DOI: 10.1002/chem.200903053

The Construction of Open Gd^{III} Metal–Organic Frameworks Based on Methanetriacetic Acid: New Objects with an Old Ligand

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In memoriam of Prof. Dr. Xavier Solans (Universitat de Barcelona, Spain)

Abstract: The preparation, X-ray crystallography and magnetic investigation of the first examples of methanetriacetate (mta)-containing lanthanide(III) complexes of formulae $[Gd(mta)(H_2O)_3]_n\cdot 4n\,H_2O$ (**1**) $[Gd(mta)(H_2O)_3]_n\cdot 2n\,H_2O$ (**2**) and $[Gd_2(mta)_2(H_2O)_2]_n\cdot 2n\,H_2O$ (**3**) are described herein. This tripodal ligand promotes the formation of 6^3 networks; thus **1** consists of a honeycomb structure, whereas in **2** two of these layers are condensed to form a rare five-connected two-dimensional (4^86^2) network. Compound **3** can be seen as an aggregation of 6^3 layers leading to a three-dimensional (6,6)-connected binodal ($4^{12}6^3$)(4^96^6)-**nia** net, in which the gadolinium(III) ions and the mta ligands act as octahedral and as trigonal prismatic nodes, respectively. The magnetic properties of **1**–**3** were investigated in the temperature range 1.9–300 K. A close fit to the Curie law (**1**) and weak either antiferro- [$J=-0.0063(1)$ cm^{-1} (**2**)] or ferromagnetic [$J=+0.0264(6)$ cm^{-1} (**3**)] interactions between the Gd^{III} ions are observed; the different exchange pathways involved [extended tris-bidentate mta (**1**) and μ-*O*(1);κ^2*O*(1),*O*(2) (**2** and **3**) plus single *syn*–*syn* carboxylate-mta (**3**)] accounting for these magnetic features. The nature and magnitude of the magnetic interactions, between the Gd^{III} ions in **1**–**3**, agree with the small amount of data existing in the literature for these kind of bridges.

Keywords: gadolinium · magnetic properties · metal–organic frameworks · topology · X-ray diffraction

Introduction

The self-assembly of metal–organic frameworks (MOFs) has attracted much attention in recent years not only for the potential discovery of novel functional materials, which may have applications in the areas including gas storage, molecular sieves, ion-exchange, catalysis, optoelectronics, and magnetism, but also for their intriguing variety of architectures and topologies, such as molecular grids, bricks, herringbones, diamondoids or honeycombs.[1–4] The functionality in these

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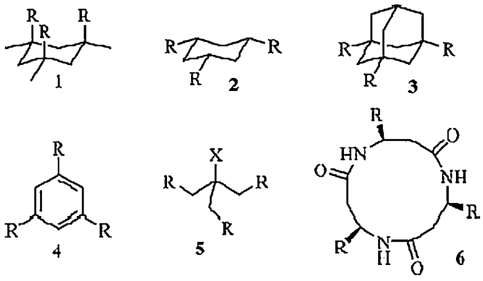
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903053.

materials can be introduced either through inorganic species or organic linkers. Construction of multidimensional frameworks has been demonstrated to produce materials with cooperative effects and improved thermal stabilities.[5] However, most of the current efforts in this area have focused on the design of infinite MOFs with transition-metal (TM) ions.[6] Unfortunately, in contrast to the fruitful production of transition-metal–organic frameworks, the design and control of high-dimensional lanthanide-based hybrids are still challenging tasks, owing to the higher coordination numbers and poorer stereochemical preferences of the lanthanide cations. The high and variable coordination numbers and flexible coordination geometry of these heavy elements provide unique opportunities to get unusual network topologies.[7]

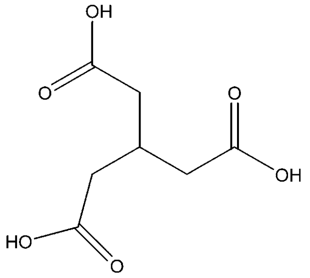
The complex formation between highly-symmetrical multi-topic ligands and suitable metal salts to construct supramolecular architectures is of great interest.[7,8] In general, rigid, symmetrical, multi-topic ligands, which have been intensively investigated, can lead to more predictable structures, but their diversity has been limited to some extent, owing to the fact that a few or even no conformational changes can be observed for them in their metal complexes. By contrast, flexible ligands can adopt different conformations and coordination modes according to the geometric requirements of the different metal ions and they may afford unpredictable, but interesting, coordination networks. Their reactivity and coordination chemistry have been less explored and the investigation of MOFs based on flexible ligands is still a great challenge.[8]

Under this premise, different C_3-symmetry scaffolds have been reported so far and some selected examples, **1**–**6**, are shown in Scheme 1. The shape of the scaffolds varies significantly from flexible tripodal molecules like **5**[9] to relatively rigid cyclohexane motifs such as **1**[10] (derived from Kemps' triacid) or **2**[11,12] and absolutely rigid and planar aromatic structures like **4**.[12] Finally, cyclic α- and β-peptides like **6**[13] have been used for biochemical applications.



Scheme 1. Examples of common C_3-symmetry scaffolds.

To extend our previous work in this field,[14] we have turned our attention to an unexplored C_3-scaffold ligand, the methanetriacetic acid $HC(CH_2CO_2H)_3$ (hereafter noted H_3mta; see Scheme 2). This ligand consists of three acetic groups attached to a central methane core. Coordination of two of these arms to the same metal ion, which can diminish the size of the final pore structure, is mostly precluded due to their great separation. Its fully deprotonated form, mta^{3-}, is a flexible tripodal ligand with a C_3 symmetry core, which can induce a three-fold axis in the resulting metal complex. Previous studies on rigid C_3-scaffold ligands, such as 1,3,5-benzenetricarboxylic acid (H_3btc),[15,16] have shown that predictable networks of the 6^3 kind (brick-wall, honeycomb, herringbone, ladder-like, etc.) are highly favoured. However, the flexible mta^{3-} ligand is expected, not only to reproduce the results obtained with rigid ligands, but also to build new hexagonal topologies. This latter characteristic makes this ligand an excellent candidate to build hexagonal cavities in crystal architectures when combined with the appropriate cation. The high coordination number of the lanthanide cations together with the expected variety of coordination modes of the mta^{3-} group constitutes a likely route toward the design of high-dimensional systems.



Scheme 2. Methanetriacetic acid (H_3mta).

A survey of the literature shows that the crystal structure and coordination chemistry of H_3mta remain unknown and only a spectroscopic study of H_3mta has been reported.[17] MOFs with other flexible C_3-scaffold type tricarboxylic acids have been prepared, in particular with H_3bta and lanthanide cations,[18] illustrating the potential interest of this strategy.

In the present work, we report the synthesis, crystallographic analysis and magnetic properties of the first examples of mta-containing lanthanide complexes of formulae $[Gd(mta)(H_2O)_3]_n{\cdot}4nH_2O$ (**1**), $[Gd(mta)(H_2O)_3]_n{\cdot}2nH_2O$ (**2**) and $[Gd_2(mta)_2(H_2O)_2]_n{\cdot}2nH_2O$ (**3**) (see Table S1 in the Supporting Information).

Results and Discussion

Description of the structures: $[Gd(mta)(H_2O)_3]_n{\cdot}4nH_2O$ (1): The structure of compound **1** consists of 6^3-hcb layers[19] (in extended Schläfli notation) constructed by $[Gd(H_2O)_3]^{3+}$ ions as three-fold nodes and mta^{3-} ions as three-fold connectors (Figure 1 a). These sheets are stacked along the *c* axis following an *ABAB* sequence, two consecutive layers being related by *c*-glide planes parallel to the (1−10), (120) and (210) crystallographic planes (Figure 1 b,c). The layers are held together by means of hydrogen bonds involving two crystallisation water molecules [O(2w) and O(3w)], the co-

