

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.281 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$\Delta\rho_{\min} = -0.265 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.116$	Extinction correction:
$S = 1.053$	<i>SHELXTL</i> (Siemens, 1994a)
9513 reflections	Extinction coefficient:
501 parameters	0.00164 (14)
Only coordinates of H atoms refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 2.7861P]$	<i>International Tables for Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute structure:
$(\Delta/\sigma)_{\max} = 0.006$	Flack (1983)
	Flack parameter = 0.23 (8)

All H atoms were treated as riding, with relative isotropic displacement parameters. The less-than-optimum mounting contributed to an unexpectedly large spread in the transmission coefficients.

Data collection: *SMART* (Siemens, 1994b). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994a). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the National Science Foundation for a grant in support of this research. The structure was originally determined at the Iowa State Molecular Structure Laboratory. A second data collection was completed on a Siemens SMART CCD diffractometer, to obtain a better quality structure. Final refinements were completed at the X-ray Crystallographic Facility at the University of Minnesota.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1013). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Brokaar, G., Groeneveld, W. L. & Reedijk, J. (1970). *Recl Trav. Chim. Pays-Bas*, **89**, 1117–1120.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Hoyer, M. & Hartl, H. (1992). *Z. Anorg. Allg. Chem.* **612**, 45–50.
 Raston, C. L., Whitaker, C. L. & White, A. H. (1989). *Aust. J. Chem.* **42**, 201–207.
 Reedijk, J. & Groeneveld, W. L. (1968). *Recl Trav. Chim. Pays-Bas*, **87**, 513–527.
 Siemens (1994a). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1994b). *SMART Software Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1995). *SAINT Software Reference Manual*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Yokota, Y. & Verkade, J. G. (1999). *Polyhedron*. Submitted.
 Zuur, A. P. & Groeneveld, W. L. (1967). *Recl Trav. Chim. Pays-Bas*, **86**, 1089–1102.

Acta Cryst. (1999). **C55**, 198–200

Samarium 3,5-dinitrobenzoate dihydrate

CENGİZ ARICI,^a DİNÇER ÜLKÜ,^{a*} M. NAWAZ TAHİR^a AND CANAN ÜNALEROĞLU^b

^aDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and ^bDepartment of Chemistry, Hacettepe University, Beytepe 06532, Ankara, Turkey. E-mail: dulku@eti.cc.hun.edu.tr

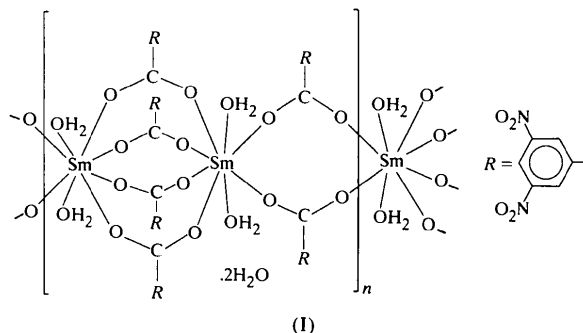
(Received 10 March 1998; accepted 28 September 1998)

Abstract

The coordination around the Sm atom in the title compound, *catena*-poly[[[tetraqua-1 κ^2 O,2 κ^2 O-tetrakis(μ -3,5-dinitrobenzoato-*O*:*O'*)disamarium]-bis(μ -3,5-dinitrobenzoato-*O*:*O'*)] dihydrate], [Sm₂(C₇H₃N₂O₆)₆(H₂O)₄].2H₂O, is eightfold. The irregular square-antiprism coordination of the Sm ion is provided by six O atoms from six carboxylate groups and two water O atoms. The Sm ions are bridged alternately by four and two ligands, resulting in linear polymeric chains with two different Sm...Sm distances of 4.2476 (7) and 5.0831 (8) Å, and Sm—O distances in the range 2.355 (4)–2.559 (4) Å. A set of hydrogen bonds exists between the nitro groups and the water molecules.

Comment

Rare earth carboxylates have been reported to show chelating, bridging and chelating–bridging modes of coordination which can be simultaneous or separate (Ma *et al.*, 1994; Hiyalov *et al.*, 1981; Bats *et al.*, 1979; Moore *et al.*, 1971; Tahir *et al.*, 1996). The title compound, (I), was synthesized in order to study the structure of Sm–carboxylate and to find out the mode of coordination around Sm. As can be seen from Fig. 1, the coor-



dination around the Sm ion is eightfold, involving six carboxylate O atoms [O1, O3, O5, O2ⁱⁱ, O4ⁱⁱ and O6ⁱ; symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$] and two water O atoms (O7 and O8). In the coordination sphere, the shortest bond length [2.355 (4) Å] is

