

$a = 9.097(2) \text{ \AA}$   
 $b = 13.940(2) \text{ \AA}$   
 $c = 8.933(3) \text{ \AA}$   
 $\alpha = 98.89(2)^\circ$   
 $\beta = 114.81(2)^\circ$   
 $\gamma = 83.16(2)^\circ$   
 $V = 1014.0(5) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 2.052 \text{ Mg m}^{-3}$   
 $D_m$  not measured

$\mu = 4.89 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Stick  
 $0.25 \times 0.25 \times 0.20 \text{ mm}$   
 Colourless

Molecular graphics: *ORTEPII* (Johnson, 1976) and *TEXSAN*.  
 Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCR  
 electronic archives (Reference: OA1022). Services for accessing these  
 data are described at the back of the journal.

#### Data collection

Rigaku AFC-7S diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  
 $\psi$  scans (North, Phillips  
 & Mathews, 1968)  
 $T_{\min} = 0.326$ ,  $T_{\max} = 0.376$   
 4957 measured reflections  
 4664 independent reflections

4385 reflections with  
 $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.013$   
 $\theta_{\max} = 27.49^\circ$   
 $h = 0 \rightarrow 11$   
 $k = -17 \rightarrow 18$   
 $l = -11 \rightarrow 10$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 4.87%

#### Refinement

Refinement on  $F$   
 $R = 0.026$   
 $wR = 0.038$   
 $S = 1.007$   
 4384 reflections  
 262 parameters  
 H atoms not refined  
 $w = 1/[\sigma^2(F_o)$   
 $+ 0.00053|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.0471$   
 $\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -2.46 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for*  
*Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Yb—O1	2.279 (2)	Yb—O9	2.337 (2)
Yb—O2	2.256 (2)	Yb—O10	2.350 (2)
Yb—O3	2.249 (2)	Yb—N1	2.506 (3)
Yb—O4	2.304 (2)	Yb—N2	2.531 (3)
O1—Yb—O2	103.78 (9)	O3—Yb—O9	148.77 (9)
O1—Yb—O3	86.20 (9)	O3—Yb—O10	74.90 (9)
O1—Yb—O4	155.86 (9)	O3—Yb—N1	77.34 (10)
O1—Yb—O9	79.81 (9)	O3—Yb—N2	69.32 (9)
O1—Yb—O10	81.35 (9)	O4—Yb—O9	83.07 (9)
O1—Yb—N1	67.69 (9)	O4—Yb—O10	77.95 (9)
O1—Yb—N2	135.71 (8)	O4—Yb—N1	136.36 (9)
O2—Yb—O3	138.74 (9)	O4—Yb—N2	67.51 (8)
O2—Yb—O4	86.85 (9)	O9—Yb—O10	75.47 (9)
O2—Yb—O9	72.16 (9)	O9—Yb—N1	121.35 (10)
O2—Yb—O10	145.61 (9)	O9—Yb—N2	137.71 (9)
O2—Yb—N1	70.26 (9)	O10—Yb—N1	139.37 (9)
O2—Yb—N2	76.39 (9)	O10—Yb—N2	123.58 (9)
O3—Yb—O4	100.15 (9)	N1—Yb—N2	71.15 (9)

The non-H atoms were refined anisotropically. H atoms were  
 included but not refined. All H atoms, except for those of the  
 water molecules, were calculated and fixed at their positions  
 relative to their parent C atoms, with C—H = 0.95  $\text{\AA}$ . The  
 water H atoms were found by the difference Fourier technique.

Data collection: *MSCIAFC Diffractometer Control Software*  
 (Molecular Structure Corporation, 1992). Cell refinement:  
*MSCIAFC Diffractometer Control Software*. Data reduction:  
*TEXSAN* (Molecular Structure Corporation, 1995). Program(s)  
 used to solve structure: *SIR92* (Altomare *et al.*, 1994)  
 and *TEXSAN*. Program(s) used to refine structure: *TEXSAN*.