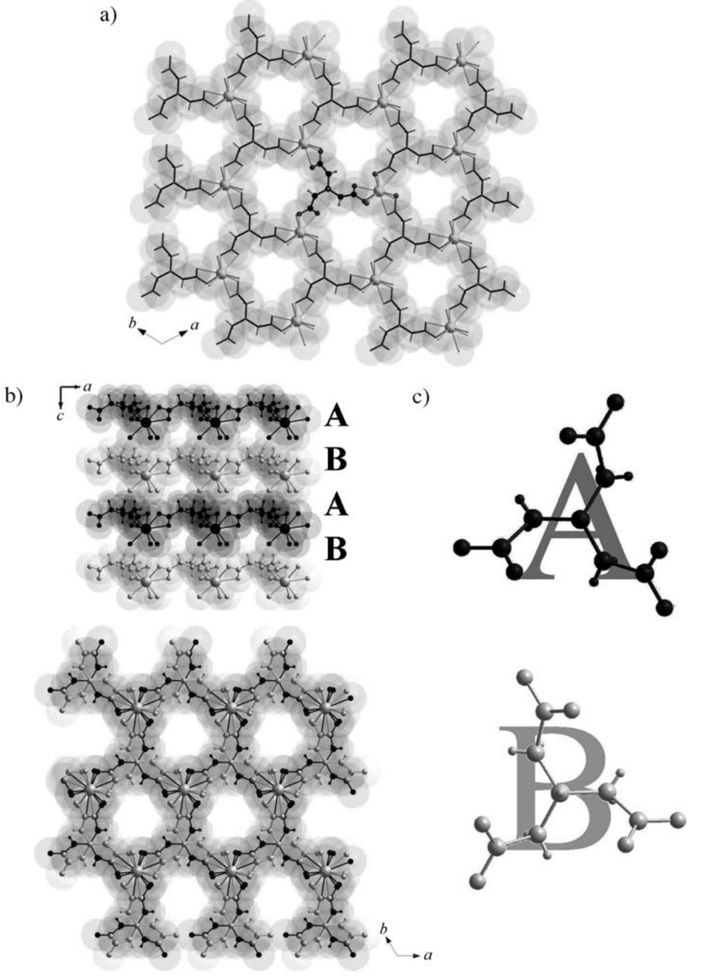


Figure 1. a) A view of a fragment of the mta-gadolinium layer of **1** growing in the *ab* plane. b) Crystal packing down the crystallographic *b* axis showing the regular alternating of the *A* and *B* layers. c) Ligand conformation in the *A* and *B* layers.

ordinated water molecule [O(1w)] and the mta carboxylate-oxygen atoms from the mta^{3-} ligand leading to a supramolecular three-dimensional network. From a topological point of view, the structure of **1** is built up from two equivalent three-fold connectors, giving rise to a uninodal network.

The 6^3 network shows hollow hexagonal tiles with a circular section of approximately 43 Å^2. They are extended along the *c* axis to form channels with solvent accessible volume of 213 Å^3 per unit cell accounting for a 28.6 % of the total cell volume.[20] These channels are occupied by the crystallisation water molecules, which form unusual trigonal pyramidal aggregates, since O(2w) is located in a three-fold axis. The values of the O···O distances for the basal edges [between the O(3w) atoms] and the basal-apex ones [between O(2w) and O(3w)] are 3.191(11) and 3.244(14) Å, respectively (see Table S2 in the Supporting Information).

The gadolinium(III) ion in **1** [Gd(1)] is located on a three-fold axis, and it is surrounded by six oxygen atoms belonging to three different mta^{3-} ligands [O(1), O(2), O(1a^1), O(2a^1), O(1b^1) and O(2b^1) with $a^1 = -x+y, -x+1, z$ and $b^1 = -y+1, x-y+1, z$] plus three water molecules [O(1w), O(1wa^1) and O(1wb^1)], the whole donor set defining a monocapped square antiprism (Figure 2 a). The O(1b^1), O(2a^1), O(2b^1) and O(1wb^1) group of atoms forms the base, whereas the O(1), O(1a^1), O(1wa^1) and O(1w) set builds the upper plane which is capped by the O(2) atom [with one of the largest Gd−O distance of 2.515(4) Å] (see Table S3 in the Supporting Information). The average Gd(1)−O bond length is 2.451(4) Å and the value of the dihedral angle between the upper and basal planes is 11.3°.

The mta^{3-} ligand adopts a tris-bidentate coordination mode, each carboxylate group chelating one Gd^{III} ion (Figure 3 a). The central carbon atom of the mta ligand [C(3)] is located on a threefold axis, a remarkable situation of constrain, as each methylene group is free to rotate respect to the central "methane" carbon atom. This axis promotes the crystallisation of the compound in a trigonal-crystal system, and in the same way, this conformation is specially suited to produce hexagonal pores in the structure. The value of the dihedral angle between the planes of the carboxylate groups of the mta^{3-} ligand is 83°. The shortest intralayer Gd···Gd separation is 8.671(3) Å, a value which is larger than the shortest interlayer metal–metal separation [5.7118(5) Å].

Let us finish the structural description of **1** with a comparison of its structure with those of the lanthanide(III) complexes prepared with other C_3-scaffold ligands, such as the 1,3,5-benzenetricarboxylate (btc^{3-}), or the more flexible tricarballylate (tca^{3-}) and 1,3,5-benzenetriacetate (bta^{3-}). The bta is the archetypical scaffold for the formation of honeycomb structures[21] and various examples can be found among the lanthanide complexes.[16] The trischelation of the lanthanide ions and the angle of 120° between the carboxylic arms of the btc ligand produces 6^3 sheets with Gd^{III}, Sm^{III} and Nd^{III},[16a,b,e] whereas 6^3 cylindrical tubes are seen for Er^{III}.[16f] The rigidity of the ligand favours the formation of these 6^3 systems. In the case of the tricarballylic acid, in which two acetate groups and one carboxylate arm are linked to a methane core, the T-shape of the ligand restrains the kind of systems that can be obtained.[14a] Thus, 6^3 systems with T nodes are highly favoured and brick-wall 6^3 nets are formed with Gd^{III} and Eu^{III}, whereas a 3D network based on ladder-like tapes are obtained with La^{III}.[14a] Remarkably, to our knowledge there is no two-dimensional 6^3 network among the lanthanide complexes of the 1,3,5-benzenetriacetate ligand.[18]

$[Gd(mta)(H_2O)_3]_n \cdot 2n H_2O$ (2): The crystal structure of compound **2** consists of dinuclear $[Gd_2(H_2O)_4]^{6+}$ units which are linked through mta^{3-} ligands to form a two-dimensional array of metal atoms extended in the *ab* plane. The topological structure of **2** is built up by two equivalent five-fold connectors, giving rise to a $(4^8 6^2)$ uninodal network. This topology is very rare and to our knowledge it has not been observed before. These layers are the result of the condensation of two of the 6^3 sheets observed in **1** (see Figure 4). If the gadolinium dinuclear units are considered as a single node, they become 6-connected, whereas the mta ligands

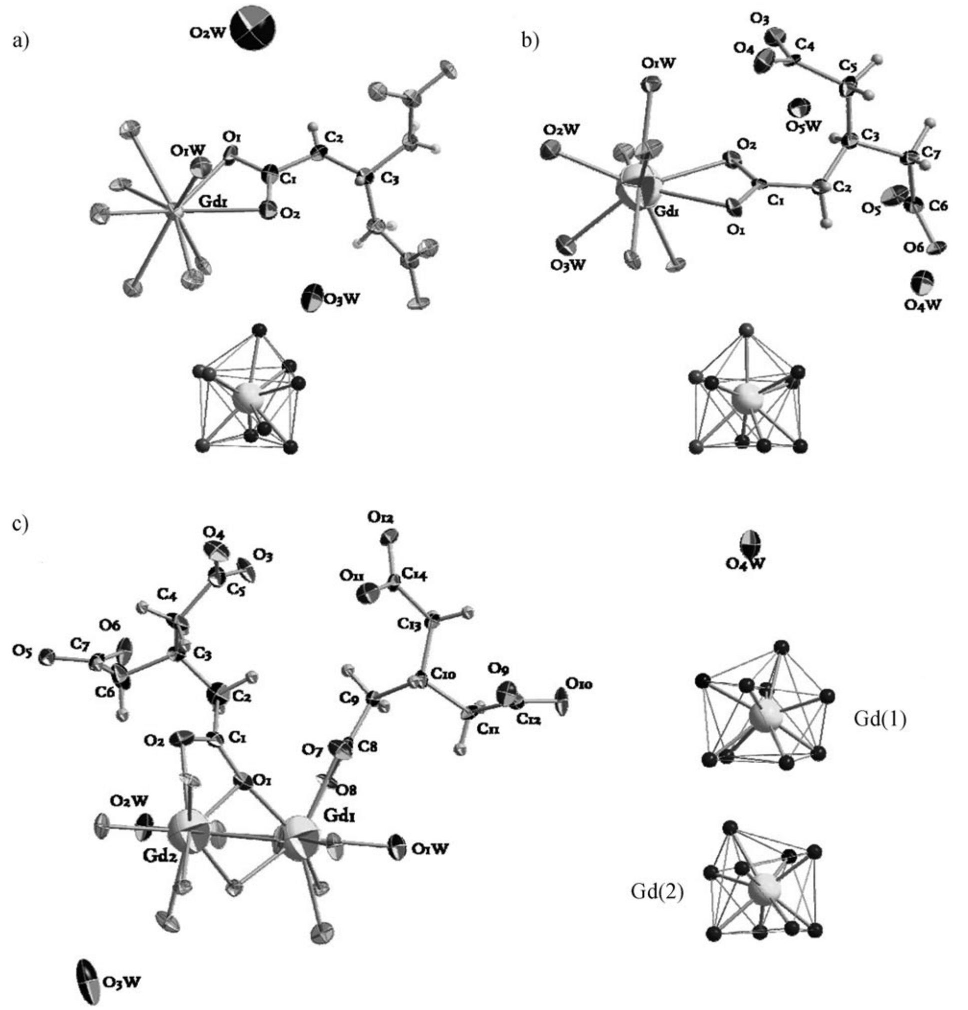


Figure 2. A view of the asymmetric unit in a) **1**, b) **2** and c) **3** showing the atom numbering together with a detail of the coordination polyhedron of the Gd^{III} ions. The unlabeled grey atoms have been generated by symmetry operations.