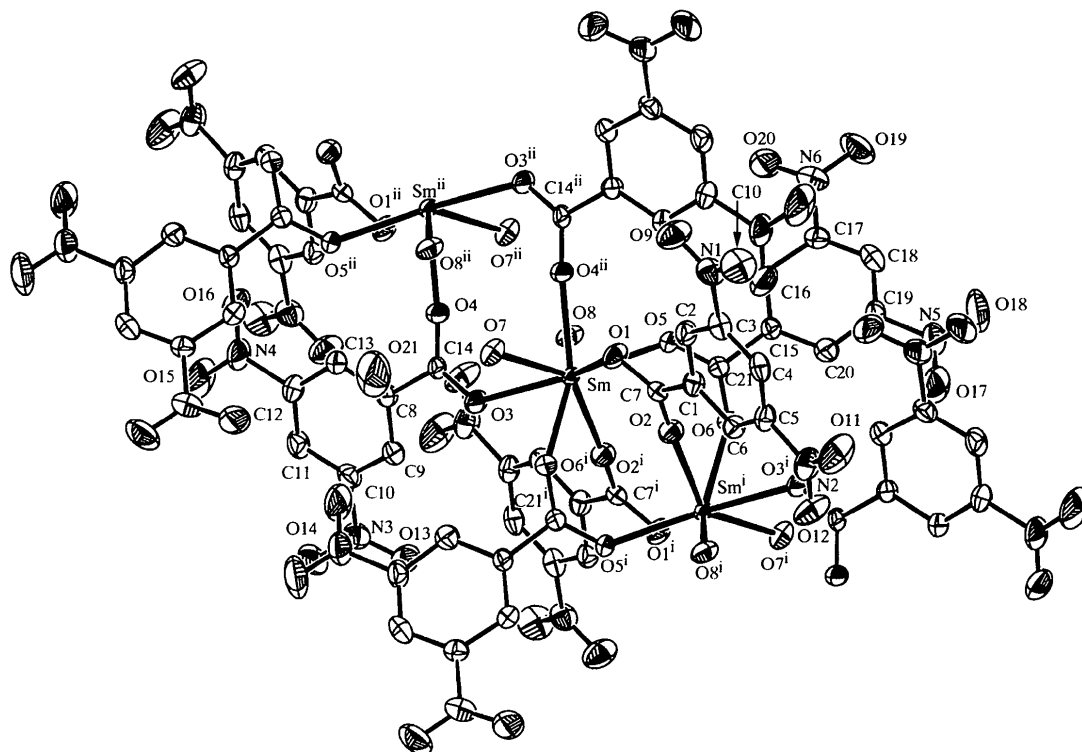


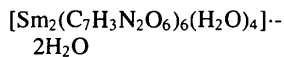
Fig. 1. The polymeric structure of the title compound showing three Sm ions bridged alternately by four and two ligands, with the atomic numbering scheme and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$.]

between the central Sm ion and the carboxylate oxygen O4ⁱⁱ, while the longest Sm—O distance [2.559 (4) Å] involves the water oxygen O7. The Sm—O(carboxylate) distances, ranging from 2.355 (4) to 2.449 (3) Å, are shorter than the Sm—O(water) distances [2.485 (4) and 2.559 (4) Å]. The Sm ions are bridged alternately by two and four carboxylate groups to form linear polymeric chains. Within the polymeric chains, only the bridging mode of coordination is observed (see Scheme). The single-mode coordination might be the result of the simultaneous occurrence of two nitro groups. The two different Sm···Sm distances of 4.2476 (7) and 5.0831 (8) Å are a consequence of alternate bridging by four and two ligands, respectively. This structure resembles the polymeric chains observed in cerium 3,5-dinitrobenzoate dihydrate (Tahir *et al.*, 1996) with the difference that the title compound has an extra lattice water molecule in the structure. The lattice water molecule, as well as the two coordination water molecules, is involved in five intermolecular hydrogen bonds to three different nitro O atoms and to two different water O atoms, so that the Sm ions are crosslinked by a variety of direct, covalent and hydrogen-bond interactions. Details of the hydrogen-bonding geometry are given in Table 2.

Experimental

3,5-Dinitrobenzoic acid (1.06 g, 5.0 mmol) and NaHCO₃ (0.42 g, 5.0 mmol) were added to hot distilled water (50 ml) and heated and stirred until complete dissolution had taken place. The solution containing Sm³⁺ was prepared by dissolving Sm(NO₃)₃·6H₂O (0.74 g, 1.66 mmol) in water (10 ml). The solutions were mixed, filtered and allowed to concentrate by evaporation. The resulting solution yielded crystals after two weeks.