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*Acta Cryst.* (1997). **C53**, 1378–1381

### Tetracaesium Bis(diethylenetriamine-*N,N,N',N'',N'''*-pentacetato)didysprosate(III) Tridecahydrate

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#### Abstract

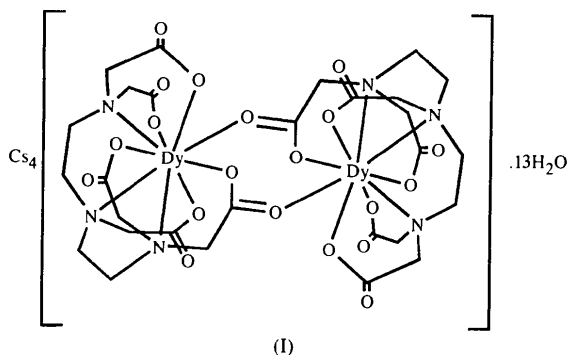
The structure of the title compound, Cs<sub>4</sub>[Dy<sub>2</sub>(C<sub>14</sub>H<sub>18</sub>-  
 N<sub>3</sub>O<sub>10</sub>)<sub>2</sub>].13H<sub>2</sub>O, is unlike that of any previously re-  
 ported Ln-DTPA complex (where DTPA is diethyl-

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enetriaminepentaacetato) and crystallizes as a dimer bridged by two carboxylate groups. Each Dy atom is nine-coordinate through the three N atoms and five O atoms of the DTPA, and one O atom of the coordinated carboxylate from the other [Dy(DTPA)] unit. The arrangement of the donor atoms around each Dy atom forms a tricapped trigonal prism.

### Comment

Accompanying the development of magnetic resonance imaging (MRI), studies have been focused on the paramagnetic lanthanide(III) (Ln) complexes as contrast agents in MRI. Complexes with polyaminocarboxylic acids such as diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid (DTPA) and its derivatives have been investigated widely. Although solution studies on the structure and dynamics of Ln–DTPA complexes have been carried out in some detail (Choppin, Baisden & Khan, 1979; Geraldès & Sherry, 1986; Peters, 1988; Jenkins & Lauffer, 1988; Aime & Botta, 1990), there is still little information on the structure in the solid state. Therefore, it is necessary to obtain crystals of new Ln–DTPA complexes in order to determine their coordination and packing patterns. We report here the crystal structure of the Cs salt of a Dy–DTPA complex, (I).



The structure of the title complex is shown in Fig. 1. In the Na salt of Gd–DTPA (Gries & Miklautz, 1984) and the Ba salt of Nd–DTPA (Stezowski & Hoard, 1984), the central lanthanide atom coordinates with the donor atoms of the DTPA and one O atom of a water molecule. In the case of the title complex, however, the ninth coordination site is occupied by a carboxylate O-atom donor of the other Dy–DTPA unit, forming a dinuclear structure which has an inversion center as shown in Fig. 1. A dimeric structure has been found also for the La(DTPA-dien) complex (Franklin & Raymond, 1994), but the bridging mode is different. In the La(DTPA-dien) dimer, a carboxylate chelates to one La ion and one O atom of the chelate is further bound to another La ion, the ligand acting in a tridentate manner, whereas in the title compound, the carboxylate bridges in a bidentate manner, described as a ‘*Z,E*

conformation’ (Ouchi, Suzuki, Ohki & Koizumi, 1988). To our knowledge, this is a new type of coordination mode for the Ln–DTPA complexes.

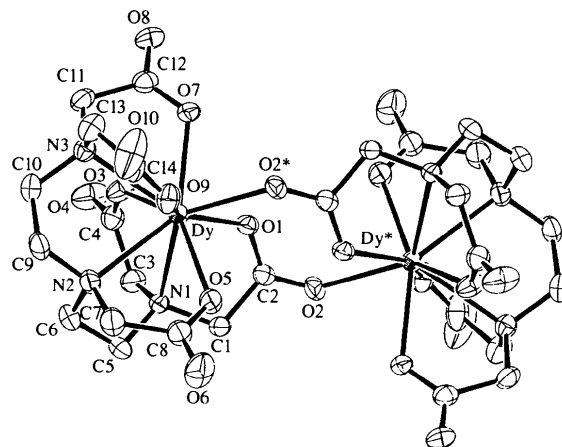


Fig. 1. ORTEP (Johnson, 1976) drawing of the Dy–DTPA dimer with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Like many other nine-coordinate Ln–DTPA-type complexes, the arrangement of the donor atoms around each Dy ion in this complex is found to be tricapped trigonal prismatic. That is, the cap positions are occupied by the O2' atom [symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ] of the bridging carboxylate and the terminal N1 and N3 atoms, while the sets of atoms N2, O5, O9 and O1, O3, O7 form the two trigonal faces of the coordination polyhedron.

The Dy–O and Dy–N distances are within the ranges observed for other polyaminocarboxylatodysprosium(III) complexes (Nassimbeni, Wright, van Niekerk & McCallum, 1979; Ehnebom & Pedersen, 1992), though Dy–O2' [2.428(4) Å] is a little longer than the other Dy–O distances [average 2.36(3) Å]. The Dy···Dy<sup>i</sup> distance is 5.6557(8) Å, which is very long compared with those in the La(DTPA-dien) dimer above [4.560(1) Å] (Franklin & Raymond, 1994), in the Dy–glutamate dimer [3.909(1) Å] (Csöreg, Kierkegaard, Legendziewicz & Huskowska, 1987, 1989) and in many carboxylate-bridged lanthanide dimers (3.8–4.6 Å).

