Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A novel three-dimensional heterometallic coordination polymer: poly[[diaquadi-μ_3-chlorido-μ_2-chlorido-tri-μ_3-nicotinato-tricopper(I)-gadolinium(III)] hemihydrate]

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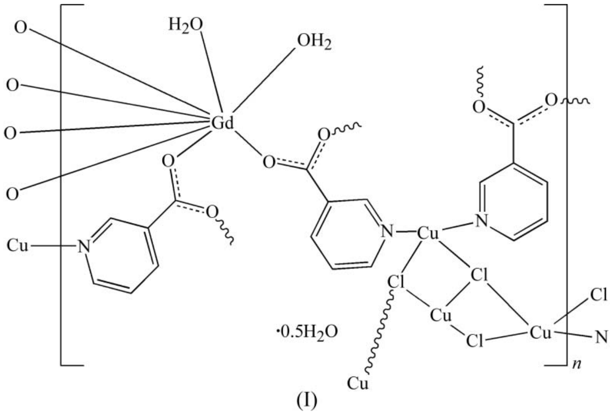
Received 8 April 2011
Accepted 7 May 2011
Online 19 May 2011

In the title polymeric heterometallic compound, $\{[Cu_3Gd(C_6H_4NO_2)_3Cl_3(H_2O)_2]\cdot0.5H_2O\}_n$, comprising copper(I) and gadolinium(III) cations bridged by nicotinate (nic) ligands and chloride anions, the Gd^{III} centers display a bicapped trigonal prismatic geometry, defined by six carboxylate O atoms and two water molecules. For copper(I), one Cu center is three-coordinated by three chloride ions and displays a trigonal–planar geometry; the other two Cu centers are four-coordinated and display a very distorted tetrahedral geometry. The chloride anions act in μ_2- and μ_3-bridging modes, linking the Cu^I ions into an infinite chain. The nic ligand exhibits a tridentate coordination mode, with the carboxylate O atoms linking to two Gd^{III} ions and the N atom linking to one Cu^I ion. Thus, a novel three-dimensional heterometallic coordination polymer is constructed from Gd–carboxylate subunits and Cu—Cl chains. In addition, intra- and intermolecular O—H···O and O—H···Cl hydrogen bonds are also observed within the three-dimensional structure. Topologically, the framework represents an unusual 3,6-connected $(4.8^2)_3(4^{10}.6^5)$ net.

Comment

Recently, new potentially multifunctional lanthanide–transition metal complexes have attracted much attention because of their fascinating structural diversity and the vast range of potential applications in many fields, such as sensors, gas storage, ion exchange, catalysis, magnetism, photoluminescence, and so on (Sabatini *et al.*, 1993; Lu, 2003; Zhou *et al.*, 2006; Cheng *et al.*, 2006; Pope *et al.*, 2004; Inanaga *et al.*, 2002; Liu, Huang *et al.*, 2011; Liu, Jia *et al.*, 2011). Lanthanide–transition metal complexes are usually constructed by assembling mixed metal ions and ligands under hydrothermal conditions, but owing to the special properties of the lanthanide ions, the ligands used should possess ligating functional groups that are able to effectively coordinate to both lanthanide and transition metal ions simultaneously. It is well known that lanthanide ions have a strong preference to bond to O-donor atoms, while soft transition metal ions, such as Ag^I or Cu^I ions, bind more easily to N-donor atoms. This different affinity for oxygen and nitrogen donors of lanthanide and transition metal ions provides the impetus to construct unusual multidimensional heterometallic coordination frameworks (Cheng *et al.*, 2007*a*; Gu & Xue, 2007*a*; Yue *et al.*, 2005). Nicotinic acid (Hnic) is one such potentially bridging ligand with O- and N-donor atoms, which can thus be used to construct high-dimensional heterometallic frameworks with the carboxylate group bonding to lanthanide ions and the N atoms bonding to transition metal ions. On the other hand, copper halides, whose anion can be used as an essential element of frameworks, are capable of meeting the special requirements of bridging ligands to construct high-dimensional coordination polymers (Song *et al.*, 2005; Cariati *et al.*, 2001; Lu *et al.*, 1999; Vega & Saillard, 2004; Li *et al.*, 2004). In this paper, we describe the synthesis of a novel 3*d*–4*f* coordination polymer, namely, poly[[diaquatri-μ_2-chlorido-tri-μ_3-nicotinato-tricopper(I)gadolinium(III)] hemihydrate], (I), by the reaction of Hnic with Gd_2O_3 and $CuCl_2$ *via* a hydrothermal method. Although the starting materials are copper(II) salts, the Cu center has an oxidation state of +1, attributable to a reduction reaction under hydrothermal conditions. Evidence for this process has been reviewed by Zenobi (Zhang *et al.*, 2003). It was found that Cu^{II} was reduced to Cu^I by gas-phase charge exchange with nicotinic acid, which is a thermodynamically favorable process. Cu^{II} can be even more efficiently reduced to Cu^I by free electron capture in the gas phase.



