

## Octaureasamarium(III) triiodide

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### Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{N}-\text{C}) = 0.008 \text{ \AA}$   
 Disorder in main residue  
 R factor = 0.036  
 wR factor = 0.058  
 Data-to-parameter ratio = 21.6

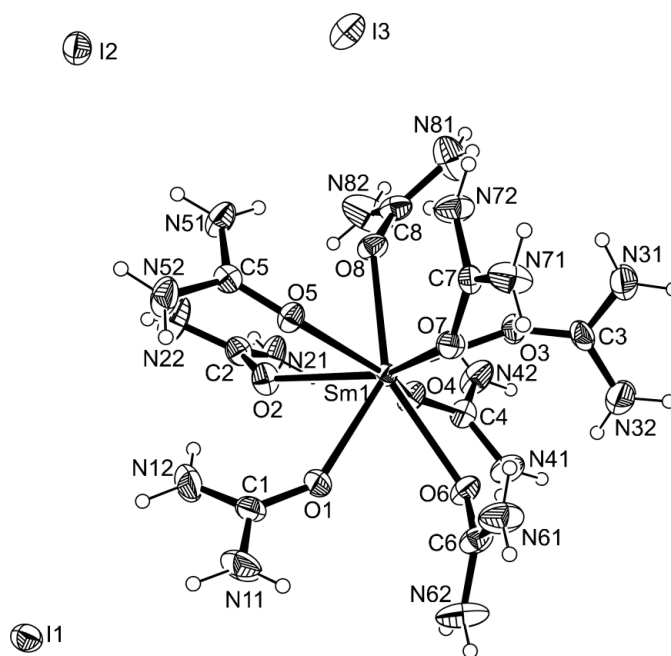
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The Sm atom of the title compound,  $[\text{Sm}(\text{CH}_4\text{N}_2\text{O})_8]\text{I}_3$ , is eight-coordinate, with eight monodentate urea ligands bound through their O atoms; the corresponding polyhedron is a distorted double-capped trigonal prism. All the urea molecules are involved in intramolecular hydrogen bonds. This compound is a rare example of a lanthanide complex containing no water and in which the anions do not serve as ligands.

### Comment

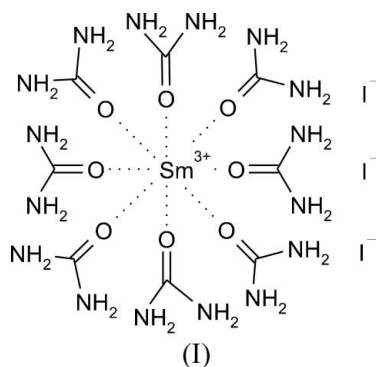
The use of samarium(II) iodide in organic chemistry has grown considerably during the last 25 years, for example in the reduction or coupling of carbonyl compounds and halides (Kagan, 2003; Lannou *et al.*, 2003). Tetrahydrofuran solutions of samarium(II) iodide are air-sensitive but stable under nitrogen or argon. A convenient method for the preparation of samarium(II) iodide is the reduction of samarium(III) iodide in an appropriate solvent. However, samarium(III) iodide is extremely moisture-sensitive, which is why a non-hygroscopic water-free samarium(III) iodide complex would be useful as an initial reagent. Such a complex with urea (Ur) was found in the  $\text{SmI}_3\text{-Ur-H}_2\text{O}$  system at 273 K (Afinogenova *et al.*, 1976); the  $\text{SmI}_3/\text{Ur}$  ratio in the water-free solid was

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**Figure 1**  
 ORTEP-3 (Farrugia, 1997) plot and numbering scheme of compound (I). Displacement ellipsoids are drawn at the 30% probability level. Only major components, namely N81 and N82, of the disordered N atoms are shown.

reported as 1:5. No structural study of this complex was performed. Our attempt to obtain the same complex at room temperature led us to the title compound, (I). The coordination number of the metal atom is eight, which is common for samarium, with the monodentate urea ligands bound to the metal *via* their O atoms. The corresponding polyhedron is a distorted double-capped trigonal prism, where atoms O1, O2, O4 and O6 form the uncapped square face. One urea ligand has the opportunity to rotate around the C—O bond so the N atoms are disordered over two sites each, with occupancies of 0.576 (10) (N81 and N82) and 0.424 (12) (N83 and N84). The urea ligands form both intra- and intermolecular hydrogen bonds to stabilize the solid-state structure (Table 2). The compound investigated here is a rare example of a lanthanide complex which contains no water and in which the anions do not serve as ligands.



## Experimental

Samarium(III) oxide (0.1 g) was dissolved in concentrated hydroiodic acid at room temperature. The resulting solution was concentrated at 373 K until formation of the first crystals of SmI<sub>3</sub> and then cooled. Urea (0.5 g) was then added to the reaction flask and the crystals were dissolved. The reaction mixture was allowed to stand at room temperature in a desiccator over potassium hydroxide for 2 d. The resulting yellow solid was recrystallized from ethanol (yield 80%).