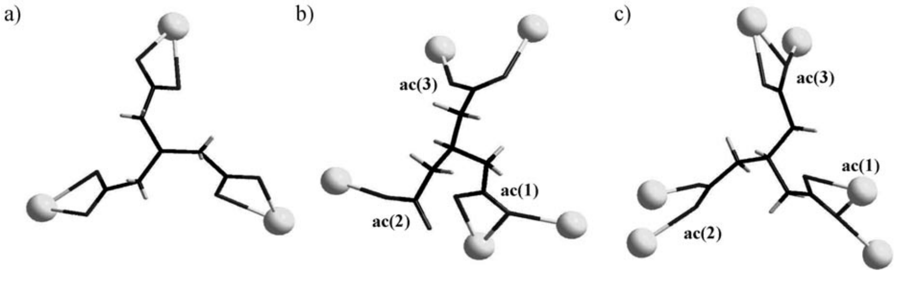


Figure 3. Coordination modes of the methanetriacetate ligand in a) **1**, b) **2** and c) **3**.

are 3-connecting nodes. Therefore, a two-dimensional (6,3)-connected binodal $(4^3)(4^6 6^6 8^3)$-**kgd** net results.[19] This $CdCl_2$ topology is common for binary inorganic compounds, but it is quite rare for metal–organic coordination polymers.[22]

The $(4^8 6^2)$ sheets are stacked regularly along the crystallographic *c* axis with a minimum interplanar separation between gadolinium atoms of 8.6750(8) Å. Six mta^{3-} ligands connect the dinuclear units to their six nearest neighbours, the shortest interdimer distance being 8.0705(7) Å. Hydrogen bonds involving the crystallisation [O(4w) and O(5w)] and coordination [O(1w), O(2w) and O(3w)] water molecules connect the sheets to form a supramolecular three-dimensional structure [intermolecular O···O distances varying in the range 2.740(11)–2.886(8) Å] (see Table S2 in the Supporting Information). The solvent available-volume per unit-cell once coordinated and uncoordinated water molecules are removed is ≈199.7 $Å^3$, a value which accounts for the 31.2 % of the total cell volume.[20]

There is one crystallographically independent gadolinium(III) ion in the structure of **2**. It is nine coordinated (see Figure 2b) with six oxygen atoms [O(1), O(2), O(1a^2), O(3b^2), O(5c^2) and O(6d^2); symmetry code: $a^2=-x, -y+1, -z$; $b^2=-x, -y+2, -z$; $c^2=x-1, y, z$; $d^2=-x+1, -y+1, -z$] from five different mta^{3-} ligands and three water molecules [O(1w), O(2w) and O(3w)] building a distorted monocapped square antiprism [Gd−O distances varying in the range 2.294(5) to 2.537(6) Å (see Table S3 in the Supporting Information)]. The O(1), O(2), O(5c^2) and O(1w) set of atoms forms the base of the polyhedron, while O(1a^2), O(3b^2), O(6d^2) and O(2w) build the upper plane and O(3w) caps the antiprism. The dihedral angle between the upper and basal planes is 3.8°.

The crystallographically independent mta^{3-} group adopts simultaneously both bidentate [through O(1) and O(2) toward Gd(1)] and tetrakis-monodentate coordination modes [through O(1), O(3), O(6) and O(5) towards Gd(1a^2), Gd(1b^2), Gd(1d^2) and Gd(1i^2), respectively; $i^2=x+1, y, z$] (Figure 3b). So, each mta^{3-} ligand connects three digadolinium(III) units. The carbon skeleton of the mta^{3-} ligand does not lay in the same plane [maximum deviation from the mean plane formed by the mta-

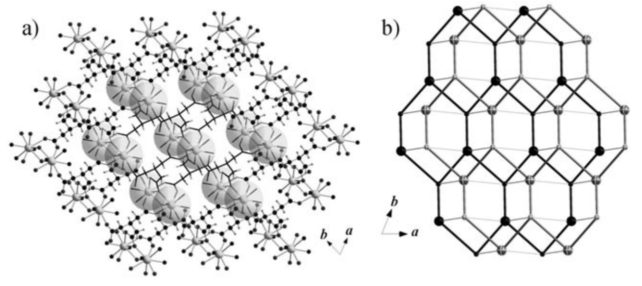


Figure 4. a) View of the structure of **2** along the *c* axis showing the layers constructed by the Gd^{III} ions and the mta^{3-} ligands; the dinuclear unit with its six nearest neighbours is emphasised. b) Topological scheme showing the condensation of the double 6^3 layer.

carbon atoms is 0.405(2) Å at C(2)]. The values of the dihedral angles between the planes of the acetate arms of the mta^{3-} ligand [C(1), C(2), O(1) and O(2) (ac(1)), C(4), C(5), O(3) and O(4) (ac(2)) and C(6), C(7), O(5) and O(6) (ac(3))] are 27.8 [ac(1)/ac(2)], 80.8 [ac(1)/ac(3)] and 53.0° [ac(2)/ac(3)].

The digadolinium(III) units in **2** are generated by an inversion centre located in the midpoint between the two metal atoms (see Figure 5). A double oxo [μ-$O(1);\kappa^2O(1),O(2)$] and two carboxylate groups [O(5c^2)-C-(6c^2)-O(6c^2)] in *syn–syn* conformation act as bridges. The value of the separation between the gadolinium(III) ions [Gd(1)···Gd(1a^2)] and that of the angle at the oxo bridge [Gd(1)-O(1)-Gd(1a^2)] are 4.0231(9) Å and 109.4(2)°, respectively.

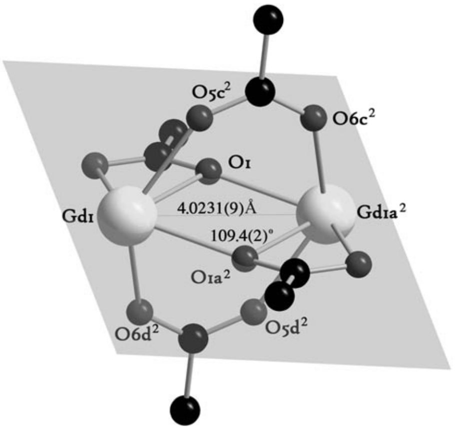


Figure 5. A detail of the bridges between the gadolinium(III) ions in **2**. The plane formed by the Gd(1), Gd(1a^2), O(1) and O(1a^2) set of atoms is also visualised.

$[Gd_2(mta)_2(H_2O)_2]_n\cdot 2n\,H_2O$ (3): The structure of compound **3** is made up of $[Gd(H_2O)]^{3+}$ ions and 6-connecting mta^{3-} ions acting as octahedral and trigonal prismatic nodes, respectively. The resulting three-dimensional network exhibits the **nia** topology (Figure 6). This (6,6)-connected binodal **nia**-net[19] with a $(4^{12}6^3)(4^96^6)$ Schläfli symbol is quite rare among MOF architectures and only three examples could be found in the recent literature.[23]

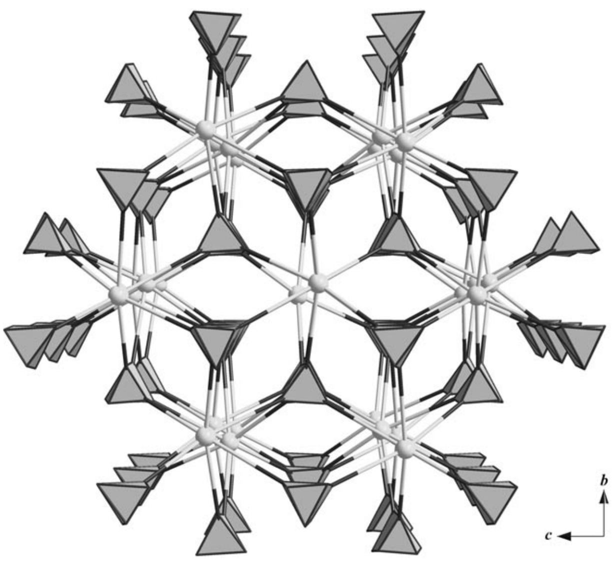


Figure 6. Topologic view of the crystal structure of **3** in which the gadolinium(III) ions and the mta^{3-} ligands are highlighted by light grey and dark grey, respectively.

The structure is formed by chains of oxo- and *syn–syn* carboxylato-bridged gadolinium (III) ions running along the *a* direction, which are further interconnected through the extended mta^{3-} ligands to afford the 3D network. Each Gd^{III} chain is linked to its six nearest neighbours within the *bc* plane with a shortest interchain separation of 7.7317(3) Å [Gd(1)···Gd(2h^3); $h^3=-x, y, z+1/2$].

