.81 \text{ \AA}$ ) reveals that the shape of B-type channel in **9** is significantly modified ( $6.10 \times 13.73 \text{ \AA}$ ). The bond lengths of Ni–N, Ni–O in **9** are 2.067(6), 2.012(5)–2.033(5) Å, respectively, comparable to those in **5**. The bond lengths of Ln–O are 2.240(5)–2.446(5) Å, shorter than those in **5**. One guest water molecule is located in each B-type "Dy<sub>6</sub>Ni<sub>2</sub>-parallelogram" channels.

Considering the synthetic conditions (ESI)<sup>†</sup> and the fact that part of the iminodiacetate ligand decomposes into  $\text{ox}^{2-}$  during the reaction, it is difficult to explain the structural differences on the basis of the concentration of  $\text{ox}^{2-}$ . In rational, the ratio Lanthanide ion: oxalate: metalloligand is 4 : 3 : 3 for Type I MOF, 4 : 2 : 4 for Type II MOF and 4 : 4 : 2 for Type III MOF, suggesting a common total of six ligand/metalloligand per four lanthanide ions. With the addition of an extra oxalate ion in the starting reaction mixture, the resulting structures appear to contain more oxalate than metalloligand. Compared to Type I MOFs, the formation of the Type III MOF would require more  $\text{ox}^{2-}$  according to their crystal structural analyses. However, several attempts to synthesize Type III MOFs in the same way as described for Type I MOFs or at higher initial concentration of  $\text{ox}^{2-}$  were unsuccessful and we obtained the previously reported 3D complex  $\text{Ln}_2(\text{ox})_3(\text{H}_2\text{O})_6$ ,<sup>10</sup> rather than the Type



**Fig. 6** Ball and stick plot showing (a) 2D structure in **9** along the *bc*-face, and (b) the 3D structure of **9** (guest water molecules and hydrogen atoms are omitted for clarity).



**Fig. 7** TGA–DSC curves for complexes **1** (a), **6** (b) and **9** (c) over the temperature range of 25–800 °C.

**III MOF.** Also, it was difficult for us to obtain Type **III MOF** for the light lanthanide ions ( $\text{La}^{3+}$ – $\text{Eu}^{3+}$ ). These facts indicate that, in addition to the concentration of  $\text{ox}^{2-}$ , the lanthanide cation itself is an important factor influencing the structure of the MOFs and we attribute it to the smaller radius of Dy(III). This is understandable, because the lanthanide ion with smaller radius would favour the coordination of  $\text{ox}^{2-}$  ligand on the basis of the Hard–Soft Acid–Base principle, while combining with more  $\text{ox}^{2-}$  would favour the heavy lanthanide ion to form the complex with lower coordination number satisfying the requirement of the coordination geometry for heavy lanthanide ion. Consistently, the coordination number of lanthanide ion in Type **II**, Type **I** and Type **III MOFs** decreases from nine, to nine/eight and to eight, respectively, with the increase of  $\text{ox}^{2-}$  ligand.<sup>8f,8e</sup>

Complexes **1**, **6** and **9** were selected for TGA to examine the thermal stability of the complexes in the temperature range 20–800 °C. As shown in Fig. 7, the TGA curve for **1** displays an initial weight loss of 8.46% between 25 and 282 °C, which corresponds to the loss of guest and coordinated water molecules (calculated, 8.30%). Between

282 and 340 °C, **1** shows no weight loss, which is an indication of its stability up to 340 °C. When the temperature is higher than 340 °C, **1** rapidly decomposes to a mixture of NiO and  $\text{La}_2\text{O}_3$  (observed residues, 45.03%; calculated, 45.05%) at 800 °C. The TGA curve for **6** displays the first weight loss of 7.3% for the loss of lattice water and coordinated molecules (calcd. 6.7%) between 25 and 305 °C. Between 305 and 345 °C, **6** shows no weight loss, indicating that the framework of **6** can be maintained over this temperature range. In contrast to those of **1** and **6**, the TGA curve for **9** displays an initial weight loss of 3.83% for the loss of guest water molecules (calculated, 4.02%) between 25 and 100 °C (Fig. 11d). The second weight loss of 4.03% for the loss of coordinated water molecules (calculated, 4.02%) occurs in the temperature range of 165 to 210 °C. Between 210 to 350 °C, **9** shows no weight loss, indicating that the framework of **9** is stable up to 350 °C.