(I)

Single-crystal structure analysis reveals that the title complex exhibits a three-dimensional heterometallic coordination framework composed of $(Cu_3Cl_3)_n$ chains, Gd centers and nic ligands. The asymmetric unit of (I) consists of one Gd^{3+} ion, three unique Cu$^+$ ions, three nic ligands, three Cl$^-$ ions, and two coordinated and one interstitial water molecule (Fig. 1). The coordination geometry around the Gd center can be described as a bicapped trigonal prism, with O—Gd—O bond angles ranging from 68.64 (16) to 146.85 (18)° and Gd—O bond lengths varying from 2.324 (5) to 2.542 (4) Å, values that

doi:10.1107/S010827011101732X

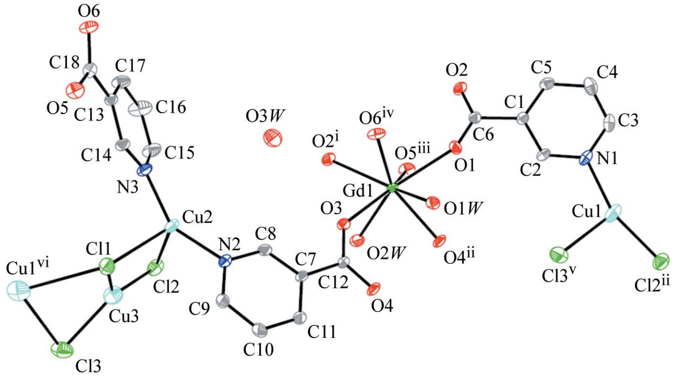


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x, -y, -z + 1$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

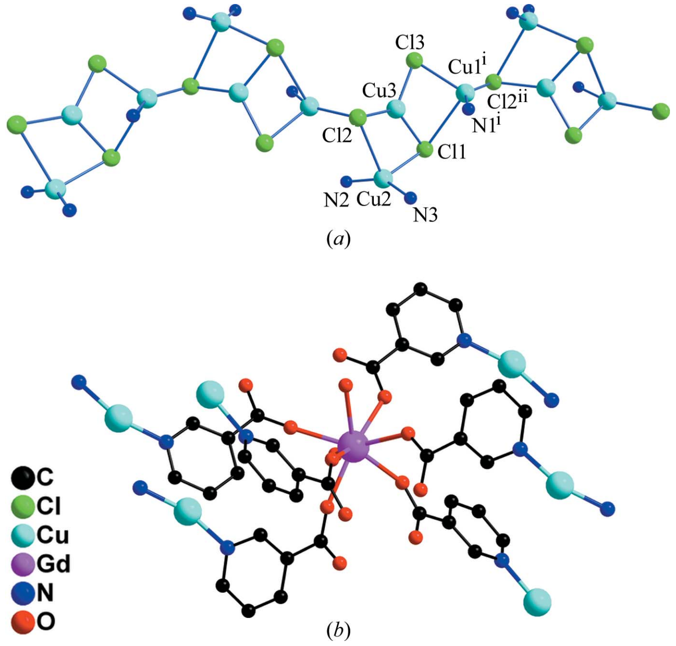


Figure 2
(*a*) A view of the one-dimensional $(Cu_3Cl_3)_n$ chain in (I). (*b*) A view of the connectivity of the Gd center. [Symmstry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.]

