

CRYSTAL STRUCTURE OF HEMIKIS(TETRAKIS(μ_2 -2-BUTENOATO)-BIS(2-BUTENOATO)-TETRA-AQUA-DI-SAMARIUM) HEMIKIS(BIS(μ_2 -BUTENOATO)-TETRAKIS(2-BUTENOATO) TETRA AQUA-DI-SAMARIUM) TRIHYDRATE

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ABSTRACT

The structure of the title compound $[\text{Sm}_2(\text{cro})_6(\text{H}_2\text{O})_4]_2 \cdot 3(\text{H}_2\text{O})$ (I), (cro= crotonate = butenoate = $\text{O}_2\text{CCHCHCH}_3$) consists of two independent, centrosymmetric dimeric units, of similar composition but diverse coordination, viz., one of them doubly bridged ($2 \times [\eta^2:\eta^1:\mu^2]$) and the remaining one quadruply bridged ($2 \times [\eta^1:\eta^1:\mu^2]$, $2 \times [\eta^2:\eta^1:\mu^2]$). The asymmetric unit is completed by three solvato water molecules, one of them depleted (occupation: 0.735 (14)). The difference in bridging strengths is readily evidenced in the two quite dissimilar Sm...Sm distances observed: 4.1402 (8) Å, (doubly bridged), 3.9439 (8) Å (quadruply bridged). SmO_9 polyhedra survey similar coordination distances which span the range 2.388 (3)-2.611 (3) Å for one of the Sm cations and 2.357 (3)-2.588 (3) Å for the other. All water hydrogens are involved in H-bonding, leading to the formation of a strongly linked 2D structure parallel to (010). These planar arrays are in turn transversally linked by one single bridging water molecule. There are in addition $\text{C}=\text{C} \cdots \text{C}=\text{C}$ p interactions providing both to intra as well as intra planar cohesion. The compound is isomorphous to its Gd isologue¹, but the present description unveils a number of molecular and supramolecular details not discussed therein.

1. INTRODUCTION

The structures of metallic carboxylates have been profusely analyzed as model materials for the study of physico-chemical properties of more complex materials, and among them carboxylate-bridged lanthanides are of relevance due to their outstanding role in molecular magnetism, etc. As a continuation of our interest on the structural and magnetic properties of carboxylate-bridged lanthanide complexes we report herein the structural study of $[\text{Sm}_2(\text{cro})_6(\text{H}_2\text{O})_4]_2 \cdot 3(\text{H}_2\text{O})$ (I), (cro= crotonate = butenoate = $\text{O}_2\text{CCHCHCH}_3$) an interesting complex containing two independent dimers in the unit cell, one of them doubly bridged ($2 \times [\eta^2:\eta^1:\mu^2]$) and the remaining one quadruply bridged ($2 \times [\eta^1:\eta^1:\mu^2]$, $2 \times [\eta^2:\eta^1:\mu^2]$). Even if the compound is isomorphous to its already reported Gd isologue¹, the present description if of relevance since it unveils a number of molecular and supramolecular details not discussed therein. In addition, it provides the second example of an homo-dinuclear Sm-crotonate reported so far, the first one being reported in Atria *et al.*²

2. Experimental

2.1. Synthesis and crystallization

Reported compound was one of the products resulting from the synthesis with crotonic acid and

