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catena-Poly[[bis(1,10-phenanthroline)samarium]-di-μ-2-hydroxybenzoato-sodium-di-μ-2-hydroxybenzoato]

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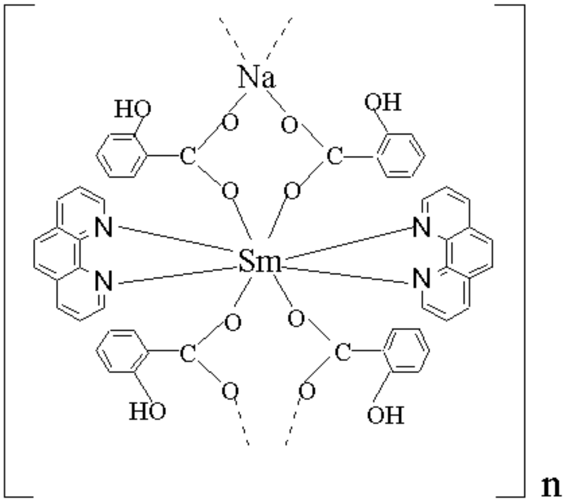
Key indicators
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.021
wR factor = 0.045
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $[NaSm(C_7H_5O_3)_4(C_{12}H_8N_2)_2]_n$, is a heteronuclear polymer. The Sm and Na atoms are bridged by two carboxylate groups. The Sm atom is eightfold-coordinated by four N atoms of two bidentate phenanthroline ligands and four O atoms of four monodentate carboxyl groups. The Na and Sm atoms lie on a twofold axis. The carboxyl groups of the hydroxybenzoate ligands act as bridges between the Na and Sm atoms, forming a one-dimensional polymer. In addition, there are intramolecular hydrogen bonds between the phenol OH group and an adjacent carboxyl O atom.

Comment

There has been a growing interest in the study of the enhancement of fluorescence of the lanthanides since the lanthanides have low absorptivity and poor quantum yields (Brito *et al.*, 2002). Luminescence investigation of RE^{3+}–aromatic acid complexes (RE = lanthanide) has increased in the past decade due to the higher efficiency of energy transfer from aromatic acid ligands to rare earth ions (Panigrahi *et al.*, 1997; Panigrahi, 2002; An *et al.*, 2004). We report here the preparation and crystal structure of the title compound, (I).



(I)

Complex (I) is a polymeric chain with crystallographically imposed C_2 symmetry, with the Na and Sm atoms lying on a twofold axis. The Sm and Na atoms are bridged by two carboxylate groups (Fig. 1). The coordination environment of the Na atom is approximately tetrahedral. Each carboxylate group acts as a bridging ligand between the Na ion and Sm, *via* the carboxylate O atoms. Each Sm atom is coordinated by four N atoms of two phenanthroline (phen) ligands and four O

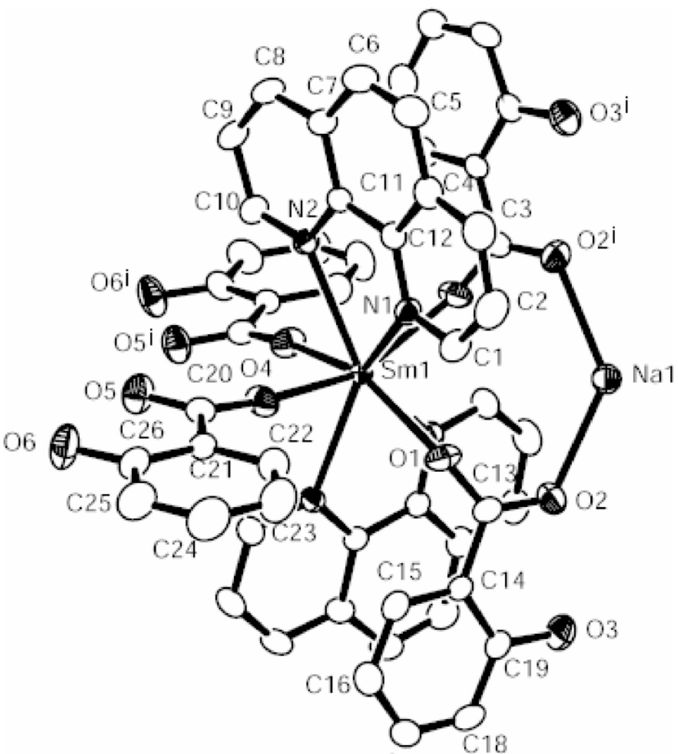


Figure 1
Twice the asymmetric unit of the title complex, showing the atomic numbering scheme and 30% probability displacement ellipsoids. H atoms and some labels have been omitted for clarity. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

