

# Synthesis and crystal structure of a bimetallic Mn<sup>II</sup>-Ce<sup>III</sup> complex bridged by oxydiacetate

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**Abstract:** A polymeric heterometallic compound  $[\{\text{Mn}(\text{H}_2\text{O})_6\}\{\text{MnCe}(\text{oda})_3\}_2] \cdot x\text{H}_2\text{O}$  containing manganese(II) and cerium(III) cations bridged by carboxylate groups of oxydiacetate (oda) is presented. It was prepared by direct reaction of oda in aqueous solution with stoichiometric amounts of Mn(II) and Ce(III). The structure of the complex exhibits a highly ordered 3D structure with  $[\text{MnCe}(\text{oda})_3]^-$  as building blocks. The charge is balanced with  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ions which occupy the holes of the anionic framework. The complex is thermally stable up to 230° C.

**Supporting information:** FT-IR, TGA diagram, X-Ray

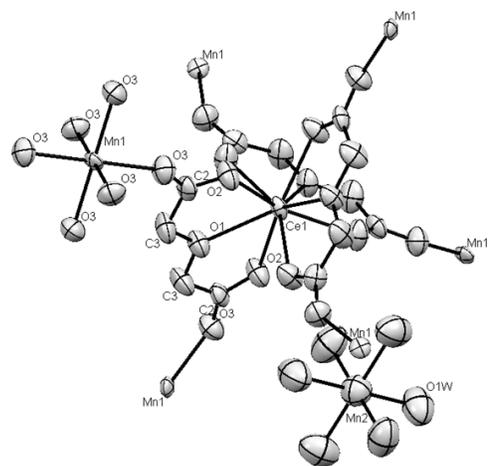
**Keywords:** Heterometallic coordination polymers; Lanthanide ions; X-ray crystal structure; Oxydiacetate

## 1. INTRODUCTION

The oxydiacetate anion (oda,  $\text{O}(\text{CH}_2\text{COO})_2^{2-}$ ) is a versatile ligand having five potential oxygen donors, four from two carboxylate groups and the fifth from an ether group. It may bind to metal ions in mono-, bi-, tri- and multidentate coordination modes. A number of oda complexes with lanthanide ions have interesting physical and chemical properties as well as fascinating structures [1].

We are interested in the synthesis and characterization of heterodimetallic complexes containing a lanthanide ion (Ln), a bivalent cation and oda as bridging ligand [1, 2]. The first compound of this group of polynuclear complexes was reported in 1997,  $[\text{Gd}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$  [3]. The structure (hexagonal crystal system, space group P6/mcc) is made by  $[\text{Gd}(\text{oda})_3]$  building blocks. These blocks still have uncoordinated O-carboxylate donor atoms which are able to link  $[\text{Cu}(\text{H}_2\text{O})_2]$  units, forming a supramolecular structure. The most interesting feature in the structures is the formation of a network containing large hexagonal channels (average diameter 10.7 Å). Isostructural complexes were also found for most of the Ln cations and other M(II) ions such as Co and Zn [1, 2].

Ten years later, a different self-assembling was obtained by using Gd(III) and Mn(II),  $[\{\text{Mn}(\text{H}_2\text{O})_6\}\{\text{MnGd}(\text{oda})_3\}_2] \cdot x\text{H}_2\text{O}$  [4]. The solid has the same stoichiometry (Gd:Mn:oda molar ratio 2:3:6), but the solid-state symmetry is different (cubic



**Figure 1:** Coordination units in  $[\{\text{Mn}(\text{H}_2\text{O})_6\}\{\text{MnCe}(\text{oda})_3\}_2] \cdot 3\text{H}_2\text{O}$ , showing the atom numbering. Thermal ellipsoids are shown at 50% probability. H atoms and crystallization water molecules are omitted for clarity.

crystal system, space group Fd-3c). The  $[\text{Gd}(\text{oda})_3]^{3-}$  units are present, but now there are inequivalent Mn ions in the structure. Two out of three are connected to Gd(III) through a carboxylate bridge, and the third one remains as hexaquo complex, filling the voids left by and neutralizing the  $[\text{Gd}_2\text{Mn}_2(\text{oda})_6]^{2-}$  anionic network in the solid state. Eighteen structures are reported up to now in this group combining different Ln ions with Mn(II), Co(II), Mg(II) and Ca(II) [5].