### Crystal data

[Sm(CH <sub>4</sub> N <sub>2</sub> O) <sub>8</sub> ] <sub>3</sub> I <sub>3</sub>	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 1011.55	<i>D<sub>x</sub></i> = 2.173 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 10.597 (5) Å	Cell parameters from 25 reflections
<i>b</i> = 11.996 (11) Å	$\theta$ = 12–13°
<i>c</i> = 13.046 (6) Å	$\mu$ = 4.95 mm <sup>-1</sup>
$\alpha$ = 85.58 (6)°	<i>T</i> = 293 (2) K
$\beta$ = 73.76 (4)°	Prism, yellow
$\gamma$ = 76.20 (7)°	0.23 × 0.21 × 0.19 mm
<i>V</i> = 1546.2 (17) Å <sup>3</sup>	

### Data collection

Enraf–Nonius CAD-4 diffractometer	4875 reflections with <i>I</i> > 2σ( <i>I</i> )
Non-profiled ω scans	$\theta_{\max}$ = 28.0°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -13 → 13
<i>T</i> <sub>min</sub> = 0.325, <i>T</i> <sub>max</sub> = 0.394	<i>k</i> = -15 → 15
7442 measured reflections	<i>l</i> = 0 → 17
7442 independent reflections	1 standard reflection
	frequency: 60 min
	intensity decay: 2%

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.058$   
 $S = 0.93$   
 7442 reflections  
 344 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0192P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.12 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -1.21 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Sm1—O4	2.378 (4)	O4—C4	1.250 (6)
Sm1—O8	2.391 (4)	C4—N42	1.327 (6)
Sm1—O1	2.395 (4)	C4—N41	1.337 (6)
Sm1—O3	2.418 (4)	O5—C5	1.250 (6)
Sm1—O5	2.441 (4)	C5—N52	1.315 (7)
Sm1—O6	2.445 (4)	C5—N51	1.329 (6)
Sm1—O2	2.448 (4)	O6—C6	1.253 (6)
Sm1—O7	2.448 (3)	C6—N61	1.323 (7)
O1—C1	1.261 (6)	C6—N62	1.330 (7)
C1—N12	1.308 (7)	O7—C7	1.256 (6)
C1—N11	1.327 (7)	C7—N71	1.325 (6)
O2—C2	1.268 (6)	C7—N72	1.327 (6)
C2—N21	1.302 (7)	O8—C8	1.266 (6)
C2—N22	1.308 (7)	C8—N82	1.281 (12)
O3—C3	1.229 (6)	C8—N81	1.350 (14)
C3—N31	1.321 (7)	C8—N83	1.271 (19)
C3—N32	1.339 (8)	C8—N84	1.356 (17)
O4—Sm1—O8	83.47 (13)	O5—Sm1—O6	132.43 (12)
O4—Sm1—O1	110.92 (14)	O4—Sm1—O2	73.05 (14)
O8—Sm1—O1	143.97 (13)	O8—Sm1—O2	78.41 (14)
O4—Sm1—O3	73.70 (14)	O1—Sm1—O2	74.99 (12)
O8—Sm1—O3	74.11 (14)	O3—Sm1—O2	138.70 (12)
O1—Sm1—O3	140.82 (12)	O5—Sm1—O2	74.90 (13)
O4—Sm1—O5	144.63 (12)	O6—Sm1—O2	119.21 (14)
O8—Sm1—O5	75.80 (13)	O4—Sm1—O7	142.61 (13)
O1—Sm1—O5	74.12 (14)	O8—Sm1—O7	96.62 (13)
O3—Sm1—O5	125.50 (14)	O1—Sm1—O7	90.86 (13)
O4—Sm1—O6	77.56 (13)	O3—Sm1—O7	70.47 (13)
O8—Sm1—O6	147.96 (13)	O5—Sm1—O7	69.19 (13)
O1—Sm1—O6	67.82 (14)	O6—Sm1—O7	83.67 (13)
O3—Sm1—O6	75.90 (14)	O2—Sm1—O7	143.82 (13)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N12—H12A...O2	0.86	2.14	2.910 (8)	149
N21—H21A...O4	0.86	2.19	2.895 (8)	139
N32—H32A...N41	0.86	2.46	3.234 (10)	150
N41—H41A...O6	0.86	2.19	2.920 (8)	143
N51—H51A...O8	0.86	2.29	3.030 (8)	145
N52—H52A...O5 <sup>i</sup>	0.86	2.43	3.224 (7)	154
N52—H52A...O7 <sup>i</sup>	0.86	2.60	3.111 (8)	119
N61—H61A...O7	0.86	2.27	3.002 (8)	143
N62—H62A...O1 <sup>ii</sup>	0.86	2.52	3.310 (9)	153
N72—H72A...O8	0.86	2.44	3.270 (8)	163
N82—H82A...N21	0.86	2.41	3.227 (15)	159
N83—H83A...O3	0.86	2.23	2.959 (17)	143

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

H atoms bound to N atoms were included in calculated positions and refined as riding atoms, with *U*<sub>iso</sub> values set to 1.2*U*<sub>eq</sub> of the parent atoms. N—H bond lengths were set at 0.86 Å. The maximum and minimum electron-density peaks are located at 0.85 Å from atom I3 and 0.06 Å from Sm1, respectively.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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