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Tetra-μ-L-isoleucine-bis[tetraaquasamarium(III)] hexaperchlorate

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The title complex, $[Sm_2(C_6H_{13}NO_2)_4(H_2O)_8](ClO_4)_6$, contains dimeric $[Sm_2(Ile)_4(H_2O)_8]^{6+}$cations (Ile is L-isoleucine) and perchlorate anions. The two Sm^{3+} cations lie on a crystallographic twofold rotation axis. The four isoleucine molecules act as bridging ligands, linking two Sm^{3+} ions through their carboxyl O atoms. Each Sm^{3+} ion is also coordinated by four water molecules to complete eightfold coordination in a square antiprismatic fashion. One of the three perchlorate anions in the asymmetric unit is disordered.

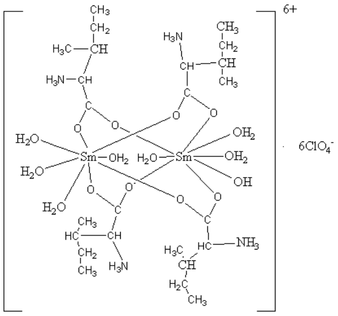
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.024 Å
H-atom completeness 77%
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.139
Data-to-parameter ratio = 10.1

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

Comment

The increasing effort to better understand the biological effects of rare earth elements has led to considerable interest in amino acid complexes of rare earth elements. In recent years, more than 50 structures of such complexes have been reported (Ni, 2002; Wang *et al.*, 1996). The crystal structures of rare earth complexes with amino acids show some interesting characteristics. For example, at low pH the amino acid ligands are bonded to the rare earth elements through their carboxyl groups, while the amino groups are protonated and are not involved in the coordination. These complexes adopt one of three types of structures, namely, dinuclear dimer, chain or network polymer; see, for example, Legendziewicz *et al.* (1984), Csoregh *et al.* (1989), Glowiak *et al.* (1991), Hu *et al.* (1995), Ma *et al.* (1995), Wang *et al.* (1994) and Wang *et al.* (2003). However, at high pH, amino groups may participate in coordination, and these complexes show tetranuclear and pentadecanuclear forms (Wang *et al.*, 1999; Ma *et al.*, 2000; Zhang *et al.*, 2000*a*,*b*). However, studies of the crystal structures of rare earth element–isoleucine complexes have rarely been reported (Zhao *et al.*, 1995). In this work, the crystal structure of a samarium(III) complex with L-isoleucine, (I), has been studied as part of our crystallographic studies of rare earth–amino acid complexes.



(I)

The compound crystallizes in the monoclinic system, and consists of C_2-symmetric dimeric $[Sm_2(Ile)_4(H_2O)_8]^{6+}$ complex

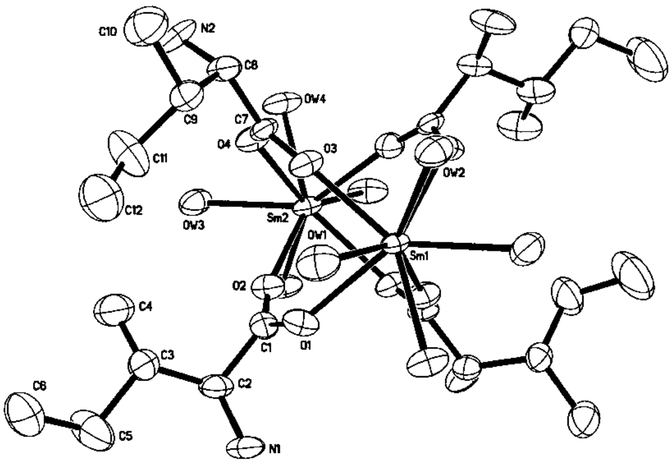


Figure 1

The structure of the $[Sm_2(Ile)_4(H_2O)_8]^{6+}$ cation of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted

cations and ClO_4^- anions. The structure of the cation is illustrated in Fig. 1 and selected geometric parameters are listed in Table 1. The two Sm^{3+} ions lie on a twofold rotation axis. The L-isoleucine molecules exist in zwitterionic form, with the amino groups protonated and the carboxyl groups deprotonated. The two Sm^{3+} ions in the dimeric $[Sm_2(Ile)_4(H_2O)_8]^{6+}$ complex cation are connected by four bridging carboxylate groups, the Sm···Sm distance being 4.446 (5) Å, indicating that there is no metal–metal bond in the complex. The average length of Sm—O(carboxylate) is 2.35 (6) Å. Each *trans* pair of carboxylate groups is coplanar with the two Sm^{3+} ions and the dihedral angle between the two planes is 85.1 (1)°, showing almost perpendicularity of the two planes. The coordination polyhedron around each Sm^{3+} ion is a square antiprism, with four of the sites occupied by the O atoms from the carboxylate groups and the other four by the O atoms from four coordinated water molecules to complete an eightfold coordination, and the average length of $Sm—O_{water}$ is 2.47 (2) Å. The perchlorate anions reside in the cavities between cations. Two O atoms of perchlorate form hydrogen bonds with NH_3^+ and coordinated H_2O O atoms from two $[Sm_2(Ile)_4(H_2O)_8]^{6+}$ cations. This contributes to the stability of the crystal.