There is an extensive network of hydrogen bonds formed *via* the water molecules. The O···O close contacts are in the range 2.704(8)–3.058(7) Å. The Cs<sup>+</sup> ion is eightfold coordinated to surrounding O atoms and the Cs<sup>+</sup>···O distances are in the range 3.087(6)–3.424(9) Å.

### Experimental

An aqueous solution of DTPA neutralized by Cs<sub>2</sub>CO<sub>3</sub> was added to an aqueous solution of Dy(CH<sub>3</sub>COO)<sub>3</sub>·H<sub>2</sub>O (1:1

molar ratio) and stirred for 2 h at room temperature. Single crystals were obtained by allowing the concentrated solution to stand in a refrigerator for a few weeks.

### Crystal data

Cs <sub>4</sub> [Dy <sub>2</sub> (C <sub>14</sub> H <sub>18</sub> N <sub>3</sub> O <sub>10</sub> ) <sub>2</sub> ].13H <sub>2</sub> O	Mo K $\alpha$ radiation
$M_r = 1867.44$	$\lambda = 0.7107 \text{ \AA}$
Monoclinic	Cell parameters from 21 reflections
C2/c	$\theta = 14.8\text{--}15.0^\circ$
$a = 22.01 (1) \text{ \AA}$	$\mu = 5.482 \text{ mm}^{-1}$
$b = 9.573 (3) \text{ \AA}$	$T = 296.2 \text{ K}$
$c = 25.895 (4) \text{ \AA}$	Short needle
$\beta = 96.37 (2)^\circ$	$0.35 \times 0.25 \times 0.25 \text{ mm}$
$V = 5423 (2) \text{ \AA}^3$	Colorless
$Z = 4$	
$D_x = 2.287 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Rigaku AFC-7S diffractometer	5390 reflections with $I > 3\sigma(I)$
$\omega$ -2 $\theta$ scans	$R_{\text{int}} = 0.042$
Absorption correction: $\psi$ scans (North, Phillips & Mathews, 1968)	$\theta_{\text{max}} = 27.52^\circ$
$T_{\text{min}} = 0.181$ , $T_{\text{max}} = 0.254$	$h = 0 \rightarrow 28$
6795 measured reflections	$k = 0 \rightarrow 12$
6620 independent reflections	$l = -33 \rightarrow 33$
	3 standard reflections every 150 reflections
	intensity decay: $-0.52\%$

### Refinement

Refinement on $F$	$\Delta\rho_{\text{max}} = 2.06 \text{ e \AA}^{-3}$
$R = 0.033$	(adjacent to Dy and Cs)
$wR = 0.037$	$\Delta\rho_{\text{min}} = -1.29 \text{ e \AA}^{-3}$
$S = 1.262$	(adjacent to Dy and Cs)
5390 reflections	Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
331 parameters	Extinction coefficient: 0.00085 (3)
H atoms not refined	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o) + 0.00250 F_o ^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.002$	

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Dy—O1	2.392 (4)	Dy—O9	2.361 (4)
Dy—O2'	2.428 (4)	Dy—N1	2.724 (5)
Dy—O3	2.363 (4)	Dy—N2	2.609 (5)
Dy—O5	2.324 (4)	Dy—N3	2.648 (5)
Dy—O7	2.362 (4)		
O1—Dy—O2'	72.9 (1)	O3—Dy—O7	73.9 (1)
O1—Dy—O3	77.1 (1)	O3—Dy—N2	86.8 (2)
O1—Dy—O5	92.3 (1)	O5—Dy—O9	74.9 (2)
O1—Dy—O7	86.8 (1)	O5—Dy—N2	67.4 (2)
O2'—Dy—O5	77.6 (1)	O7—Dy—O9	88.8 (2)
O2'—Dy—O7	73.0 (1)	O9—Dy—N2	74.4 (2)
O2'—Dy—O9	73.0 (1)	N1—Dy—N2	68.6 (2)
O2'—Dy—N1	123.9 (1)	N1—Dy—N3	116.5 (1)
O2'—Dy—N3	119.4 (1)	N2—Dy—N3	69.4 (2)