Hydrogen bonds involving the crystallisation [O(3w) and O(4w)] and coordination [O(1w) and O(2w)] water molecules and carboxylate-oxygen atoms of the mta^{3-} ligand contribute to the stabilisation of the structure [O···O contacts covering the range 2.754(10)–2.852(10) Å] (see Table S2 in the Supporting Information). The O(3w) and O(4w) water molecules are placed between the central carbon atoms of the mta^{3-} ligands along the *a* direction, in such a way that no residual space is allowed for more solvent molecules. A solvent available volume of about 424.5 Å^3 per unit cell results in this compound after removal of the crystallisation and coordination water molecules. This empty space accounts for the 21 % of the total cell volume.[20]

Two crystallographically independent gadolinium atoms [Gd(1) and Gd(2)] in **3** (see Figure 2c), are nine-coordinated with distorted monocapped square antiprism environments. Gd(1) is surrounded by eight oxygen atoms [O(1), O-(3a^3), O(5b^3), O(7), O(8), O(10c^3), O(11a^3) and O(12a^3); $a^3=x, y-1/2, -z+1/2$; $b^3=-x, y-1/2, -z$; $c^3=-x+1, y, z-1/2$] from six mta^{3-} ligands, and one water molecule [O(1w)]. The O(1), O(7), O(8) and O(10c^3) set of atoms forms the base of the polyhedron, whereas O(3a^3), O(5b^3), O(12a^3) and O(1w) build the upper plane and O(11a^3) caps the antiprism. The mean value of the Gd(1)−O bond distance is 2.451(8) Å (see Table S3 in the Supporting Information) and the dihedral angle between the upper and basal planes amounts 10.5°. Gd(2) is surrounded also by eight oxygen atoms [O(1), O(2), O(4a^3), O(5b^3), O(6b^3), O(8d^3), O(9e^3) and O(12f^3); d^3=x−1, y, z; e^3=−x, y, z−1/2; f^3=x−1, y−1/2, −z+1/2] from six mta^{3-} ligands and one water molecule [O(2w)]. The basal and upper planes at the Gd(2) atom are built by the O(1), O(2), O(4a^3) and O(8d^3) and O-(5b^3), O(9e^3), O(12f^3) and O(2w) set of atoms respectively, whereas O(6b^3) caps the antiprism. The mean Gd(2)−O distance is 2.445(8) Å and the dihedral angle between the basal an upper mean planes is 9.5° (see Table S3 in the Supporting Information).

Two crystallographically independent mta^{3-} ligands, both exhibiting the same bis-bidentate/tetrakis-monodentate coordination mode, occur in **3** (Figure 3c). The one containing the C(3) atom [mta(1)] is chelating Gd(2) [through O(1) and O(2)] and Gd(2k^3) [through O(5) and O(6)], connecting Gd(1) to Gd(2) [through O(1)] and to Gd(1l^3) [through O(3)] and binding to Gd(2l^3) [through O(4)] and Gd(1k^3) [through O(5)] (symmetry code: l^3=x, y+1/2, −z+1/2; k^3=−x, y+1/2, −z). The second mta ligand [mta(2)] which contains the methane carbon atom C(10) shows the same coordination mode chelating Gd(1) [through O(7) and O(8)], and Gd(1l^3) [through O(11) and O(12)] and linking Gd(2), Gd(2h^3), Gd(1j^3) and Gd(2m^3) (h^3=−x, y, z+1/2; j^3=−x+1, y, z+1/2; m^3=x+1, y+1/2, −z+1/2), by means of O(8), O(9), O(10) and O(12), respectively. The mean planes of the acetate arms of the mta(1) ligand [ac(1): C(1), C(2), O(1) and O(2); ac(2): C(4), C(5), O(3) and O(4)]; ac(3): C(6), C(7), O(5) and O(6)] form dihedral angles of 61.8 [ac(1)/ac(2)], 54.8 [ac(1)/ac(3)] and 63.5° [ac(2)/ac(3)], values that are all close to those from the mta(2) ligand [ac(1): C(13), C(14), O(11) and O(12); ac(2): C(11), C(12), O(9) and O(10); ac(3): C(9), C(8), O(7) and O(8)], which are 60.4 [ac(1)/ac(2)], 53.8 [ac(1)/ac(3)] and 79.6° [ac(2)/ac(3)]. A regular alternation of the mta(1) and mta(2) groups in the six ligands around each Gd^{III} chain takes place in **3** as shown in Figure 7.

Regular alternating Gd(1) and Gd(2) occurs within each chain of gadolinium atoms with two crystallographically different bridges among them. Gd(1) and Gd(2) are linked through μ-O(1);κ^2O(1),O(2) and μ-O(5b^3);κ^2O(5b^3),O(6b^3) bridges and by a single carboxylate bridge in a *syn–syn* conformation [O(3)-C(5)-O(4)]. Gd(2) and Gd(1d^3) are connected by the same kind of bridges, μ-O(8d^3);κ^2O(8d^3),O-(7d^3), μ-O(12f^3);κ^2O(12f^3),O(11f^3), and the *syn–syn* carboxylate bridge O(9e^3)-C(12e^3)-O(10e^3) (see Figure 8).

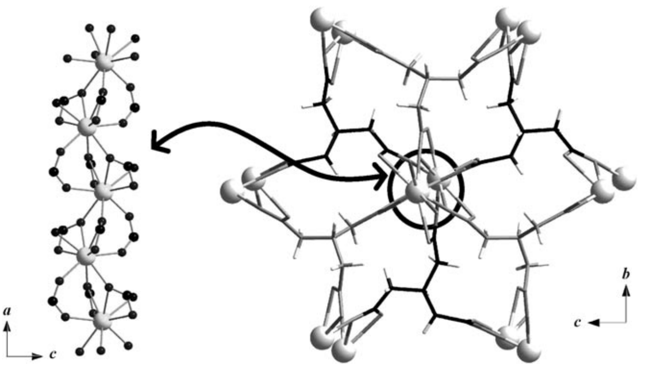


Figure 7. A view of the arrangement of the two crystallographically independent methanetricarboxylate ligands [mta(1) (grey) and mta(2) (black)] in **3**.

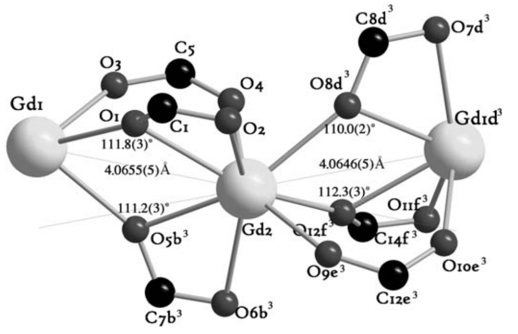


Figure 8. Detail of the bridges between the gadolinium(III) ions in **3**.

Magnetic properties of 1–3

Compound 1: The temperature dependence of the $\chi_M T$ product for **1** [χ_M is the magnetic susceptibility per one Gd^{III} ion] is shown in Figure 9. At room temperature, $\chi_M T$ is equal 7.75 cm^3 mol^{-1} K, a value which is as expected for a magnetically isolated Gd^{III} ion. Upon cooling, this value remains constant until about 50 K and then it smoothly decreases to 7.22 cm^3 mol^{-1} K at 1.9 K. This plot corresponds to a quasi Curie law behaviour. The analysis of the magnetic data of **1** through the Curie–Weiss law in Equations (1), (2) and (3) led to θ=0.16(1) K and g=1.99(1):

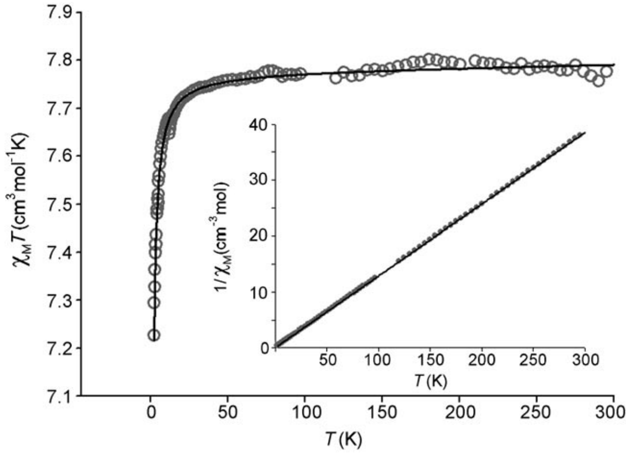


Figure 9. Temperature dependence of the $\chi_M T$ product for **1** :(○) experimental data; (——) best-fit curve (see text). Inset: 1/χ_M versus T plot.

$$\chi = \frac{C}{(T - \theta)} \tag{1}$$

$$C = \frac{N\beta^2 g^2}{3k} S(S+1) \tag{2}$$

$$\theta = \frac{zjS(S+1)}{3k} \tag{3}$$

Taking into account that $z=6$ in **1** (z = number of neighbours), a value of $j=-0.003(2)\,\text{cm}^{-1}$ results. Such a very weak magnetic coupling between the Gd^{III} ions **1** is as expected having in mind the large separation between the spin carriers through the tris-bidentate mta^{3-} ligand in this compound.