Crystal data



$M_r = 1675.5$

Triclinic

$P\bar{1}$

$a = 9.2836 (12) \text{ \AA}$

$b = 11.4842 (13) \text{ \AA}$

$c = 13.7777 (12) \text{ \AA}$

$\alpha = 106.896 (2)^\circ$

$\beta = 90.436 (3)^\circ$

$\gamma = 93.930 (2)^\circ$

$V = 1401.6 (3) \text{ \AA}^3$

$Z = 1$

$D_x = 1.985 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 11.46\text{--}20.81^\circ$

$\mu = 2.205 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Needle

$0.40 \times 0.12 \times 0.10 \text{ mm}$

Colourless

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction:
empirical via ψ scans
(Fair, 1990)
 $T_{\min} = 0.725$, $T_{\max} = 0.801$
5655 measured reflections
5290 independent reflections
4423 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\max} = 26.24^\circ$
 $h = -11 \rightarrow 0$
 $k = -14 \rightarrow 14$
 $l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity variation:
negligible

Refinement

Refinement on F
 $R = 0.035$
 $wR = 0.038$
 $S = 1.12$
4423 reflections
442 parameters
H atoms: see below
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.0002$
 $\Delta\rho_{\max} = 1.37 \text{ e } \text{\AA}^{-3}$ (0.99 \AA
from Sm)
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA)

Sm \cdots Sm ⁱ	4.2476 (7)	Sm—O4 ⁱⁱ	2.355 (4)
Sm \cdots Sm ⁱⁱ	5.0831 (8)	Sm—O5	2.438 (3)
Sm—O1	2.449 (3)	Sm—O6 ⁱ	2.358 (4)
Sm—O2 ⁱ	2.372 (4)	Sm—O7	2.559 (4)
Sm—O3	2.412 (3)	Sm—O8	2.485 (4)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
O7—H71 \cdots O11 ⁱ	0.854	2.207	2.981 (6)	150.8
O7—H72 \cdots O21	0.877	1.882	2.753 (7)	171.8
O8—H81 \cdots O9 ⁱⁱⁱ	0.986	2.527	3.184 (6)	123.9
O8—H82 \cdots O7 ⁱⁱⁱ	0.891	1.926	2.787 (5)	162.2
O21—H212 \cdots O20 ^{iv}	0.838	2.435	3.148 (7)	143.5

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x, y - 1, z$; (iii) $1 - x, -y, 1 - z$; (iv) $x, y, z - 1$.

The water H atoms were found from a difference map. H atoms bonded to C atoms were placed geometrically 0.95 \AA from their parent atoms. A riding model was used for all H atoms and their H-atom displacement parameters were fixed as $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{parent})$.

Data collection and cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program used to solve structure: *MolEN*. Program used to refine structure: *MolEN*. Molecular graphics: *MolEN* version of *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*. Other programs include *PLATON* (Spek, 1990).

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1246). Services for accessing these data are described at the back of the journal.

References

- Bats, J. W., Kalus, R. & Fuess, H. (1979). *Acta Cryst.* **B35**, 1225–1227.
Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Hiyalov, M. S., Amirasanov, I. R., Mamedov, Ch. S. & Mõvsümov, E. M. (1981). *J. Struct. Chem. (USSR)*, **T22**, 113–119.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1994). *Acta Cryst.* **C50**, 1008–1010, 1010–1012.
Moore, J. W., Glick, M. D. & Baker, W. A. Jr (1971). *J. Am. Chem. Soc.* **94**, 1858–1865.
Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
Tahir, M. N., Ülkü, D., Ünaleroğlu, C. & Mõvsümov, E. M. (1996). *Acta Cryst.* **C52**, 1449–1451.

Acta Cryst. (1999). **C55**, 200–202

Tricarbonyl[(6a,7,8,9,10,10a- η)-3,3-diphenyl-3H-benzo[*f*]chromene]chromium

PATRICK HANNESSCHLAGER,^a PIERRE BRUN^a AND GÉRARD PÈPE^b

^a*GCOPL, Université d'Aix-Marseille II, Campus de Luminy, Case 901, 13288 Marseille CEDEX 9, France, and*
^b*Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Universités d'Aix-Marseille II et III, Campus de Luminy, Case 913, 13288 Marseille CEDEX 9, France.*
E-mail: genmol@crmc2.univ-mrs.fr

(Received 26 May 1998; accepted 22 September 1998)

Abstract

The title compound, [Cr(C₂₅H₁₈O)(CO)₃], belongs to a new family of chromenes complexed with tricarbonylchromium and exhibiting photochromic properties. The molecular geometry is compared to that of a similar structure [Hannesschlager *et al.* (1998). *Acta Cryst.* **C54**, 221–223] in which one of the phenyl groups is replaced by a methyl group.

Comment

The photochromic properties of 3H-naphthopyrans (2H-benzochromenes) (Becker & Michl, 1966) can be modulated by introducing selected substituents onto the different positions of the aromatic system. The complexation of aromatic rings with tricarbonylchromium modifies the reactivity and also the electronic distribution on such structures, which affects the photochromic