Experimental

Samarium perchlorate and isoleucine were mixed in a 1:1 molar ratio in aqueous solution and the pH value was adjusted to 4.0 with NaOH. The solution was evaporated slowly at room temperature, yielding colorless prismatic crystals.

Crystal data

$[Sm_2(C_6H_{13}NO_2)_4(H_2O)_8](ClO_4)_6$
$M_r = 1566.22$
Monoclinic, $C2$
$a = 21.682\ (3)$ Å
$b = 10.3815\ (19)$ Å
$c = 15.177\ (4)$ Å
$\beta = 120.03\ (3)°$
$V = 2957.7\ (14)$ Å^3
$Z = 2$

$D_x = 1.759$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 5.2–13.8°$
$\mu = 2.34$ mm^{-1}
$T = 293\ (2)$ K
Prism, colorless
0.52 × 0.40 × 0.32 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Siemens, 1994)
$T_{min} = 0.398$, $T_{max} = 0.473$
6875 measured reflections
3400 independent reflections
3009 reflections with $I > 2\sigma(I)$

$R_{int} = 0.037$
$\theta_{max} = 26.0°$
$h = -25 \rightarrow 26$
$k = -1 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.139$
$S = 1.03$
3400 reflections
338 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.050$
$\Delta\rho_{max} = 1.17$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.00 (3)

Table 1

Selected geometric parameters (Å, °).

Sm1—O3	2.310 (10)	Sm2—O2	2.279 (13)
Sm1—O*W*2	2.445 (12)	Sm2—O4	2.412 (9)
Sm1—O1	2.411 (12)	Sm2—O*W*3	2.446 (12)
Sm1—O*W*1	2.474 (13)	Sm2—O*W*4	2.505 (13)
O3^i—Sm1—O3	107.7 (5)	O2—Sm2—O4	79.7 (4)
O3—Sm1—O*W*2^i	145.9 (4)	O2^i—Sm2—O4	77.0 (4)
O3^i—Sm1—O*W*2	145.9 (4)	O4^i—Sm2—O4	135.5 (5)
O3—Sm1—O*W*2	84.8 (4)	O2—Sm2—O*W*3^i	142.2 (4)
O*W*2^i—Sm1—O*W*2	102.7 (6)	O4—Sm2—O*W*3^i	138.0 (4)
O3—Sm1—O1^i	73.1 (4)	O2—Sm2—O*W*3	79.2 (5)
O*W*2—Sm1—O1^i	74.4 (5)	O2^i—Sm2—O*W*3	142.2 (4)
O3^i—Sm1—O1	73.1 (4)	O4^i—Sm2—O*W*3	138.0 (3)
O3—Sm1—O1	79.1 (4)	O4—Sm2—O*W*3	71.6 (4)
O*W*2^i—Sm1—O1	74.4 (5)	O*W*3^i—Sm2—O*W*3	111.2 (8)
O*W*2—Sm1—O1	141.0 (4)	O2—Sm2—O*W*4	143.8 (4)
O1^i—Sm1—O1	131.9 (7)	O2^i—Sm2—O*W*4	80.1 (5)
O3^i—Sm1—O*W*1	141.2 (4)	O4^i—Sm2—O*W*4	139.2 (4)
O3—Sm1—OW1	81.4 (4)	O4—Sm2—O*W*4	72.2 (4)
O*W*2^i—Sm1—O*W*1	70.2 (4)	O*W*3^i—Sm2—O*W*4	70.0 (4)
O*W*2—Sm1—O*W*1	70.8 (4)	O*W*3—Sm2—O*W*4	70.7 (5)
O1^i—Sm1—O*W*1	138.3 (4)	O2—Sm2—O*W*4^i	80.1 (5)
O1—Sm1—O*W*1	71.8 (5)	O4—Sm2—O*W*4^i	139.2 (4)
O3—Sm1—O*W*1^i	141.2 (4)	O*W*3—Sm2—O*W*4^i	70.0 (4)
O*W*2—Sm1—O*W*1^i	70.2 (4)	O*W*4—Sm2—O*W*4^i	106.9 (7)
O1—Sm1—O*W*1^i	138.3 (4)	C1—O1—Sm1	132.4 (10)
O*W*1—Sm1—O*W*1^i	115.4 (7)	C1—O2—Sm2	157.7 (12)
O2—Sm2—O2^i	115.5 (7)	C7—O3—Sm1	163.0 (10)
O2—Sm2—O4^i	77.0 (4)	C7—O4—Sm2	129.5 (9)

Symmetry code: (i) $1 - x, y, 1 - z$.

The perchlorate group containing Cl3 was found to be disordered. The occupancy factors for the disordered atoms were refined so that the sum of the occupancy factors was equal to 1. Finally, refinement gave the occupancy factors for Cl3 and the four O atoms of the perchlorate group in the two positions as 0.805 (11) and 0.195 (11), respectively. All non-H atoms were refined anisotropically, except for those with occupancy factors less than 0.5, which were refined isotropically. Amino acid H atoms were added at calculated positions and those of water molecules were not located. H atoms were refined using a riding mode [$U_{iso}(H) = 1.2U_{eq}(C,N)$]. $\Delta\rho_{max}$ was located near the disordered perchlorate anion and $\Delta\rho_{min}$ was located 0.72 Å from the Cl3 atom.

Data collection: *P*4 *Software* (Siemens, 1995); cell refinement: *P*4 *Software*; data reduction: *P*4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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