Compounds 2 and 3: The temperature dependence of the $\chi_\text{M}T$ product for **2** [χ_M is the magnetic susceptibility per one Gd^{III} ion] is shown in Figure 10. At room temperature, $\chi_\text{M}T$ for **2** is about $7.80\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$, a value that is as expected for a magnetically isolated Gd^{III} ion with local spin $S=7/2$ and $g=2.0$. Upon cooling the sample, this value practically remains constant until 15 K after which decreases abruptly to $7.48\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ at 1.9 K. This behaviour is indicative of the existence of weak antiferromagnetic interactions between the gadolinium(III) ions. According to the crystal structure of **2** described above and because of the shortest interdimer separation inside the layers through the mta^{3-} ligand is quite large [≈8.6750(8) Å], this complex can be considered magnetically as an isolated digadolinium(III) unit with a double μ-oxo and two carboxylato in *syn–syn* conformation as bridges (see Figure 5). So, the analysis of its magnetic data has been done through a simple dimer law for two local spin octets which is derived from the isotropic spin Hamiltonian $\hat{H}=-J\hat{S}_1\cdot\hat{S}_2$. The least-squares best-fit parameters are $J=-0.0063(1)\,\text{cm}^{-1}$ and $g=1.99(1)$. The calculated curve matches very well the experimental data over the whole temperature range, as shown in Figure 10. This very-weak antiferromagnetic interaction is confirmed by the magnetisation versus H data at 2.0 K which closely follow the Brillouin function for a magnetically isolated gadolinium(III) ion with $g=2.0$ and tend to a saturation value of 7.0 μ_B (inset of Figure 10).

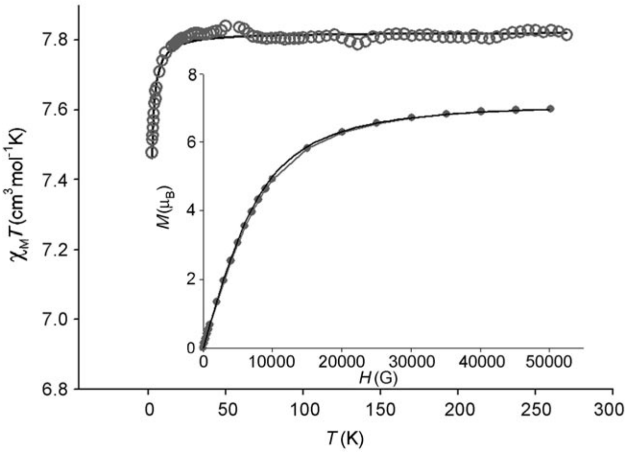


Figure 10. Temperature dependence of the $\chi_\text{M}T$ product for **2**: (○) experimental data; (——) best-fit curve. Inset: field dependence (grey points) of the magnetisation for **2** at 2.0 K; the solid line is the Brillouin function for a magnetically isolated $S=7/2$ with $g=2.0$.

The temperature dependence of the $\chi_\text{M}T$ product for **3** [for which χ_M is the magnetic susceptibility per one Gd^{III} ion] is shown in Figure 11. This plot is as expected for a weak ferromagnetic interaction. The value of $\chi_\text{M}T$ at room temperature is about $7.80\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$. It remains practically constant upon cooling until 28 K and at lower temperatures it increases reaching a value of $9.74\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ at 1.9 K. This plot is indicative of the occurrence of a weak ferromagnetic interaction between the gadolinium(III) ions in **3**.

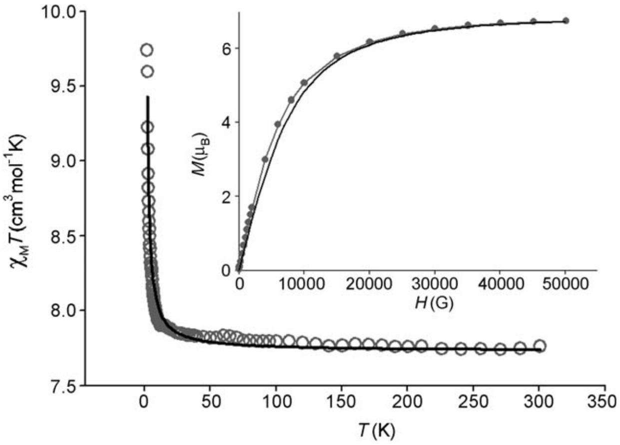


Figure 11. Temperature dependence of the $\chi_\text{M}T$ product for **3**: (○) experimental data; (——) best-fit curve (see text). Inset: field dependence of the magnetisation for **3** at 2.0 K [grey points]; the solid line is the Brillouin function for a magnetically isolated $S=7/2$ with $g=2.0$.

Looking at the structure of **3**, it seems clear that this ferromagnetic coupling occurs within the chains of gadolinium(III) ions which run parallel to the *a* axis and which are well separated from each other through the skeleton of the mta^{3-} ligands [the interchain Gd···Gd distance is ≈7.7317(3) Å]. Having this in mind and taking into account the large value of the local interacting spins [S = 7/2], the classical spin expression derived by Fisher to describe the magnetic behaviour of a uniform chain applies for **3** [Eq. (4)]:[24]

$$\chi = \frac{N\beta^2 g^2}{3kT} S(S+1) \frac{1+u}{1-u} \tag{4}$$

In this expression, u is the Langevin function, defined in Equation (5):

$$u = \coth\left(\frac{JS(S+1)}{kT}\right) - \frac{kT}{JS(S+1)} \tag{5}$$

in which N, β, k and g represent their regular meanings and J is the exchange coupling parameter between adjacent spins. Least-squares best-fit parameters are $J=+$

0.026(1) cm^{-1} and $g=1.98(1)$. The calculated curve (solid line in Figure 11) matches quite well the experimental data over the whole temperature range. This very-weak ferromagnetic interaction is visualised by the magnetisation versus H data at 2.0 K, which is slightly above the Brillouin function for a magnetically isolated gadolinium(III) ion with $g=2.0$, both tending to a saturation value of 6.7 μ_B (inset of Figure 11).

At first sight, the different nature of the weak magnetic coupling between the Gd^{III} ions in **2** (antiferromagnetic) and **3** (ferromagnetic) seems a bit surprising because of the same bridging groups [μ-oxo(carboxylate) and carboxylato in the *syn–syn* conformation] provide the exchange pathways in them. The subtle difference is the occurrence of two *syn–syn* carboxylato bridges in **2** versus only one in **3**. This circumstance is certainly responsible for the shortening of the angle at the oxo(carboxylate) bridge (η), 109.2(2)° (**2**) and 111.8(3) and 111.2(3)° (**3**). Previous magneto-structural studies on compounds containing the double μ-oxo(carboxylate) digadolinium(III) core suggest that there exists an antiferromagnetic interaction when the angle Gd-O-Gd is small, and ferromagnetic when it is greater.[25] The magnetic behaviour of compounds **2** and **3** follows this prediction. This agreement is also observed when looking at the previous cases in which the μ-$O(1);\kappa^2O(1),O(2)$/double *syn–syn* carboxylato (**2**)[26] or the μ-$O(1);\kappa^2O(1),O(2)$/single *syn–syn* carboxylato (**3**)[27] bridge occur.

Conclusions

Three novel gadolinium(III) compounds (**1**–**3**) have been synthesised and single crystals suitable for X-ray analysis have been obtained. They are the first examples that illustrate the use of methanetriacetic acid, as a scaffold for the construction of MOFs. Compounds **1** and **2** have layered structures, the former being a 6^3-**hcb** network, whereas the latter can be viewed as a condensation of **1** in bilayers to build (4^86^2) sheets. In **3** the 3D framework is of the **nia**-type, where both the $[Gd(H_2O)]^{3+}$ ions and the mta^{3-} ions act as six-fold nodes. The complexes **1** and **2** have been obtained in a gel medium varying slightly the pH value, whereas **3** was prepared by hydrothermal synthesis. This result supports that high-pressure preparative routes favour high dimensional architectures.

Concerning the magnetic properties, a relationship between the nature of the magnetic coupling and the type of bridge that links the Gd^{III} centres has been proposed on the basis of magneto-structural data for digadolinium(III) motifs with carboxylate-type ligands.[24] Compounds **2** and **3** exhibit weak antiferro- [$J=-0.0063\ cm^{-1}$ (**2**)] and ferromagnetic [$J=+0.026\ cm^{-1}$ (**3**)] interactions that agree with the above prediction.