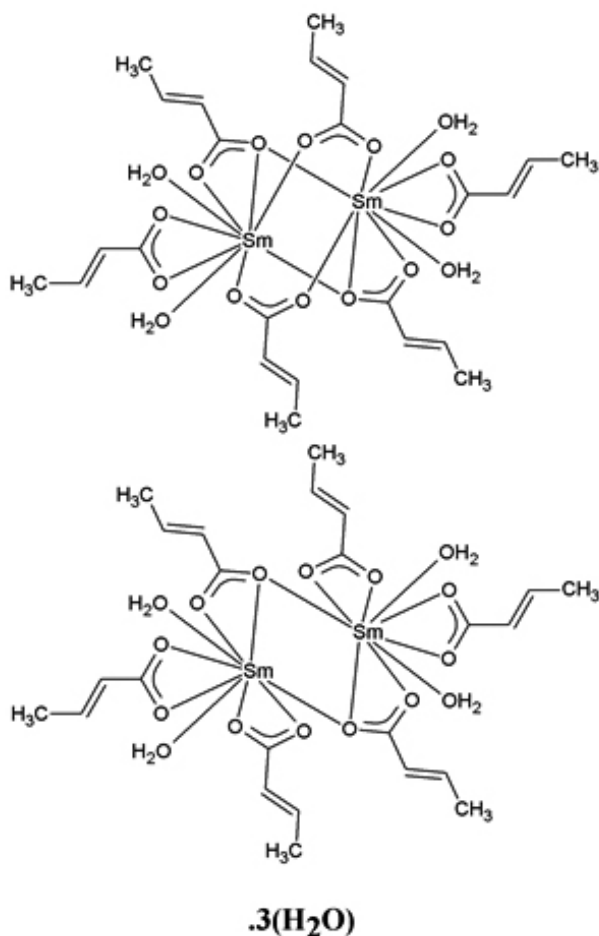
(R)-(+)- α -methylbenzylamine. The procedure used was as follows:

A mixture of Sm_2O_3 (0.3487 g, 1 mmol) and crotonic acid (0.5165 g, 6 mmol) was dissolved in water (100 mmol), and then (R)-(+)- α -methylbenzylamine (0.1211 g, 1 mmol) dissolved in ethanol (10 ml) was added. The resulting mixture was refluxed for 24 h, filtered while hot. The filtrate was left at room temperature. On standing, a two phase crystalline system was obtained consisting on a major fraction of ill crystallized material, useless for x-ray diffraction (where probably the methylbenzylamine resided) and a few well developed, colourless crystals suitable for single crystal diffraction, which correspond to the Sm-crotonate herein reported. We are working at present in the crystallization of the remaining fase

All chemicals and solvents were reagent grade, and used without further purification

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All the H atoms included in the model were originally found in a difference Fourier, but treated differently in refinement: C—H's were repositioned in their expected positions and thereafter allowed to ride [$d(\text{C}-\text{H}_{\text{aromatic}}) = 0.95$ Å, $d(\text{C}-\text{H}_{\text{methyl}}) = 0.98$ Å], while O—H's were refined with restrained $d(\text{O}-\text{H}) = 0.85$ (1) Å, $d(\text{H} \cdots \text{H}) = 1.35$ (2) Å. In all cases, $[U_{\text{iso}}(\text{H}) = 1.2 \times (1.5 \times \text{for methyl})U_{\text{eq}}(\text{host})]$. Water molecule O7W appeared depleted, and the oxygen occupation factor refined to 0.735 (14); since the corresponding H's could not be confidently located they were not included in the model. One of the butenoate anions (trailing number 6) appeared split



into two sites sharing the same carboxylate group (occupation factors: 0.645 (6), 0.355 (6) respectively). Both groups were refined with similarity restraints in distances and displacement factors.

The final difference map showed rather large peaks and holes (Extreme values: 1.13, -1.80 eÅ⁻³ at 0.74, 0.67Å from Sm2

3. RESULTS AND DISCUSSION

As ditto, the structure of [Sm₂(cro₆(H₂O)₄)₂·3(H₂O) (I) consists of two independent, centrosymmetric dimeric units, of similar composition but diverse coordination (Fig. 1). The asymmetry unit is completed by three water solvates, one of them (O7W) appearing depleted with a refined occupation of 0.735 (14).

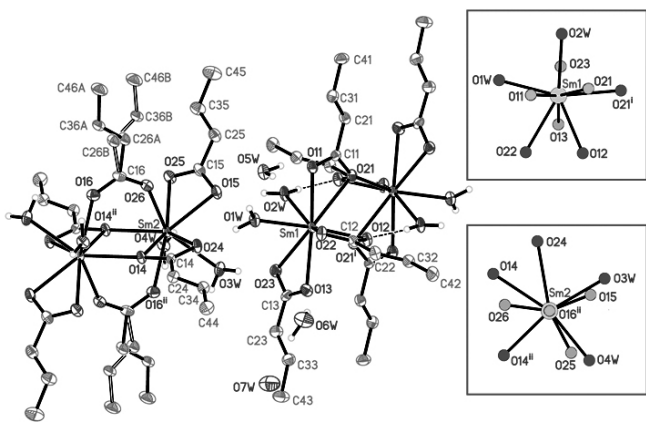


Figure 1. Molecular diagram of (I), with ellipsoids drawn at a 40% probability level. In open bonds, the minor part of the split butenoate anion. In broken lines, the intradimeric H-bond.