are similar to those reported in the literature (Zhu & Zeng, 2010). For the copper centers, Cu1 is four-coordinated by three different chloride ions and one N atom from a nic ligand; Cu2 is also four-coordinated by two different chloride ions and two N atoms from two nic ligands. Both Cu1 and Cu2 display a very distorted tetrahedral geometry; Cu3 is three-coordinated by three different chloride ions and displays a trigonal–planar geometry. The Cu—Cl and Cu—N bond lengths in (I) are in the ranges 2.215 (2)–2.9022 (19) and 1.928 (6)–1.982 (6) Å, respectively, which are all within the range observed for related Cu^I complexes with chloride donor ligands (Deng *et al.*, 2008). The Cl1 and Cl2 anions exhibit μ_3-bridging modes to link three Cu^I cations, while Cl3 has a μ_2-bridging mode between two Cu^I ions. Thus, the combination results in the formation of a (Cu_3Cl_3) unit. The (Cu_3Cl_3) units connect through μ_3-Cl2 to form a $(Cu_3Cl_3)_n$ chain (Fig. 2*a*). Similar examples of $(Cu_xCl_y)_n$ chains can be found in the structures of $(C_8H_{20}N)_3[Cu_7Cl_{10}]$ and $(C_{12}H_{12}N)[Cu_2Cl_3]$, which contain $(Cu_7Cl_{10})_n$ and $(Cu_2Cl_3)_n$ chains, respectively (Asplund & Jagner, 1984; Pavlyuk *et al.*, 2001). The structure of $[(CuCl)(4,4'\text{-bpy})_2]_n(NO_3)_n$ (bipy is bipyridine) contains a $(Cu_2Cl)_n$ chain (Hao *et al.* 2008). (I) is therefore a new important member of Cu—Cl chains. The nic ligand in (I) exhibits a tridentate coordination mode with the carboxylate O atoms bridging two Gd^{III} ions and the N-atom end coordinating to one Cu^I ion (Fig. 2*b*).

In the complicated polymeric structure of (I), the carboxylate groups of the nic ligands link adjacent Gd^{III} ions

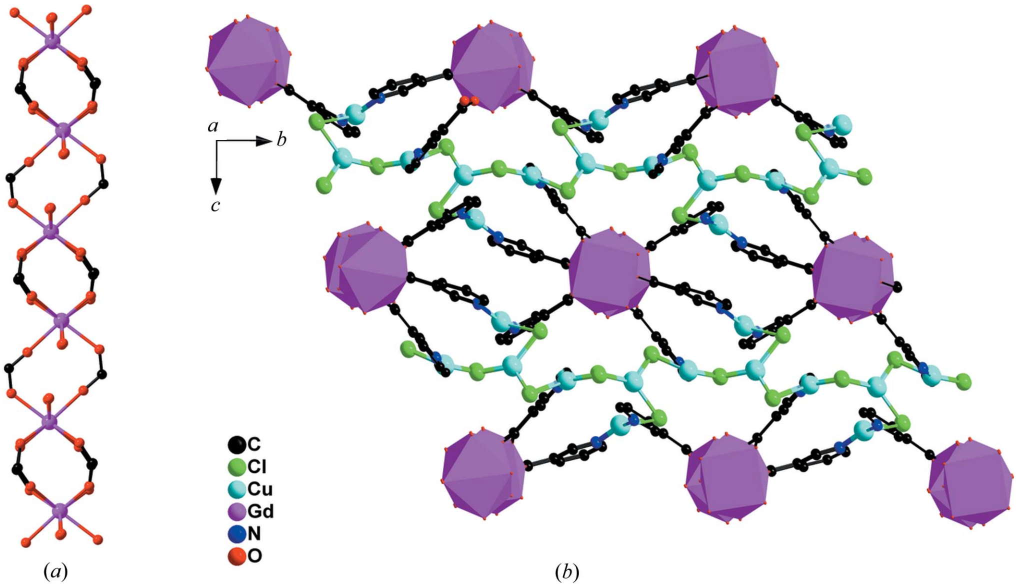


Figure 3
(*a*) A view of an extended Gd–carboxylate chain. (*b*) A view of the three-dimensional heterometallic coordination frameworks along the *bc* plane. The polyhedra (pink in the electronic version of the paper) represent the GdO_8 coordination environments.

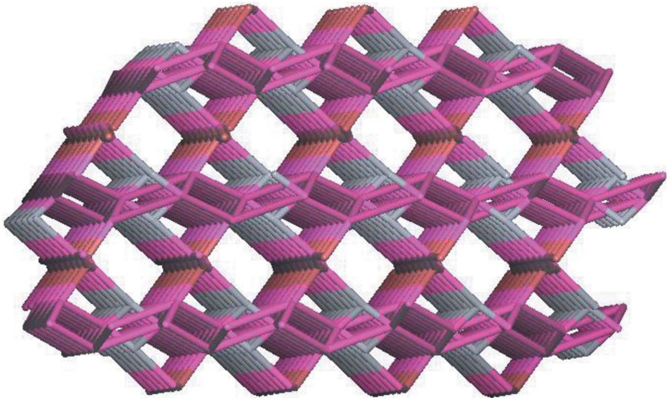


Figure 4
A view of the topology of the title compound.