Experimental Section

Materials and physical characterisations: Methanetriacetic acid (H_3tmc) was prepared by using a method reported previously.[28] The compounds were characterised by using ^1H NMR (at 400 and 300 MHz) and ^{13}C NMR (at 75 MHz) spectra, the chemical shifts are reported relative to internal Me_4Si, at room temperature. Column chromatography was performed on silica gel, 60 Å and 0.2–0.5 mm. The intermediate organic compounds were visualised by using UV light and vanillin with acetic and sulfuric acids in ethanol with heating. All solvents were purified by standard techniques.[29] Reactions requiring anhydrous conditions were performed under a dinitrogen atmosphere. Anhydrous magnesium sulfate was used for drying solutions. The rest of reagents and solvents used in the synthesis of compounds **1**–**3** were purchased from commercial sources and used without further purification. Single crystals of **1** and **2** were grown in silica gel medium through the techniques described by Henish,[30] whereas those of compound **3** were obtained in hydrothermal conditions. Elemental analyses (C and H) were performed on an EA 1108 CHNS-O microanalytical analyser. Magnetic susceptibility measurements on polycrystalline samples of **1**–**3** were performed in the temperature range of 1.9–300 K by using a Quantum Design SQUID magnetometer. The measurements in all compounds were made with a field of 100 G between 1.9 and 50 K, and 10000 G in the range of 50 K to RT. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[31] to be -196×10^{-6} (**1**), -170×10^{-6} (**2**) and $-131\times10^{-6}\ cm^3mol^{-1}$ (**3**) per one Gd^{III} ion. Experimental susceptibilities were also corrected for the magnetisation of the sample holder.

Preparation of dimethyl-3-cyanomethyleneglutarate: A mixture of dimethyl-1,3-acetonedicarboxylate (10 g, 57.4 mmol), cyanoacetic acid (6.38 g, 86.1 mmol), ammonium acetate (0.77 g, 1.2 mmol), dry benzene (50 mL) and acetic acid (3.4 mL) was refluxed under stirring for 24 h using a Dean-Stark to remove water the formed in the reaction azeotropically. The reaction mixture was cooled and washed with water (2× 15 mL) and then with a saturated $NaHCO_3$ solution (2×10 mL). The aqueous washings were extracted with ether (2×20 mL) and the combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by silica gel flash-chromatography, yielding dimethyl-3-cyanomethyleneglutarate (10.3 g, 90% yield) as an oil. ^1H NMR ($CDCl_3$): $\delta=3.36$ (d, $J=1.2$ Hz, 2H), 3.59 (s, 2H), 3.69 (s, 3H), 3.70 (s, 3H), 5.49 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta=39.6$ (t), 41.4 (t), 52.8 (q), 52.8 (q), 103.4 (d), 115.8 (s), 152.2 (s), 169.3 (s), 169.5 ppm (s); LRMS (EI): *m/z*: (%): 197 [M^+] (0.5), 166 (71), 165 (100), 138 (23), 80 (38); HRMS (EI): *m/z*: calcd: $C_9H_{11}NO_4$ [M^+]: 197.0688; found: 197.0695.

Preparation of methanetriacetic acid: A mixture of the α,β-unsaturated cyanide (10 g, 50.7 mmol) and $Pd(OH)_2$ (200 mg) in MeOH (150 mL) was placed under H_2 atmosphere. The reaction mixture was vigorously stirred until TLC showed complete conversion to the dimethyl-3-(cyanomethyl)pentanedioate. The mixture was filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was used without further purification. A 60 mL 5 M NaOH solution was added to the residue oil leading a two-phase system. The mixture was heated and vigorously stirred for 2 h. After cooling, the clear solution was acidified with 5 M sulfuric acid and then evaporated to dryness. The solid was extracted several times with diethyl ether and the combined extracts were dried with $MgSO_4$. After filtration, the evaporation of the solvent afforded the tricarboxylic acid as a white solid (9.35 g, 96% yield from the dimethyl-3-cyanomethileneglutarate). ^1H NMR ([D_6]acetone): $\delta=2.50$ (d, $J=6.4$ Hz, 6H), 2.67 ppm (m, 1H); ^{13}C NMR ([D_6]acetone): $\delta=28.4$ (d), 36.6 (t), 172.8 ppm (s); elemental analysis calcd (%) for $C_7H_{10}O_6$ (190.0): C 44.21, H 5.30; found: C 44.22, H 5.99.

Complex $[Gd(mta)(H_2O)_3]_n\cdot4nH_2O$ (1): An aqueous solution of NaOH was poured into a 0.07 M solution of methanetriacetic acid [H_2O (3 mL) and ethanol (4 mL)] for which the pH was adjusted to 5.08. Afterwards, tetramethoxysilane (0.7 mL) was added to the resulting solution. The mixture was introduced into test tubes, covered, and stored for one day at room temperature to allow the formation of the gel. Once the gel has been formed, an aqueous solution of gadolinium(III) nitrate hexahydrate 0.1 M (2.5 mL) was placed on the gel, care being taken to avoid damaging the surface of the gel, and it was stored at 30 °C. White prisms of **1** suitable for single-crystal X-ray diffraction appeared in the test tubes a few days later. They were separated mechanically, washed with water/ethanol and air dried. Single crystals of **1** are shown in picture 1 (see the Supporting Information). Elemental analysis (%) calcd for $C_7H_{21}GdO_{13}$ (**1**): C 17.85, H 4.46; found: C 17.80, H 4.48.

Complex $[Gd(mta)(H_2O)_3]_n \cdot 2nH_2O$ (2): Compound **2** was obtained by a similar procedure to that used for **1**, but adjusting the pH of the solution to 4.50. X-ray quality crystals of **2** as colourless needles formed in the gel after a few days. They were collected, washed with water/ethanol and air dried. Elemental analysis (%) calcd for $C_7 H_{17} Gd O_{11}$ **2**: C 19.33, H 3.91; found: C 19.29, H 3.93.

Complex $[Gd(mta)(H_2O)_3] \cdot 4nH_2O$ (3): Aqueous solutions of methanetriacetic acid 0.1 M (10 mL) and gadolinium(III) nitrate hexahydrate 0.05 M (20 mL) were mixed and the resulting mixture was sealed in a 45 mL stainless-steel reactor with a Teflon liner, and heated at 170 °C for 48 h.[32] After cooling, yellow cubic crystals, suitable for X-ray analysis, were manually selected from the Teflon-liner and air dried. Elemental analysis (%) calcd for $C_{14} H_{22} Gd_2 O_{16}$ **3**: C 22.08, H 2.89; found: C 22.03, H 2.86.

Crystallographic data collection and structural determination: Single crystals of **1**–**3** were mounted on a Nonius Kappa CCD diffractometer and the data were collected at 293(2) K by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å).[33] A summary of the crystallographic data and structure refinement is given in Table S1 in the Supporting Information. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 by using the SHELXS-97 and SHELXL-97 programs[34] included in the WINGX software package.[35] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the mta^{3-} ligand were located from difference Fourier maps in **1** and **2**, whereas they were set in calculated positions in **3**. All hydrogen atoms were refined isotropically. The final geometrical calculations and the graphical manipulations were carried out with PARST95,[36] PLATON[21] and DIAMOND[37] programs. Hydrogen bonds and selected-bond lengths and angles of compounds **1**–**3** are listed in Tables S2 and S3 in the Supporting Information.

Acknowledgements

This work was funded by the Ministerio Español de Ciencia e Innovación through projects MAT2007–60660, CTQ2007–61690 and “Factoría de Cristalización” (Consolider-Ingenio2010, CSD2006–00015). Pre-doctoral (O. F.) fellowships from Ministerio Español de Educación y Ciencia and from the Agencia Canaria de Investigación, Innovación y Sociedad de la Información (L.C.-D.) are acknowledged. J. P. also thanks the CSD2006–00015 for a postdoctoral contract.

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[1] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) *Comprehensive Supramolecular Chemistry, vol. 1–11* (Eds.: J. M. Lehn, J. L. Atwood, E. D. J. Davis, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1990–1996**.

[2] Review articles: a) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502–518; b) C. Janiak, *Angew. Chem.* **1997**, *109*, 1499–1502; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431–1434; c) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484; d) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375–1405; e) A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466–3492; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292; f) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; g) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; h) G. S. Papaefstathiou, L. R. MacGillivray, *Coord. Chem. Rev.* **2003**, *246*, 169–184; i) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; j) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273–282.

[3] a) A. Corma, *Chem. Rev.* **1997**, *97*, 2373–2420; b) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.* **2000**, *112*, 2161–2164; *Angew. Chem. Int. Ed.* **2000**, *39*, 2081–2084; c) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; e) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; f) L. Pan, K. M. Adams, H. E. Hernandez, X. T. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067; g) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490–1521; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496; h) B. B. Ding, Y. Q. Weng, Z. W. Mao, C. K. Lam, X. M. Chen, B. H. Ye, *Inorg. Chem.* **2005**, *44*, 8836–8845; i) E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374–6381 and references cited therein; j) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748–4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679.

[4] a) G. S. Hanan, D. Volkmer, U. S. Schubert, J. M. Lehn, G. Baum, D. Fenske, *Angew. Chem.* **1997**, *109*, 1929; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1842- 1844; b) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186–2187; c) V. Tangoulis, C. P. Raptopoulou, V. Psycharis, A. Terzis, K. Skorda, S. P. Perlepes, O. Cador, O. Kahn, E. G. Bakalbassis, *Inorg. Chem.* **2000**, *39*, 2522–2529; d) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2002**, *114*, 3545–3548; *Angew. Chem. Int. Ed.* **2002**, *41*, 3395–3398; e) D. L. Liang, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, C. Wilson, M. Schroder, *Chem. Eur. J.* **2003**, *9*, 1384–1391; f) K. E. Holmes, P. F. Kelly, M. R. J. Elsegood, *Dalton Trans.* **2004**, 3488–3494; g) C. W. Liu, B. J. Liaw, L. S. Liou, J. C. Wang, *Chem. Commun.* **2005**, 1983–1985; h) D. F. Sun, S. Q. Ma, Y. X. Ke, T. M. Petersen, H. C. Zhou, *Chem. Commun.* **2005**, 2663–2665; i) J. J. M. Amoore, C. A. Black, L. R. Hanton, M. D. Spicer, *Cryst. Growth Des.* **2005**, *5*, 1255–1261; j) Z. He, E. Q. Gao, Z. M. Wang, C. H. Yan, M. Kurmoo, *Inorg. Chem.* **2005**, *44*, 862–874.