Insets: schematic representation of both SmO₉ coordination polyhedra, where SmO₅ basal planes (oxygen atoms coloured in red) are capped from the top by oxygens in cyan and from the bottom by oxygens in grey.

Symmetry codes: i: -x, 1-y, 1-z; ii: 1-x, 1-y, -z

Both cation environments are of the SmO₉ type, and the coordination polyhedra are similar in their being based on doubly capped (above and below) SmO₅ pentagons (In red in the insets of Figure 1). Even if both SmO₅ basal planes are rather similar, the way in which they are capped is not, being in a 2+2 fashion around Sm1 (Fig 1, upper inset), and 1+3 around Sm2.

Sm1 has its SmO₉ environment defined by six oxygens from three chelating crotonates (atoms O1n, O2n from crotonates n=1,2,3), one extra bond from the centrosymmetric image of one of these, O21ⁱ, i: -x, 1-y, 1-z), which acting as a short Sm—O—Smⁱ bridge between neighbouring centrosymmetry related Sm centers defines one of the dimers, and finally two aqua molecules, O1W and O2W.

The second samarium cation Sm2 is also nine coordinated, this time to four carboxylate oxygens from two chelate crotonato anions (O1n, O2n from crotonates n=4,5) and one extra bond from the centrosymmetric image of one of them, O14ⁱⁱ, ii: 1-x, 1-y, -z), which also here acts as a short Sm—O—Smⁱⁱ bridge between neighbouring centrosymmetry related Sm centers constituting one of the links defining the second dimer. The second link is provided by crotonato n=6 which via O16ⁱⁱ and O26 acts as a long -O—C—O- bridge between adjacent cations. Thus, this second dimer is held together by two pairs of centrosymmetric bridges, two short and two long, which define two closed, almost perpendicular loops (87.5 (2)°) around the symmetry center. The coordination is completed by two aqua molecules, O3W and O4W.

The difference in bridging strengths in both dimers is readily evidenced by the two quite dissimilar Sm...Sm distances: Sm1...Sm1ⁱ (single bridge): 4.1402 (8)Å, Sm2...Sm2ⁱⁱ (double bridge): 3.9439 (8)Å. Sm—O Coordination distances span the range 2.388 (3)-2.611 (3)Å for Sm1 and 2.357 (3)-2.588 (3)Å for Sm2. The three independent oxygens involved in the formation of the Sm2 dimer present the shortest Sm—O distances. The one subtending the single bridge in the Sm1 dimer is in turn the second shortest, at a distance very similar to these of the monodentate ligands O1W and O2W.

Table 1. Experimental details.

Crystal data	
Chemical formula	C ₄₈ H ₇₆ O ₃₂ Sm ₄ ·3H ₂ O
M _r	937.29
Crystal system, space group	Triclinic, P ⁻ 1
Temperature (K)	123
a, b, c (Å)	10.454 (2), 10.514 (2), 15.908 (3)
α, β, γ (°)	88.098 (4), 81.944 (3), 86.033 (3)
V (Å ³)	1726.6 (6)
Z	2
Radiation type	Mo Kα
μ (mm ⁻¹)	3.44
Crystal size (mm)	0.33 × 0.17 × 0.15
Data collection	
Diffractometer	Bruker Smart II diffractometer
Absorption correction	Multi-scan SADABS in SAINT-NT (Bruker, 2002)
T _{min} , T _{max}	0.82, 0.85
No. of measured, independent and observed [I > 2σ(I)] reflections	7766, 7766, 7130
R _{int}	0.032
(sin θ/λ) _{max} (Å ⁻¹)	0.668
Refinement	
R[F ² > 2σ(F ²)], wR(F ²), S	0.026, 0.066, 1.13
No. of reflections	7766
No. of parameters	460
No. of restraints	20
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.22, -1.83

Computer programs: SMART⁹, SAINT¹⁰ SAINT, SHELXS97 (Sheldrick, 2008), SHELXL97 Sheldrick, 2008), SHELXTL (Sheldrick, 2008)¹¹, SHELXTL; PLATON¹²