Consistent with TGA results, PXRD study (Fig. S2–S3)† reveals that **1** retains its crystallinity when heated to 300 °C, suggesting that the framework of **1** is maintained at that temperature. When cooled to 25 °C and exposed to air for 24 h, the initial X-ray pattern was

**Table 1** Crystal data and details of data collection and refinement for complexes **1** to **9**

Complex	<b>1</b>	<b>1a</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	$\text{C}_{15}\text{H}_{24}\text{La}_2\text{N}_3\text{Ni}_{1.5}\text{O}_{22.5}$	$\text{C}_{15}\text{H}_{21}\text{La}_2\text{N}_3\text{Ni}_{1.5}\text{O}_{21}$	$\text{C}_{15}\text{H}_{23}\text{N}_3\text{Nd}_2\text{Ni}_{1.5}\text{O}_{22}$	$\text{C}_{15}\text{Eu}_2\text{H}_{23}\text{N}_3\text{Ni}_{1.5}\text{O}_{22}$	$\text{C}_{15}\text{Gd}_2\text{H}_{23}\text{N}_3\text{Ni}_{1.5}\text{O}_{22}$
$M_r$	972.26	945.23	973.91	989.35	999.93
$T/\text{K}$	123(2)	298(2)	123(2)	223(2)	123(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	7.201(2)	7.223(1)	7.118(2)	7.0976(19)	7.072(1)
$b/\text{Å}$	12.813(3)	12.769(2)	12.650(3)	12.604(3)	12.517(3)
$c/\text{Å}$	14.723(3)	14.766(2)	14.633(3)	14.654(4)	14.536(3)
$\alpha/^\circ$	74.624(4)	74.862(2)	74.922(4)	74.981(5)	74.901(4)
$\beta/^\circ$	89.392(4)	89.617(2)	89.513(4)	89.720(5)	89.669(4)
$\gamma/^\circ$	87.687(3)	87.493(2)	87.403(4)	87.365(5)	87.133(4)
$V/\text{Å}^3$	1308.7(5)	1313.3(3)	1270.9(5)	1264.7(6)	1240.7(4)
$Z$	2	2	2	2	2
$D_s/\text{g cm}^{-3}$	2.467	2.390	2.545	2.598	2.676
$\mu/\text{mm}^{-1}$	4.376	4.353	5.227	6.107	6.515
Data/params	4976/412	5017/385	4848/403	4868/394	4716/394
$\theta/^\circ$	2.46–26.00	1.43–26.00	1.44–26.00	1.44–26.00	1.45–25.99
Obsd reflns	4554	4787	4427	4079	4519
$R_1 [I > 2\sigma(I)]$	0.0397	0.0270	0.0445	0.0430	0.0415
$wR_2$ (all data)	0.1046	0.0820	0.0980	0.1020	0.1087

Complex	<b>5</b>	<b>5a</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
Formula	$\text{C}_{18}\text{H}_{28}\text{N}_4\text{Ni}_2\text{O}_{24}\text{Pr}_2$	$\text{C}_{18}\text{H}_{24}\text{N}_4\text{Ni}_2\text{O}_{22}\text{Pr}_2$	$\text{C}_{18}\text{H}_{28}\text{La}_2\text{N}_4\text{Ni}_2\text{O}_{24}$	$\text{C}_{18}\text{H}_{28}\text{N}_4\text{Nd}_2\text{Ni}_2\text{O}_{24}$	$\text{C}_{18}\text{Eu}_2\text{H}_{28}\text{N}_4\text{Ni}_2\text{O}_{24}$	$\text{C}_{12}\text{Dy}_2\text{N}_2\text{H}_{18}\text{NiO}_{20}$
$M_r$	1083.68	1047.65	1079.68	1090.34	1105.78	894.0
$T/\text{K}$	123(2)	298(2)	298(2)	123(2)	298(2)	298(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	7.113(2)	7.153(2)	7.225(1)	7.163(2)	7.124(2)	7.403(2)
$b/\text{Å}$	8.519(2)	8.569(3)	8.647(2)	8.577(2)	8.578(2)	8.224(2)
$c/\text{Å}$	12.641(4)	12.570(4)	12.836(2)	12.728(3)	12.695(3)	9.822(2)
$\alpha/^\circ$	74.748(5)	75.026(6)	74.971(3)	74.789(4)	74.769(4)	81.482(4)
$\beta/^\circ$	88.024(5)	87.787(6)	87.847(3)	87.820(4)	87.335(5)	81.709(4)
$\gamma/^\circ$	86.919(5)	85.779(6)	86.518(3)	86.685(4)	86.314(5)	83.254(4)
$V/\text{Å}^3$	737.8(4)	742.2(4)	772.9(2)	753.1(3)	746.7(3)	582.3(2)
$Z$	1	1	1	1	1	1
$D_s/\text{g cm}^{-3}$	2.439	2.344	2.320	2.404	2.459	2.549
$\mu/\text{mm}^{-1}$	4.612	4.575	4.014	4.730	5.494	7.248
Data/params	2363/238	2411/220	2946/238	2847/238	2800/229	2237/169
$\theta/^\circ$	1.67–24.99	1.68–25.00	2.44–25.99	1.66–26.00	1.66–26.00	2.11–25.99
Obsd reflns	2310	2200	2906	2782	2705	2189
$R_1 [I > 2\sigma(I)]$	0.0371	0.0531	0.0248	0.0390	0.0422	0.0358
$wR_2$ (all data)	0.1121	0.1360	0.0654	0.1011	0.1069	0.0915