[5] a) C. Livage, C. Egger, G. Fe'rey, *Chem. Mater.* **1999**, *11*, 1546–1550; b) D. J. Price, S. Tripp, A. K. Powell, P. T. Wood, *Chem. Eur. J.* **2001**, *7*, 200–208; c) S. O. H. Gutschke, D. J. Price, A. K. Powell, P. T. Wood *Angew. Chem.* **2001**, *113, 1974–1977; Angew. Chem. Int. Ed.* **2001**, 40, 1920–1923; *Angew. Chem. Int. Ed.* **2001**, *40*, 1920–1923; d) N. Guillou, Q. Gao, P. M. Forster, J. S. Chang, S. E. Park, G. Fe'rey, A. K. Cheetham *Angew. Chem.* **2001**, *113, 2913–2916; Angew. Chem. Int. Ed.* **2001**, 40, 2831–2834; *Angew. Chem. Int. Ed.* **2001**, *40*, 2831–2834.

[6] a) N. Guillou, C. Livage, M. Drillon, G. Férey *Angew. Chem.* **2003**, *115, 5472–5475; Angew. Chem. Int. Ed.* **2003**, 42, 5314–5317; *Angew. Chem. Int. Ed.* **2003**, *42*, 5314–5317; b) P. M. Forster, A. K. Cheetham *Angew. Chem.* **2002**, *114, 475–477; Angew. Chem. Int. Ed.* **2002**, 41, 457–459; *Angew. Chem. Int. Ed.* **2002**, *41*, 457–459; c) W. Schmitt, J. P. Hill, M. P. Juanico, A. Caneschi, F. Costantino, C. E. Anson, A. K. Powell *Angew. Chem.* **2005**, *117, 4259–4264; Angew. Chem. Int. Ed.* **2005**, 44, 4187–4192; *Angew. Chem. Int. Ed.* **2005**, *44*, 4187–4192; d) S. C. Xiang, X. T. Wu, J. J. Zhang, R. B. Fu, S. M. Hu, X. D. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16352–16353; e) A. C. Sudik, A. P. Coté, O. M. Yaghi, *Inorg.Chem.* **2005**, *44*, 2998–3000; f) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518.

[7] a) D. L. Long, A. J. Blake, N. R. Champness, C. Wilson, M. Schröder *Angew. Chem.* **2001**, *113, 2509–2513; Angew. Chem. Int. Ed.* **2001**, 40, 2443–2447; *Angew. Chem. Int. Ed.* **2001**, *40*, 2443–2447; b) D. L. Long, A. L. Blake, N. R. Champness, P. Hubberstey, D. M. Proserpio, M. Wilson, *Angew. Chem.* **2004**, *116*, 1887–1890; *Angew. Chem. Int. Ed.* **2004**, *43*, 1851–1854; c) Y. Cui, H. L. Ngo, P. S. White, W. Lin, *Chem. Commun.* **2002**, 1666–1667; d) C. Qin, X. L. Wang, E. B. Wang, Z. M. Su, *Inorg. Chem.* **2005**, *44*, 7122–7129; e) M. B. Zhang, J. Zhang, S. T. Zheng, G. Y. Yang, *Angew. Chem.* **2005**, *117*, 1409–1412; *Angew. Chem. Int. Ed.* **2005**, *44*, 1385–1388; f) G. B. Gardner, D. Ventakaraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792–795; g) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar, D. Venkataraman, *J. Am. Chem. Soc.* **1996**, *118*, 6946–6953; h) B. F. Abrahams,

S. J. Egan, R. Robson, *J. Am. Chem. Soc.* **1999**, *121*, 3535–3536; i) A. Markus, *Angew. Chem.* **1999**, *111*, 3671–3674; *Angew. Chem. Int. Ed.* **1999**, *38*, 3463–3465; j) B. L. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021- 1023; k) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983.

[8] a) M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649–1650; b) B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins, R. Robson, *Angew. Chem.* **1999**, *111*, 1538–1540; *Angew. Chem. Int. Ed.* **1999**, *38*, 1475–1477; c) M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou, A. S. C. Chan, *Angew. Chem.* **2000**, *112*, 2586–2588; *Angew. Chem. Int. Ed.* **2000**, *39*, 2468–2470; d) C. Y. Su, Y. P. Cai, C. L. Chen, F. Lissner, B. S. Kang, W. Kaim, *Angew. Chem.* **2002**, *114*, 3519–3523; *Angew. Chem. Int. Ed.* **2002**, *41*, 3371–3375; e) J.-P. Costes, F. Dahan, F. Nicodeme, *Inorg. Chem.* **2003**, *42*, 6556–6563; f) S. Y. Wan, Y. Z. Li, T. Okamura, J. Fan, W. Y. Sun, N. Uevama, *Eur. J. Inorg. Chem.* **2003**, 3183- 3189; g) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim, H. C. zur Loye, *J. Am. Chem. Soc.* **2003**, *125*, 8595–8613; h) W. Zhao, Y. Song, T. A. Okamura, J. Fan, W. Y. Sun, N. Ueyama, *Inorg. Chem.* **2005**, *44*, 3330–3336.

[9] a) N. Weibel, L. Charbonniere, R. Ziessel, *Tetrahedron Lett.* **2006**, *47*, 1793–1796; b) P. R. Ashton, S. E. Boyd, C. L. Brown, N. Jayaraman, S. A. Nepogodiev, J. F. Stoddart, *Chem. Eur. J.* **1996**, *2*, 1115–1128; c) G. R. Newkome, R. K. Behera, C. N. Moorefield, G. R. Baker, *J. Org. Chem.* **1991**, *56*, 7162–7167.

[10] a) D. S. Kemp, K. S. Petrakis, *J. Org. Chem.* **1981**, *46*, 5140–5143; b) E. A. Jefferson, E. Locardi, M. Goodman, *J. Am. Chem. Soc.* **1998**, *120*, 7420–7428.

[11] J. B. Bialecki, L.-H. Yuan, B. Gong, *Tetrahedron* **2007**, *63*, 5460–5469.

[12] a) R. Welti, F. Diederich, *Helv. Chim. Acta* **2003**, *86*, 494–503; b) K. H. Lee, J.-I. Hong, *Tetrahedron Lett.* **2000**, *41*, 6083–6087; c) A. Vacca, C. Nativi, M. Cacciarini, R. Pergoli, S. Roelens, *J. Am. Chem. Soc.* **2004**, *126*, 16456–16465; d) W. C. Still, R. Liu, *Philos. Trans. R. Soc. London Ser. A* **1993**, *345*, 97–104.

[13] a) A. Bianco, S. Fournel, S. Wieckowski, J. Hoebeke, G. Guichard, *Org. Biomol. Chem.* **2006**, *4*, 1461–1463; b) J. Bitta, S. Kubik, *Org. Lett.* **2001**, *3*, 2637–2640.

[14] a) L. Cañadillas-Delgado, O. Fabelo, J. Pasán, F. S. Delgado, M. Déniz, E. Sepúlveda, M. M. Laz, M. Julve, C. Ruiz-Pérez, *Cryst. Growth Des.* **2008**, *8(4)*, 1313–1318; b) L. Cañadillas-Delgado, J. Pasán, O. Fabelo, M. Hernández-Molina, F. Lloret, M. Julve, C. Ruiz-Pérez, *Inorg. Chem.* **2006**, *45*, 10585–10594; c) L. Cañadillas-Delgado, O. Fabelo, C. Ruiz-Pérez, F. S. Delgado, M. Julve, M. Hernández-Molina, M. M. Laz, P. Lorenzo-Luis, *Cryst. Growth Des.* **2006**, *6(1)*, 87–93; d) M. Hernández-Molina, C. Ruiz-Pérez, T. López, F. Lloret, M. Julve, *Inorg. Chem.* **2003**, *42*, 5456–5458; e) M. Hernández-Molina, P. Lorenzo-Luis. C. Ruiz-Pérez, T. López-Couros, I. M. Martín, K. M. Anderson, A. G. Orpen, E. H. Bocanegra, F. Lloret, M. Julve, *J. Chem. Soc. Dalton Trans.* **2002**, 3462–3470; f) M. Hernández-Molina, P. Lorenzo-Luis. T. López, C. Ruiz-Pérez, F. Lloret, M. Julve, *CrystEngComm* **2000**, *31*, 169–174.