In this work we prepared and characterized a novel heterodimetallic compound containing Ce(III), Mn(II) and oda as bridging ligand. It was studied by x-ray diffraction, IR spectroscopy and thermal analysis.

## 2. EXPERIMENTAL

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. The infrared spectra, as KBr pellets, were obtained in the range 4000 – 400  $\text{cm}^{-1}$  from a Bomem MB 102 FT-IR spectrophotometer. Elemental analysis (C, H) was performed on a Flash 2000 instrument. Thermal analysis (25 – 300 °C) was

performed on a Shimadzu TGA-50 instrument with a TA 50I interface, using a platinum cell and nitrogen atmosphere. Experimental conditions were 0.5 °C min<sup>-1</sup> temperature ramp rate, and 50 mL min<sup>-1</sup> nitrogen flow rate.

Synthesis of [Ce<sub>2</sub>Mn<sub>3</sub>(oda)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>].4H<sub>2</sub>O. CeCl<sub>3</sub>.7H<sub>2</sub>O (0.37 g, 1.0 mmol) and MnCl<sub>2</sub>.4H<sub>2</sub>O (0.30 g, 1.5 mmol) were dissolved in 5 mL of water. 2,2-oxydiacetic acid (0.40 g, 3.0 mmol) were dissolved in another 5 mL of water, and the pH value was adjusted to 8.0 with ammonium hydroxide. Both solutions were mixed, and a clear solution was obtained. The solution was allowed to evaporate slowly at room temperature. After some weeks, cubic crystals were obtained. Yield 50–70%. Anal. Calc. for C<sub>24</sub>H<sub>44</sub>O<sub>40</sub>Mn<sub>3</sub>Ce<sub>2</sub>: C, 20.3; H, 3.1. Found: C, 20.5; H, 3.2 %.

The X-ray diffraction data were collected at 293(2) K with an Agilent SuperNOVA diffractometer with micro-focus X-ray using Mo radiation ( $\lambda = 0.71073$  Å). CrysAlisPro [6] software was used to collect, index, scale and apply analytical absorption corrections based on faces of the crystal.

The structure solution was obtained by direct methods, using the SIR2011 [7] program and refined using the SHELXL-97 [8] program. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least-squares procedures on F<sup>2</sup>. All hydrogen atoms were allowed to ride on their parent atoms with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) except for the water molecules, in which idealized positions were determined using the Olex2 program [9].

Crystal data, collection procedures and refinement results are summarized in Table S1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 913420.

### 3. RESULTS AND DISCUSSION

The direct reaction of oda in aqueous solution with the stoichiometric amounts of Mn(II) and Ce(III) salts led to the formation of a complex with general formula [Ce<sub>2</sub>Mn<sub>3</sub>(oda)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>].4H<sub>2</sub>O. This composition is supported by the elemental analysis. TGA diagram (Figure S1) shows two weight losses. The first one appears between room temperature and 140 °C and corresponds to 4 crystallization water molecules (Anal. Calc.: 5.1; Found: 5.4%). The second mass loss appears from 140 to 190 °C and corresponds to the 6 coordinated water molecules (Anal. Calc.: 7.6; Found: 6.8%). The anhydrous material appears stable up to 230 °C (constant mass observed). Then, a further loss mass is evidenced, probably due to the beginning of the ligand decomposition.

IR main peaks appear at 1608, 1439, 1311, 1115, 1045, 937, and 559 cm<sup>-1</sup> (Figure S2). It is noticeable the shift of  $\nu$ COO (1724, 1419 cm<sup>-1</sup>) of the free ligand to 1608 and 1439 cm<sup>-1</sup>. Besides, upon complexation,  $\nu$ COC of 1149 cm<sup>-1</sup> for the free ligand is shifted to 1115 cm<sup>-1</sup>. The signal at 937 cm<sup>-1</sup> can be assigned to coordinated water, while Ce-O mode appears at 559 cm<sup>-1</sup>.

