

Polymeric hexaaqua-hexakis- $(\mu_3-2,2'$ -oxydiacetato)trizinc(II)-digadolinium(III) dodecahydrate

Ricardo Baggio,^{a*} Mireille Percec^b and Maria Teresa Garland^c

^aDepartamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, ^bDepartamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Facultad de Ciencias Exactas y Naturales, UNBA, Buenos Aires, Argentina, and ^cDepartamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile
Correspondence e-mail: baggio@cnea.gov.ar

Received 17 February 2003

Accepted 14 March 2003

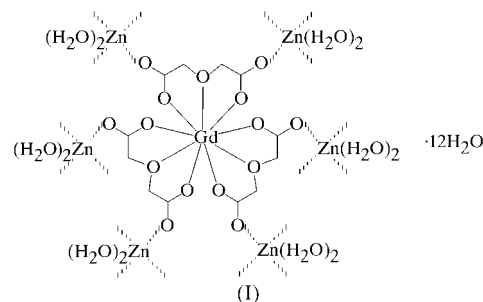
Online 10 April 2003

A polymeric heterometallic compound, $[\{[\text{Gd}_2\text{Zn}_3(\text{C}_4\text{H}_4\text{O}_5)_6(\text{H}_2\text{O})_6]\cdot 12\text{H}_2\text{O}\}]_n$, comprising zinc(II) and gadolinium(III) cations bridged by carboxylate groups from oxydiacetate ligands, is presented. The Gd^{III} cations lie at sites with crystallographic 32 symmetry and display a tricapped trigonal-prism arrangement, which is defined by six carboxyl and three ether O atoms. The Zn^{II} cations lie at sites with imposed $2/m$ symmetry and are octahedrally coordinated by four carboxyl O atoms and two apical water ligands, which form strong intramolecular hydrogen bonds. Comparison is made with the previously reported isostructural homologous copper–gadolinium complex.

Comment

The design of new compounds with specific architectures is a rapidly developing field in modern inorganic chemistry. One successful strategy is based on the use of both the building-bonding approach and the hydrogen-bonding capability of the ligands (Lehn, 1995). The oxydiacetate anion (oda) is a well known and versatile ligand that is able to chelate and bridge metal ions in a variety of ways, leading to the formation of polynuclear and low-dimensional systems (Grirrane *et al.*, 2002). We have recently reported the study of a series of oxydiacetate-bridged copper(II)–lanthanide(III) three-dimensional polymers, formulated as $[\{\text{Cu}_3\text{Ln}_2(\text{oda})_6(\text{H}_2\text{O})_6\}\cdot 12\text{H}_2\text{O}]_n$ [$\text{Ln} = \text{Y}, \text{Gd}, \text{Eu}, \text{Nd}$ and Pr (Baggio *et al.*, 2000); $\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}$ and Y (Rizzi *et al.*, 2002)]. These polymers crystallize in the hexagonal system, with space group $P6/mcc$ (No. 192). Replacement of copper by zinc ions to obtain isostructural zinc–lanthanide compounds appears possible, in principle, in spite of the lack of crystal-field stabilization of the Zn^{II} cation. Such compounds should be of interest in the study of magnetic exchange interactions

between lanthanide ions, since Zn^{II} has no unpaired electrons. The first Zn–Gd compound bridged by carboxylate groups has been reported for the propionate derivative $[\text{Zn}_2\text{Gd}_2(\text{O}_2\text{CC}_2\text{H}_5)_8(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (Cui *et al.*, 2001). The structure consists of two triply propionate-bridged dinuclear Zn–Gd subunits, linked together by two tridentate propionate groups bridging the neighboring Gd^{III} ions. We report here the isolation and X-ray structure of the title compound, (I). The crystallographic results reveal that the Zn–Gd complex is isostructural with the other members of the copper–lanthanide series, in particular the Cu–Gd member, (II).



The structure of (I) consists of two distinct types of building block, *viz.* GdO_9 and ZnO_6 , as illustrated in Fig. 1. Two GdO_9 and three ZnO_6 cores form the unit cell that generates an extended, highly symmetric, three-dimensional structure. The Gd atom lies at the intersection of a three- and a twofold axis and is coordinated by the carboxylate O1 and O1' atoms (where the prime denotes the twofold-related part of the oda ligand) and by the ether O3 atoms of three symmetry-related oda ligands [$\text{Gd}-\text{O}_{\text{carboxyl}} = 2.402(2) \text{ \AA}$ and $\text{Gd}-\text{O}_{\text{ether}} = 2.475(3) \text{ \AA}$; Table 1], leading to the usual tricapped trigonal-prismatic geometry (TCTP; Albertsson, 1968). The gadoli-