These two types of coordination, doubly and quadruply bridged (type 1 and type 2, respectively) are usual in dimeric Ln carboxylates in general and crotonates in particular. A search in the CSD³ revealed that among these latter dimers, those bridged solely through “type 1” links have only been reported for Nd⁴ and Dy, Sm², all of them surveying two water molecules as ancillary ligands. Quadruply bridged (“type 2”) dimers seem to be more often found in compounds with organic ancillary ligands, as phenanthroline (Gd)¹; Dy⁵ or Eu, Tb⁶) and bispyridine (Gd, Ho)⁷ even though there are also examples with water (Gd)⁷. The concurrent appearance of both bridging types in the same structure, as found in the present Sm structure is much more rare and has only been found before in the Gd isologue¹.

Regarding packing interactions, all the hydrogen atoms attached to fully

occupied water molecules (see refinement section for details) take part in H-bonding (Table 3), linking dimers together into tight 2D structures parallel to (010). Fig 3 shows the resulting planar array: entries 1 to 11 in Table 3 describe bonds which take part in the substructure cohesion; in particular, the $O2W-H2WB \cdots O12'$ one is intradimeric (see Fig. 1) and the $R(8)_2^2$ H-bonding ($Sm1-O-H \cdots O$)₂ loop it generates in the Sm1 dimer ("A" in Fig. 2, pale gray) mimics the covalent ($Sm2-O-C-O$)₂ loop ("B" in Fig 2, cyan) in the second dimer (Sm2) (For graph set nomenclature see Bernstein *et al.*⁸). The intricate H-bonding scheme results in a tight mesh of H-bonding rings building up near, or around, the four relevant inversion centres in the structure, viz. those halving both dimers, ("A" and "B" in Fig. 2) and those at the centres of the hydrophobic regions ("C" and "D"). These latter "C" and "D" centres lodge the largest, centrosymmetric $R(22)_8^8$, $R(18)_6^6$ rings in the structure, but in spite of the large number of donors and acceptors there are no closed H-bonding loops surveying only light atoms (C,H,O): all of the generated rings include at least a couple of Sm atoms and, accordingly, they effectively provide to interdimeric linkage.

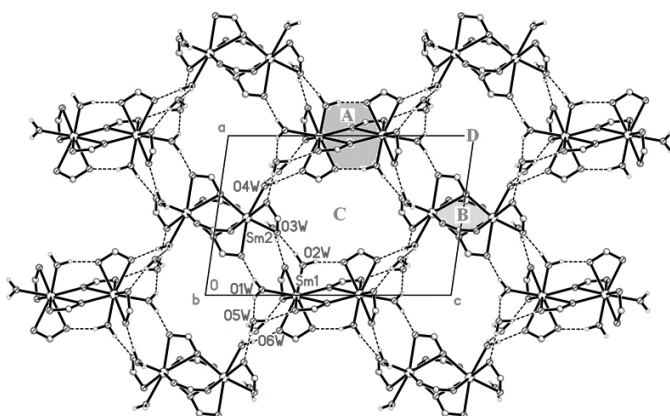


Figure 2. A simplified packing view drawn along [010] showing the intricate H-bonding network giving rise to the 2D (010) structure (butenoate $CH=CH-CH_3$ tails removed, for clarity). Grey and cyan loops are discussed in the text.

These strongly bound planar arrays are in turn weakly connected to each other via a single bridging water molecule: the (depleted) O7W. In this bridge, the molecule acts as acceptor in the $O6W-H6WB \cdots O7W$ bond (Table 2, last entry) and as donor to a bond having O5E as acceptor, no directly detectable since the corresponding H7W atoms could not be found in the difference map; however, the interaction is evidenced by the short distance between oxygens ($O7W \cdots O5W[x, -1+y, z] = 2.830(7) \text{ \AA}$). Fig 3 shows the way in which the planes are linked along [010] by way of these two interactions. It is perhaps worth mentioning that O7W and, accordingly, this latter water \cdots water interplanar interaction, run undetected in the previous (room temperature) Gd structure determination by Rizzi and coworkers¹.