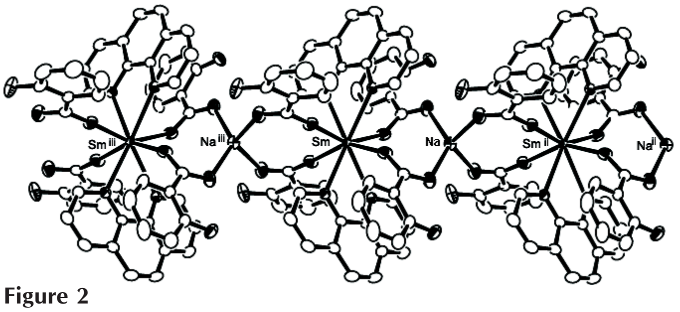


Figure 2
A view of the structure of the one-dimensional chain of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted. [Symmetry codes: (ii) $x, y - 1, z$; (iii) $x, y + 1, z$.]

atoms of four carboxylate groups, which further coordinate to two neighboring Na atoms, forming a one-dimensional chain structure (Fig. 2). The plane of the phenanthroline ring system formed by atoms N1, N2 and C1–C12 makes a dihedral angle of 80.5 (1)° with the C14–C19 benzene ring, and an angle of 89.9 (1)° with the C21–C26 benzene ring. The Sm—O distances [2.270 (2) and 2.318 (2) Å; Table 1] are much shorter than the values found in an analogous compound $[Sm_2(C_{12}H_8N_2)_2(C_6H_5COO)_6]$, (II) [2.355 (4)–2.866 (4) Å; Niu & Jin, 1999]. The difference may be due to their different coordination modes. The Sm—N distances are comparable with the corresponding values found in (II). The Na—O distances are 2.348 (2) and 2.383 (3) Å.

In many cases, carboxylate groups are coordinated simultaneously to metal ions in three modes, *viz.* bridging, chelating and bridging–chelating. In (I), however, all the carboxylate groups are coordinated in the bridging mode, in which the two C—O bond lengths of the carboxylate are slightly different. The longer C—O bond is linked to the Sm atom while the shorter one is linked to the Na atom.

Experimental

2-Hydroxybenzoic acid (2.0 mmol, 276.2 mg) and 1,10-phenanthroline (1.0 mmol, 180.0 mg) were dissolved in ethanol (20 ml). The pH of the solution was adjusted to 6–7 with 2 *M* NaOH solution. To the resulting solution was added $SmCl_3·6H_2O$ (0.5 mmol, 182.4 mg) in ethanol (5 ml). The reaction mixture was stirred for 4 h at 343 K. A white precipitate was formed. Crystals of (I) suitable for X-ray analysis were obtained from the mother liquor at room temperature after a few days (m.p. 524–529 K). IR (KBr, cm^{-1}): 3435.6 ν(Ar—OH), 1597.2 and 1389.2 $\nu(COO^-)$, 1561.3 ν(C═N), 806.1, 760.0 and 727.8 ν(C—H, phen).

Crystal data

$[NaSm(C_7H_5O_3)_4(C_{12}H_8N_2)_2]$
$M_r = 1082.27$
Monoclinic, $C2/c$
$a = 28.4989 (7)$ Å
$b = 9.3347 (2)$ Å
$c = 22.7954 (5)$ Å
$\beta = 132.4010 (8)$°
$V = 4478.1 (2)$ Å^3
$Z = 4$

$D_x = 1.605$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17110 reflections
$\theta = 2.4$–27.5°
$\mu = 1.40$ mm^{-1}
$T = 295 (1)$ K
Chunk, colorless
0.21 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.687$, $T_{max} = 0.811$
20367 measured reflections

5126 independent reflections
3612 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.037$
$\theta_{max} = 27.5$°
$h = -36 \rightarrow 36$
$k = -12 \rightarrow 12$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.045$
$S = 1.01$
3612 reflections
317 parameters

H-atom parameters constrained
$w = 1/[0.0002F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sm1—O1	2.318 (2)	Sm1—N2	2.652 (2)
Sm1—O4	2.270 (2)	Na1—O2	2.383 (3)
Sm1—N1	2.681 (1)	Na1—O5^{ii}	2.348 (2)
O1^i—Sm1—O1	92.05 (8)	N2^i—Sm1—O1	77.69 (7)
O4—Sm1—O1	95.70 (8)	N2—Sm1—O4	75.63 (8)
O4^i—Sm1—O1	149.04 (6)	N2^i—Sm1—O4	76.09 (6)
N1—Sm1—O1	73.22 (6)	N1—Sm1—O4^i	137.70 (7)
N1^i—Sm1—O1	74.28 (6)	Sm1—O1—C13	142.5 (2)
N2—Sm1—O1	134.86 (5)	Sm1—O4—C20	171.1 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O3—H17···O2	0.98	1.71	2.566 (4)	144
O6—H18···O5	0.95	1.74	2.560 (4)	142

The hydroxy H atoms were located in difference Fourier maps, while the C-bound H atoms were placed in calculated positions, with C—H = 0.96 or 0.97 Å, and refined as riding, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}$(carrier atom).

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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