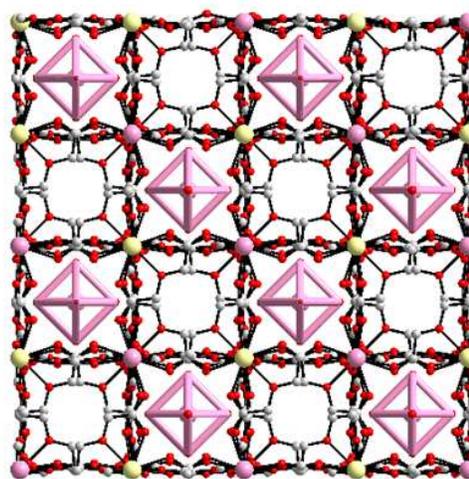
The structure contains an anionic network [MnCe(oda)<sub>3</sub>]<sup>-</sup>, [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations to balance the charge, and three crystallization water molecules. The number of crystallization water molecules found in the measured single crystal is not coincident with that determined in the bulk solid (four, see Experimental). The pres-

ence of very weakly bound water molecules (as reflected in the TGA profiles) would account for this fact.

Selected bond lengths and angles for [Mn(H<sub>2</sub>O)<sub>6</sub>]{MnCe(oda)<sub>3</sub>]<sup>-</sup>.3H<sub>2</sub>O are presented in Table 1. Cerium(III) ion is nine-coordinated, being surrounded by O atoms from three independent oda ligands. [Ce(oda)<sub>3</sub>]<sup>3-</sup> building blocks are clearly distinguished in the structure (Figure 1). The coordination geometry of the cerium atom can be described as a distorted tricapped trigonal prism. The six carboxylate oxygen atoms form a trigonal prism (Ce-O distance 2.474(7) Å) with three ether oxygen atoms as capping ones at a longer distance, 2.536(8) Å. Each [Ce(oda)<sub>3</sub>]<sup>3-</sup> unit is connected to six Mn atoms through the free (non-bonded to Ce) oxygen atoms in an *anti-anti* configuration, forming the anionic network [MnCe(oda)<sub>3</sub>]<sup>-</sup>. Mn(II) (labeled Mn1 in Figure 1) is six-coordinated with a regular octahedral geometry, which is composed of six carboxylate oxygen O3 atoms from six [Ce(oda)<sub>3</sub>]<sup>3-</sup> units (Mn1-O3 distance 2.157(7) Å).

**Table 1.** Selected bond lengths (Å) and angles (°) for [Mn(H<sub>2</sub>O)<sub>6</sub>]{MnCe(oda)<sub>3</sub>]<sup>-</sup>.3H<sub>2</sub>O

Ce-O1	2.536(8)
Ce-O2	2.474(7)
Mn1-O3	2.157(7)
Mn2-O1W	2.196(13)
C3-O1	1.415(10)
C2-O2	1.257(9)
C2-O3	1.263(10)
O1-Ce-O2	62.58(15)
O3-C2-O2	121.2(9)
Mn1-O3-C2	142.9(7)



**Figure 2.** Packing view of [Mn(H<sub>2</sub>O)<sub>6</sub>]{MnCe(oda)<sub>3</sub>]<sup>-</sup>.2 along the crystallographic *a* axis. Crystallization water molecules are omitted for clarity. Color code: Ce, yellow; Mn, pink; O, red; C, grey.

Cubic-like holes are formed in the anionic structure (Figure 2). They are limited by alternating Mn1 and Ce atoms in the vertices at 6.610(9) Å, and the oda ligands, almost planar, in the faces of the cubes. The  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ions (labeled Mn2 in Figure 1) provide charge balance to the compound and occupy half of the holes. Mn2 is also in a regular octahedral geometry (Mn2-O1W distance 2.196(13) Å). The smaller holes of the anionic network (empty in Figure 2) are filled by the crystallization water molecules.

The compound presented in this work should be described as  $[\{\text{Mn}(\text{H}_2\text{O})_6\}\{\text{MnCe}(\text{oda})_3\}_2] \cdot x\text{H}_2\text{O}$ . It belongs to the group of heterometallic Ln-M(II)-oda complexes exhibiting a cubic structure with inequivalent M(II) in the structure. Eighteen other complexes  $[\{\text{M}(\text{H}_2\text{O})_6\}\{\text{MLn}(\text{oda})_3\}_2] \cdot x\text{H}_2\text{O}$  (M = Mn, Co, Mg, and Ca; Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have been reported with this cubic structure [5]. This is the first report of a Ce(III) complex in this group. The presence of a symmetric aquocation  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  which could fix the cubic holes of the structure seems to be a decisive factor to obtain this kind of structure, as previously discussed [5].

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