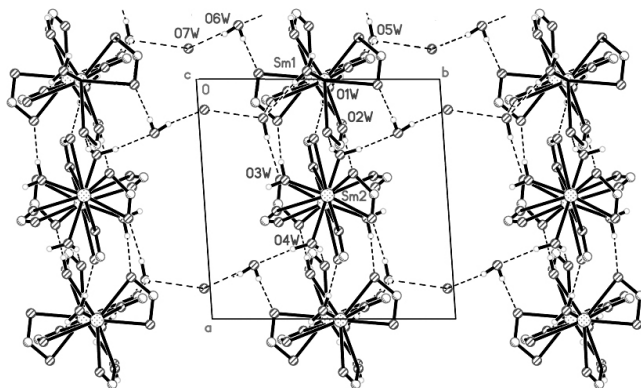


Figure 3. A simplified packing view drawn along [001] showing the way in which planar arrays are connected with each other (butenoate $CH=CH-CH_3$ tails removed, for clarity).

In addition to H-bonding interactions there are a number of $C=C \cdots C=C$ π contacts between inversion related butenoate anions, depicted in Fig. 4, where the complete, H-removed dimers have been represented. The most significant interactions, with $Cg \cdots Cg < 3.60 \text{ \AA}$, are of an intra-plane nature, while the weaker one represented in the third place provides to the inter-planar linkage.

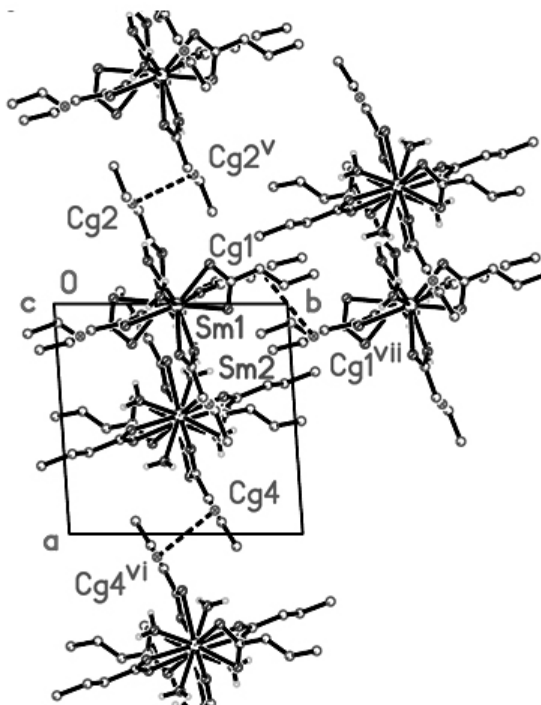


Figure 4. Same view as in Fig 3, now with full butenoate anions, showing the $C=C \cdots C=C$ π interactions.

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REFERENCES

- Rizzi, A., Baggio, R., Garland, M. T., Peña, O. & Perec, M. *Inorg. Chim. Acta* **353**, 315-319, (2003).
- Atria, A. M., Garland, M. T. & Baggio, R. *Acta Cryst.* **C68**, m80-m84, (2012).
- Allen, F. H., *Acta Cryst.* **B58**, 380-388, (2002).
- Atria, A. M., Astete, A., Garland, M. T. & Baggio, R. *Acta Cryst.* **E67**, m1191-m1192, (2011).
- Baggio, R., Perec, M. & Garland, M. T. *Acta Cryst.* **E59**, m1121-m1123, (2003).
- Barja, B., Aramendia, P., Baggio, R., Garland, M. T., Pena, O. & Perec, M. (2003). *Inorg.Chim.Acta* ,355,183-190.
- Atria, A. M., Baggio, R., Garland, M. T., Munoz, J. C. & Pena, O. *Inorg. Chim. Acta*, **357**,1997-2006. (2004).
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. *Angew. Chem. Int. Ed. Engl.* **34**, 1555-1573, (1995).
- Bruker *SMART*, V5.624. Data Collection Software. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. (2001).
- Bruker (*SAINT*, V6.22A (Including *SADABS*)). Data Reduction Software. Siemens. Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. (2002).
- Sheldrick, G. M. *Acta Cryst.* **A64**, 112-122. (2008).
- Spek, A. L. *J. Appl. Cryst.* **36**, 7-13. (2009).