recovered, indicating that the dehydration and rehydration processes for **1** are reversible. The high thermal stability of **1** was mainly attributed to the rigid oxalate ligands which prevent the framework from collapsing. The XRPD study reveals that complex **5** has similar thermal stability and reversible sorption process as **1**.

Based on the stability of the frameworks, **1** and **5** were selected for investigation of their dehydration and rehydration behaviour. Although thermogravimetric analyses suggest that these frameworks are stable when the guest and coordinated water molecules are removed, the anhydrous crystals obtained after these measurements were severely damaged with cracks that it was difficult to perform X-ray data collections. However, when the crystals were gently heated to 230 °C and kept for 30 min followed by cooling to room temperature, the crystals were less damaged and we were able to obtain the partially dehydrated **1** (namely **1a**) and **5** (namely **5a**). The crystal structures obtained from the single crystal diffraction data collected at room temperature reveal that the frameworks are maintained but only the non-coordinated water molecules were removed. The range of bond lengths for Ni–N, Ni–O and La–O in **1a** are 2.035(2)–2.062(3), 2.003(3)–2.067(2) and 2.381(2)–2.699(2) Å, while those in **5a** are 2.010(7)–2.052(7), 2.013(6)–2.047(6) and 2.313(6)–2.630(7) Å, respectively. These are comparable to the corresponding ones in **1** and **5**. Analyses using Platon<sup>11</sup> gave an estimated void volume of 62 and 55 Å<sup>3</sup> per mole for **1** and **5** without the guest water, respectively. The attempt to perform similar measurements for crystals of **9** has so far been unsuccessful.

In summary, using organic ligand and metalloligand as building units in association with lanthanide cations, we have synthesized three structural kinds of 3d-4f MOFs, in which complexes **1** to **4** contain two kinds of channels, *i.e.*, A- and B-type, complexes **5** to **8** contain only the A-type channel, while complex **9** contains only a B-type channel. The structural differences of the complexes reveal that the shape and dimensions of the channels of MOFs may be changed by adjusting the reaction conditions.

## Acknowledgements

We thank the NNSFC (Grant Nos. 20471050, 20531050, and 20721001), the 973 project (Grant 2007CB815304) from MSTC and the CNRS-France for financial support.