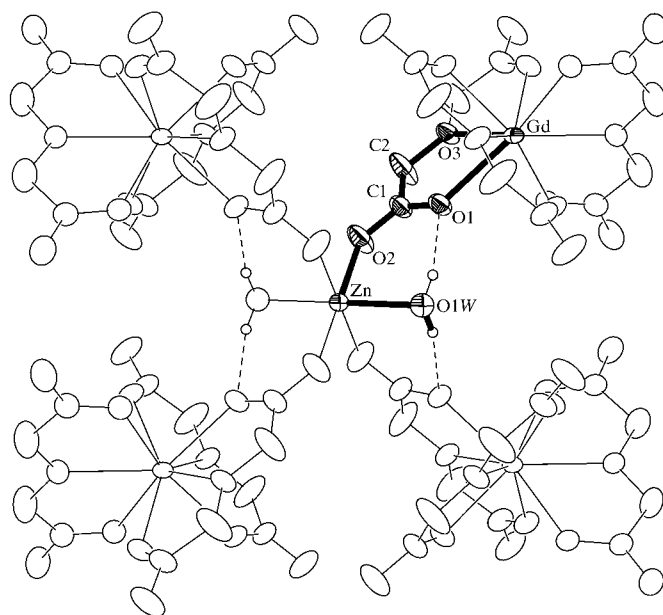


Figure 1

The molecular structure of (I), showing the way in which the three-dimensional network forms. Intramolecular hydrogen bonds are represented by dashed lines. Displacement ellipsoids are shown at the 40% probability level.

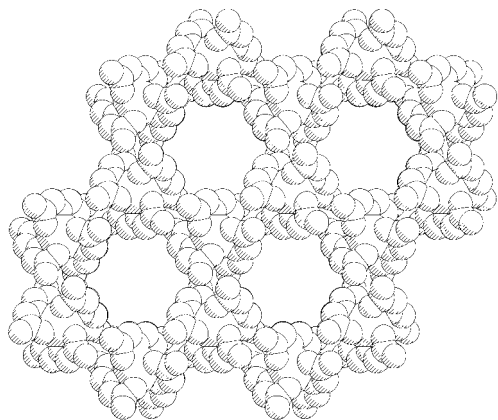


Figure 2
Space-filling diagram of the structure of (I), viewed along the z axis. Note the columnar voids where the disordered water molecules reside. Projections of the hexagonal unit-cell nodes lie at the void centers.

nium coordination polyhedron is similar to that found in (II), to the extent that a superposition of the two entities (*XP* in *SHELXTL*; Bruker, 1999) matched within an average deviation of less than 0.045 Å.

Each Zn atom lies at the intersection of a twofold axis and a mirror plane, and is coordinated by the outer carboxylate O2 and O2' atoms of four oda ligands [$\text{Zn}-\text{O}_{\text{basal}} = 2.052(2)$ Å], which define the equatorial plane. The apical sites are occupied by two water molecules at a Zn–O distance of 2.152(1) Å, similar to the basal bonds. The geometries of the GdO₉ and ZnO₆ coordination polyhedra are unexceptional and their average bonding distances are similar to those obtained in a search for similarly coordinated cores in the Cambridge Structural Database (CSD; Allen, 2002); mean Gd–O and Zn–O distances in the CSD (49 and 125 structures, respectively): 2.45(8) and 2.10(7) Å; measured for (I): 2.43(4) and 2.09(5) Å.

The most noteworthy differences between (I) and (II) are found in the vicinity of the octahedral site, where the nearly isometric coordination of Zn in (I) contrasts with the strong Jahn–Teller distortion around copper in (II) [$\text{Cu}-\text{O}_{\text{basal}} = 1.956(4)$ Å and $\text{Cu}-\text{O}_{\text{apical}} = 2.519(2)$ Å]. These bond-length differences propagate through the connecting chains, linking the three-dimensional structure in such a way as to modify the cell constants by decreasing a by ~1.4% and increasing c by ~4.5% when replacing copper with zinc. Therefore, the corresponding Zn···Zn and Gd···Gd separations have different values along different directions. Distances taken along the two-dimensional structures, nearly parallel to the apical O–Cu–O bonds ([100], [010] and [110]), shrink, while distances taken normal to the two-dimensional structures, almost along the diagonal of the basal coordination plane ([001]), expand when replacing Cu by Zn. The intramolecular Zn···Gd separation of 5.753(1) Å, however, is very similar to the corresponding Cu···Gd distance in (II) [5.695(1) Å], because the interatomic vector is nearly parallel to the almost invariant [111] direction.

All the outer carboxylate O atoms link to Zn atoms, so that each Gd atom is surrounded by six Zn atoms as nearest

neighbors, while the Zn atoms have four Gd atoms in their vicinity, as expected from the Zn/Gd molar relationship. Through this connectivity pattern, the Gd polyhedra create a two-dimensional planar honeycomb structure, parallel to (001), at z heights of $\sim\frac{1}{4}$ and $\frac{3}{4}$. Each pair of polyhedra at one side of the hexagonal motif is connected to the homologous pair one layer below (above) *via* a Zn atom bonded to four outer carboxylate O atoms (two from above and two from below). As a result of the translational symmetry along z , the two-dimensional structure develops into a three-dimensional honeycomb structure with columnar voids with a diameter of almost 6 Å (Fig. 2). These, in turn, are occupied by a number of highly disordered water molecules. Their interaction with the main structure could not be studied, since the H atoms of the water molecules were not found. On the other hand, the only independent water H atom in the zinc coordination sphere binds strongly to atom O1 of the ligand, and this H atom was clearly resolved in a difference Fourier map (Table 2).