[15] a) O. M. Yaghi, H. Li, T. L. Groy, *J. Am. Chem. Soc.* **1996**, *118*, 9096–9101; b) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; c) M. Eddaoudi, H. L. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397; d) J. W. Ko, K. S. Min, M. P. Suh, *Inorg. Chem.* **2002**, *41*, 2151–2157; e) T. J. Prior, M. J. Rosseinsky, *Inorg. Chem.* **2003**, *42*, 1564–1575; f) D. Cheng, M. A. Khan, R. P. Houser, *Cryst. Growth Des.* **2004**, *4*, 599–604; g) H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **2004**, *126*, 15844–15851; h) L. H. Xie, S. X. Liu, B. Gao, C. D. Zhang, C. Y. Sun, D. H. Li, Z. M. Su, *Chem. Commun.* **2005**, 2402–2404.

[16] a) Q.-L. Wang, M. Liang, D.-Z. Liao, S.-P. Yan, Z.-H. Jiamg, P. Cheng, *Z. Anorg. Allg. Chem.* **2004**, *630*, 613–616; b) C. Daiguebonne, Y. Gerault, O. Guillou, A. Lecerf, K. Boubekeur, P. Batail, M. Kahn, O. Kahn, *J. Alloys Compd.* **1998**, *275–277*, 50–53; c) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518; d) C. Daiguebonne, O. Guilloa, Y. Gerault, A. Lecerf, K. Boubekeur, *Inorg. Chim. Acta* **1999**, *284*, 139–145; e) C. Daiguebonne, Y. Gerault, F. Le Dret, O. Guillou, K. Boubekeur, *J. Alloys Compd.* **2002**, *344*,179–185; f) C. Daiguebonne, O. Guillou, K. Boubekeur, *Inorg. Chim. Acta* **2000**, *304*, 161–169; g) C. Serre, G. Ferey, *J. Mater. Chem.* **2002**, *12*, 3053–3057; h) J. Yang, Q. Yue, G.-D. Li, J.-J. Cao, G.-H. Li, J.-S. Chen, *Inorg. Chem.* **2006**, *45*, 2857–2865; i) X. Guo, G. Zhu, Z. Li, F. Sun, Z. Yang, S. Qiu, *Chem. Commun.* **2006**, 3172–3174; j) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693–1696.

[17] a) N. Bland and J. F. Thorpe, *J. Chem. Soc.* **1912**, *101*, 1557–1570; b) J. F. Thorpe and A. S. Wood, *J. Chem. Soc. Trans.* **1913**, *103*, 1579–1586; c) C. K. Ingold, *J. Chem. Soc. Trans.* **1921**, *119*, 341–354; d) C. K. Ingold and L. C. Nickolls, *J. Chem. Soc. Trans.* **1922**, *121*, 1638–1648; e) F. R. Goss, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc. Trans.* **1923**, *123*, 327–361; f) M. H. Dreifuss and C. K. Ingold, *J. Chem. Soc. Trans.* **1923**, *123*, 2964–2968; g) E. P. Kohler and G. H. Reid, *J. Am. Chem. Soc.* **1925**, *47*, 2803–2811; h) H. Stetter and H. Stark, *Chem. Ber.* **1959**, *92*, 732–735; i) R. Lukeš and K. Syhora, *Collect. Czech. Chem. Commun.* **1953**, *18*, 654; j) R. Lukeš and J. Pale ek, *Collect. Czech. Chem. Commun.* **1964**, *29*, 1073; k) J. Font, F. López and F. Serratosa, *Tetrahedron Lett.* **1972**, *13*, 2589–2590.

[18] a) Z.-H. Zhang, Z.-L. Shen, T. Okamura, H.-F. Zhu, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* **2005**, *5(3)*, 1191–1197; b) Z.-H. Zhang, T. Okamura, Y. Hasegawa, H. Kawaguchi, L.-Y. Kong. W.-Y. Sun, N. Ueyama, *Inorg. Chem.* **2005**, *44*, 6219–6227; c) Z.-H. Zhang, W. Li, T. Okamura, L.-Y. Kong, W.-Y. Sun, N. Ueyama, *Supramol. Chem.* **2006**, *18(4)*, 317–325; d) Z.-H. Zhang, G.-X. Liu, T. Okamura, W.-Y. Sun, N. Ueyama, *Struct. Chem.* **2006**, *17*, 3–11.

[19] a) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182; b) http://rcsr.anu.edu.au/home.

[20] A. L. Spek , *PLATON, J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[21] C. Janiak, *Dalton Trans.* **2003**, 2781–2804.

[22] a) M. Du, Z.-H. Zhang, L.-F. Tang, X.-G. Wang, X.-J. Zhao, S. R. Batten, *Chem. Eur. J.* **2007**, *13*, 2578–2586; b) V. Niel, A. Galet, A. B. Gaspar, M. C. Muñoz, J. A. Real, *Chem. Commun.* **2003**, 1248–1249; c) B. Yan, C. S. Day, A. Lachgar, *Chem. Commun.* **2004**, 2390–2391, and references therein.

[23] a) H.-K. Chae, M. Eddaoudi, J.-K. Kim, S. I. Hauck, J. F. Hartwig, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 11482–11483; b) Z. Wang, X. Zhang, S. R. Batten, M. Kurmoo, S. Gao, *Inorg. Chem.* **2007**, *46*, 8439–8441; c) Y.-L. Bai, J. Tao, R.-B. Huang, L.-S. Zheng, S.-L. Zheng, K. Oshida, Y. Einaga, *Chem. Commun.* **2008**, 1753–1755.

[24] M. E. Fisher, *Am. J. Phys.* **1964**, *32*, 343–346.

[25] R. Baggio, R. Calvo, M. T. Garland, O. Peña, M. Perec, A. Rizzi, *Inorg. Chem.* **2005**, *44*, 8979–8987.

[26] a) A. Panagiotopoulos, T. F. Zafiropoulos, S. P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C. P. Raptopoulou, *Inorg. Chem.* **1995**, *34*, 4918–4920; b) S. Y. Niu, J. Jin, J. L. Jinb, Z. Z. Yanga, *Solid State Sci.* **2002**, *4*, 1103–1106; c) A. W.-H. Lam, W.-T. Wong, S. Gao, G. Wen, X.-X. Zhang, *Eur. J. Inorg. Chem.* **2003**, 149–163; d) A. Rizzi, R. Baggio, M. T. Garland, O. Peña, M. Perec, *Inorg. Chim. Acta* **2003**, *353*, 315–319; e) A. M. Atria, R. Baggio, M. T. Garland, J. C. Muñoz, O. Peña, *Inorg. Chim. Acta* **2004**, *357*, 1997–2006; f) D. John, W. Urland, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2635–2637; g) D. John, W. Urland, *Eur. J. Inorg. Chem.* **2005**, 4486–4489; h) A. Rohde, W. Urland, *Dalton Trans.* **2006**, *24*, 2974–2978; i) D. John, W. Urland, *Eur. J. Inorg. Chem.* **2006**, 3503–3509.

[27] a) J.-P. Costes, J.-M. Clemente-Juan, F. Dahan, F. Nicodème, *Dalton Trans.* **2003**, 1272–1275; b) S. C. Manna, E. Zangrando, A. Bencini, C. Benelli, N. R. Chaudhuri, *Inorg. Chem.* **2006**, *45*, 9114–9122.

[28] a) K. A. Gupta, A. K. Saxena, P. C. Jain, N. Anand, *Indian Journal of Chemistry* **1987**, *26B*, 341–343; b) J. M. Baumeister; R. Alberto; K. Ortner; B. Spingler; P. A. Schubiger; T. A. Kaden, *J. Chem. Soc. Dalton Trans.* **2002**, 4143–4151; R. Alberto; K. Ortner; B. Spingler; P. A. Schubiger; T. A. Kaden, *J. Chem. Soc. Dalton Trans.* **2002**, 4143–4151.

[29] W. L. F. Armarego; D. D. Perrin, Purification of Laboratory Chemicals, 4th ed.; Butterworth-Heinemann: Oxford, **1996**.
[30] H. K. Henisch, in *Crystal Growth in Gels*, The Pennsylvania State Univ. Press, Pittsburg, **1970**.
[31] R. L. Carlin in *Magnetochemistry* Springer, Heidelberg, Germany, **1986**.
[32] K. Byrappa, M. Yoshimura in *Handbook of Hydrothermal Technology: Technology for Crystal Growth and Materials Processing*, William Andrew Inc. **2001**.
[33] a) EVALCCD: A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220–229; b) SADABS, Bruker Analytical X-Ray Systems, Inc., Madison, WI, USA, **1998**, 10.
[34] G. M. Sheldrick, SHELXL-97 and SHELXS-97; Universität Göttingen: Göttingen, Germany, **1998**.
[35] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[36] PARST95: M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659–660.
[37] DIAMOND 2.1d, Crystal Impact GbR, CRYSTAL IMPACT, K. Brandenburg & H. Putz GbR, Postfach 1251, D-53002 Bonn, Germany, **2000**.

Received: November 5, 2009