## Notes and references

- (a) A. Corma, *Chem. Rev.*, 1997, **97**, 2373; (b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (c) M. Eddaoudi, D. B. Li, H. Moler, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (d) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (e) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (f) M. Kurmoo, H. Kumagai, S. M. Hughes and C. J. Kepert, *Inorg. Chem.*, 2003, **42**, 6709; (g) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; (h) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238.
- (a) J. P. Costes, F. Dahan, A. Dupuis and J. P. Laurent, *Inorg. Chem.*, 1997, **36**, 3429; (b) D. M. J. Doble, C. H. Benison, A. J. Blake, D. Fenske, M. S. Jackson, R. D. Kay, W. S. Li and M. Schroder, *Angew. Chem., Int. Ed.*, 1999, **38**, 1915; (c) J. Lisowski and P. Starynowicz, *Inorg. Chem.*, 1999, **38**, 1351; (d) M. Sakamoto, K. Manseki and H. Okawa, *Coord. Chem. Rev.*, 2001, **219**, 379; (e) C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102**, 2369; (f) G. Li, T. Akitsu, O. Sato and Y. Einaga, *J. Am. Chem. Soc.*, 2003, **125**, 12396; (g) H. Z. Kou, B. C. Zhou, S. Gao and R. J. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 3288; (h) O. Guillou, C. Daiguebonne, M. Camara and N. Kerbellec, *Inorg. Chem.*, 2006, **45**, 8468; (i) B. Zhai, L. Yi, H. S. Wang, B. Zhao, P. Cheng, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2006, **45**, 8471.
- Y. B. Dong, M. D. Smith and H. C. zur Loye, *Angew. Chem., Int. Ed.*, 2000, **39**, 4271.
- (a) L. Pan, X. Y. Huang, J. Li, Y. G. Wu and N. W. Zheng, *Angew. Chem., Int. Ed.*, 2000, **39**, 527; (b) Q. D. Liu, J. R. Li, S. Gao, B. Q. Ma, Q. Z. Zhou, K. B. Yu and H. Liu, *Chem. Commun.*, 2000, 1685; (c) D. M. L. Goodgame, D. A. Grachvogel, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 6180; (d) S. Liu, E. A. Meyers and S. G. Shore, *Angew. Chem., Int. Ed.*, 2002, **41**, 3609; (e) A. Dimos, D. Tsaousis, A. Michaelides, S. Skoulika, S. Golhen, L. Ouahab, C. Didierjean and A. Aubry, *Chem. Mater.*, 2002, **14**, 2616; (f) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc.*, 2004, **126**, 420; (g) Y. F. Zhou, M. C. Hong and X. T. Wu, *Chem. Commun.*, 2006, 135.
- (a) S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem., Int. Ed.*, 2002, **41**, 4670; (b) J. J. Zhang, S. Q. Xia, T. L. Sheng, S. M. Hu, G. Leibeling, F. Meyer, X. T. Wu, S. C. Xiang and R. B. Fu, *Chem. Commun.*, 2004, 1186; (c) B. Zhao, P. Cheng, X. Y. Chen, C. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 3012; (d) F. He, M. L. Tong and X. M. Chen, *Inorg. Chem.*, 2005, **44**, 8285.
- J. G. Mao, L. Song and J. S. Huang, *J. Chem. Crystallogr.*, 1998, **28**, 475.
- (a) L. S. Long, Y. P. Ren, R. B. Huang, L. S. Zheng and S. W. Ng, *Appl. Organomet. Chem.*, 2003, **17**, 741; (b) F. He, M. L. Tong, X. L. Yu and X. M. Chen, *Inorg. Chem.*, 2005, **44**, 559; (c) Y. Wang, P. Cheng, J. Chen, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2007, **46**, 4530.
- (a) C. Daiguebonne, O. Guillou, M. L. Kahn, O. Kahn, R. L. Oushoorn and K. Boubekeur, *Inorg. Chem.*, 2001, **40**, 176; (b) A. M. Madalan, H. W. Roesky, M. Andruh, M. Noltemeyer and N. Stanica, *Chem. Commun.*, 2002, 1638; (c) R. Gheorghe, P. Cucos, M. Andruh, J. P. Costes, B. Donnadiu and S. Soba, *Chem.–Eur. J.*, 2006, **12**, 187; (d) B. Zhai, L. Yi, H. S. Wang, B. Zhao, P. Cheng, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2006, **45**, 8471; (e) B. Li, W. Gu, L. Z. Zhang, J. Qu, Z. P. Ma, X. Liu and D. Z. Liao, *Inorg. Chem.*, 2006, **45**, 10425; (f) T. K. Prasad, M. V. Rajasekharan and J.-P. Costes, *Angew. Chem., Int. Ed.*, 2007, **46**, 2851.
- (a) X. J. Kong, Y. P. Ren, L. S. Long, Z. P. Zheng, R. B. Huang and L. S. Zheng, *J. Am. Chem. Soc.*, 2007, **129**, 7016; (b) X. J. Kong, Y. P. Ren, W. X. Chen, L. S. Long, Z. P. Zheng, R. B. Huang and L. S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 2398; (c) X. J. Kong, Y. P. Ren, L. S. Long, Z. P. Zheng, G. Nichol, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2008, **47**, 2728.
- (a) W. Ollendorf and F. Weigel, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 263; (b) E. Hansson, *Acta Chem. Scand.*, 1973, **27**, 823.
- A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34.
- G. M. Sheldrick, *SADABS 2.05*; University of Göttingen: Göttingen, Germany.
- SHELXTL 6.10*; Bruker Analytical Instrumentation: Madison, WI, 2000.