to form an extended Gd–carboxylate chain perpendicular to the *a* axis (Fig. 3*a*). The distances between adjacent Gd^{III} ions within the chain are 4.486 (2) and 5.119 (3) Å. Each Gd center is coordinated by six different nic ligands, whilst each nic ligand links one Cu ion through an N atom (Fig. 2*b*). Therefore, the Gd centers of neighboring Gd–carboxylate chains are connected into a sandwich-like layer by nic ligands and $(Cu_3Cl_3)_n$ chains along the *bc* plane. These layers are further extended into a novel three-dimensional heterometallic coordination framework along the *bc* plane (Fig. 3*b*). Intra- and intermolecular O—H···Cl and O—H···O hydrogen bonds involving the carboxylate O atoms of the nic ligands, water molecules and Cl atoms further enhance the stability of the three-dimensional structure (Table 1). A better insight into the nature of this intricate framework can be achieved by the application of a topological approach. If the organic ligand is regarded as a three-connected node, the $[Gd_2(CO_2R)_2]^{2+}$ paddle-wheel unit may be regarded as a six-connected node and the Cu_3Cl_3 cluster and Cu1 may also be considered as three-connected nodes. The point (Schäfli) symbol for the title compound is $(4.8^2)_3(4^{10}.6^5)$ (Blatov & Shevchenko, 2006; Blatov *et al.*, 2010), which belongs to the family of 3,6-connected nets (Fig. 4). To the best of our knowledge, this type of network has not yet been reported. The overall structural motif in (I) is novel, differing from those reported previously by Cheng and co-workers involving mixed ligands (Cheng *et al.*, 2007*b*; Cheng, Zheng, Liu *et al.*, 2008; Cheng, Zheng & Yang, 2008; Liu, Wang *et al.*, 2011). In addition, there are two lanthanide–transition metal complexes containing only nic ligands and copper halides in which the copper halides are discrete (Zhu & Zeng, 2010; Gu & Xue, 2007*b*).

Experimental

A mixture of $CuCl_2·2H_2O$ (0.085 g, 0.5 mmol), Gd_2O_3 (0.087 g, 0.25 mmol), Hnic (0.0615 g, 0.5 mmol), HNO_3 (1 ml) and H_2O (10 ml) was stirred for 30 min in air and then sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 433 K for 72 h. The mixture was cooled to room temperature at a rate of 5 K h^{-1}. The yellow block-shaped crystals obtained were washed with water and dried in air.

Crystal data

$[Cu_3Gd(C_6H_4NO_2)_3Cl_3(H_2O)_2]·0.5H_2O$
M_r = 865.52
Monoclinic, $P2_1/c$
a = 9.5388 (11) Å
b = 12.6589 (14) Å
c = 21.400 (2) Å
β = 98.539 (1)°
V = 2555.4 (5) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 5.39 mm^{-1}
T = 110 K
0.30 × 0.25 × 0.21 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.228, T_{max} = 0.334
12988 measured reflections
4591 independent reflections
3561 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.106
S = 1.00
4591 reflections
334 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.64 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.41 e $Å^{-3}$

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···Cl2^{i}	0.85	2.58	3.326 (5)	148
O1*W*—H2*W*···Cl1^{ii}	0.85	2.33	3.158 (5)	165
O2*W*—H3*W*···O1*W*^{iii}	0.85	2.04	2.838 (7)	157
O2*W*—H4*W*···Cl3^{iv}	0.85	2.41	3.171 (6)	149
O3*W*—H5*W*···O6^{v}	0.85	2.37	3.168 (13)	158
O3*W*—H6*W*···O2^{vi}	0.85	2.54	3.200 (13)	136

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x, -y, -z+1$; (vi) $-x, -y+1, -z+1$.

When the site for the solvent water molecule was assumed to be fully occupied, the anisotropic displacement parameters for O3*W* were excessively large. Refinement of the site-occupation factor for this atom gave a value close to 0.5, so in subsequent refinements, the value was fixed at 0.5. Carbon-bound H atoms were placed at calculated positions and were treated as riding on the parent C atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Initially, the aqua H atoms were located in a difference Fourier map and their positions were adjusted, using the HIMP command in *XP* (*SHELXTL*; Sheldrick, 2008), to O—H = 0.85 Å. In the final cycles, these H atoms were constrained to ride on their parent O atoms, with $U_{iso}(H) = 1.5U_{eq}(O)$. The highest residual electron-density peak is located 0.98 Å from atom Gd1 and the deepest hole is located 0.74 Å from atom Cu3.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

This work was supported by ‘the Fundamental Research Funds for the Central Universities’.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3161). Services for accessing these data are described at the back of the journal.

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