In spite of the differences in their octahedral sites, the whole array in (I) is very similar to that found in (II), which suggests that Zn^{II} can replace the Cu^{II} ions in the octahedral CuO₆ sites in the Cu–Ln system, leading to an isomorphous Zn–Ln series. This could be useful in understanding the electronic and magnetic properties of these extended solids.

Experimental

Chemicals for the synthesis of (I) were used as purchased (reagent grade) without further purification. Zinc acetate dihydrate (0.35 g, 1.5 mmol) and gadolinium acetate hydrate (0.35 g, 1 mmol) were dissolved in an aqueous solution (25 ml) of oxydiacetic acid (0.60 g, 4.5 mmol) and stirred at room temperature for 4 h. After a few weeks, colorless crystals of the compound suitable for X-ray diffraction were filtered off and dried in air.

Crystal data

$[\text{Zn}_3\text{Gd}_2(\text{C}_4\text{H}_4\text{O}_5)_6(\text{H}_2\text{O})_6]\cdot 12\text{H}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 1627.33$	Cell parameters from 15 357 reflections
Hexagonal, $P6/mcc$	$\theta = 1.6\text{--}28.0^\circ$
$a = 14.5104(11)$ Å	$\mu = 3.62\text{ mm}^{-1}$
$c = 15.7725(16)$ Å	$T = 293(2)$ K
$V = 2876.0(4)$ Å ³	Polyhedra, colorless
$Z = 2$	$0.32 \times 0.30 \times 0.22$ mm
$D_x = 1.879$ Mg m ^{−3}	

Data collection

Bruker SMART CCD 1K area-detector diffractometer	1180 independent reflections
ω scans	962 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (<i>XPRED</i> in <i>SHELXTL</i> ; Bruker, 1999)	$R_{\text{int}} = 0.091$
$T_{\text{min}} = 0.35$, $T_{\text{max}} = 0.47$	$\theta_{\text{max}} = 28.0^\circ$
15 357 measured reflections	$h = -18 \rightarrow 15$
	$k = -17 \rightarrow 18$
	$l = -20 \rightarrow 19$

Table 1
Selected bond lengths (Å).

Gd–O1	2.402(2)	O1–C1	1.259(4)
Gd–O3	2.475(3)	O2–C1	1.246(3)
Zn–O2	2.052(2)	O3–C2	1.390(4)
Zn–O1W	2.152(3)	C1–C2	1.488(4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1W \cdots O1^i$	0.88 (5)	1.90 (5)	2.768 (3)	167 (4)

Symmetry code: (i) $x, y, 1-z$.**Refinement**Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.096$ $S = 1.07$

1180 reflections

74 parameters

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.947P]$
where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.007$ $\Delta\rho_{\max} = 0.78 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.72 \text{ e } \text{Å}^{-3}$

The structure of the homologous copper–gadolinium complex was used as a starting model for refinement by least squares on F^2 , using all data, with anisotropic displacement parameters for non-H atoms. H atoms belonging to the coordinated water molecules were found in the final ΔF synthesis and were fully refined with isotropic displacement parameters. H atoms attached to C atoms were included in calculated positions and allowed to ride. The water molecules appeared to be very disordered in the columnar cavities of the structure, and it was impossible to determine their overall number by X-ray techniques alone. Thermogravimetric analysis of freshly prepared samples showed a weight loss, Δm , of 19.6% (expected for 18 water molecules: 19.8%), of which 6.6% corresponds to the six water molecules and the rest (13.0%) corresponds to the remaining water of crystallization. This remainder amounts to 11.8 (~12) molecules per formula unit; only a fraction of these molecules (~75%) were found in a difference Fourier map and they appeared to be scattered into five independent positions, with a total O-atom occu-

pation of 8.9 (5). These molecules were refined with a common isotropic displacement parameter without their H atoms.

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XP* in *SHELXTL*.

We thank the Spanish Research Council (CSIC) for providing a license to the CSD system. This work was partially supported by CONICYT FONDAP grant No. 11980002 and FONDECYT grant No. 1020802 (Chile). MP is a member of CONICET.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1010). Services for accessing these data are described at the back of the journal.

References

- Albertsson, J. (1968). *Acta Chem. Scand.* **22**, 1563–1578.
 Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Baggio, R., Garland, M. T., Moreno, Y., Peña, O., Pereg, M. & Spodine, E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2061–2066.
 Bruker (1999). *SMART-NT* (Version 5.0), *SAINT-NT* (Version 5.0) and *SHELXTL-NT* (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.
 Cui, Y., Zheng, F., Qian, Y. & Huang, J. (2001). *Inorg. Chim. Acta*, **315**, 220–228.
 Grirrane, A., Pastor, A., Ienco, A., Mealli, C. & Galindo, A. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3771–3777.
 Lehn, J.-M. (1995). In *Supramolecular Chemistry: Concept and Perspectives*. Weinheim: VCH.
 Rizzi, A., Calvo, R., Baggio, R., Garland, M. T., Peña, O. & Pereg, M. (2002). *Inorg. Chem.* **41**, 5609–5614.