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

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

D—H...A	D—H	H...A	D...A	D—H...A
O51—H512...O2'	0.74	2.38	3.058 (7)	155
O51—H512...O7''	0.74	2.45	2.975 (7)	130
O51—H511...O10''	0.64	2.09	2.717 (8)	173
O52—H521...O4	1.12	1.72	2.874 (9)	158
O52—H522...O56	0.92	2.00	2.857 (9)	156
O53—H532...O52''	0.95	1.92	2.73 (1)	142
O54—H541...O10''	0.82	2.10	2.796 (9)	144
O54—H542...O57''	0.74	2.07	2.72 (1)	147
O55—H551...O54''	0.79	1.94	2.704 (8)	162
O56—H561...O4''	1.19	1.70	2.879 (8)	173
O56—H562...O55	1.11	1.70	2.806 (9)	176
O57—H572...O4	0.63	2.22	2.837 (8)	171
O57—H571...O8	0.99	1.86	2.831 (9)	167

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (iv)  $1 - x, -y, 1 - z$ ; (v)  $x, 1 + y, z$ ; (vi)  $1 - x, y, \frac{3}{2} - z$ .

The structure was solved by direct methods and expanded using Fourier techniques (*DIRDIF94*; Beurskens *et al.*, 1994). All non-H atoms were refined anisotropically; H atoms were included but not refined. All H atoms, except for water molecules, were calculated and fixed with C—H = 0.95  $\text{\AA}$ . The water H atoms were found from difference Fourier maps.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to refine structure: *DIRDIF94*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1240). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1997). **C53**, 1381–1383

## Tetrakis(ethylenediamine)yttrium(III) Hydrosulfide Iodide

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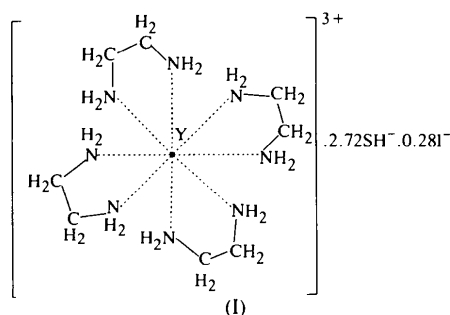
(Received 14 March 1997; accepted 19 May 1997)

### Abstract

An yttrium hydrosulfide complex,  $[Y(H_2NCH_2CH_2-NH_2)_4](SH)_{2.72}I_{0.28}$ , was synthesized by solvothermal methods. The  $Y(en)_4^{3+}$  and  $SH^-$  ions are well separated, and the Y atom is coordinated in a distorted square antiprism by the eight N atoms and lies on a twofold axis. The Y—N distances are in the range 2.488 (4)–2.520 (4) Å. There are two hydrosulfide sites, the one on the twofold axis being partially occupied by an iodide ion.

### Comment

Attempts at solvothermal crystallization of  $Y_2S_3$  in liquid anhydrous ammonia with an  $NH_4I$  mineralizer at temperatures of 473–573 K produced colorless crystals which rapidly lost solvent and crumbled when removed from the tube. In order to gain a better understanding of the identity of this product, ethylenediamine (en) was used as a high-boiling substitute for ammonia. From  $Y_2S_3$  and  $NH_4I$  at 568 K, monoclinic crystals of the title compound  $Y(en)_4(SH)_{2.72}I_{0.28}$ , (I), were isolated. Each  $Y(en)_4^{3+}$  ion in the lattice is surrounded by a total of nine  $SH^-$  or  $I^-$  ions. There are two sites for the  $SH^-$  ions, one of which lies on a twofold axis. This site is also partially occupied by an iodide ion.



The  $YN_8$  coordination polyhedron (Fig. 2) is a distorted square antiprism (Porai-Koshits & Aslanov, 1972), where (N1, N2, N1' and N2') and (N1A, N1'A, N2A and N2'A) form the rectangular faces where the mean deviation from a least-squares plane is 0.167 Å. The two planes deviate from being parallel by 0.2°. A square antiprism of approximate  $D_2$  symmetry is what one would usually expect from coordination to four bidentate ligands with a normalized bite (N··N distance/Y—N distance) between 1.07 and 1.3 (Kepert, 1978). The normalized bite of the en ligands in  $Y(en)_4(SH)_{2.72}I_{0.28}$  averages 1.11, and the bite angles are 67.3(1) and 68.1(1)°. Despite extensive use of ethylenediamine and its tetramethyl derivative as ligands, only one structurally characterized example of a metal ion surrounded by four ethylenediamine ligands,  $[La(en)_4SO_3CF_3]^{2+}(SO_3CF_3^-)_2$ , has been reported (Smith & Raymond, 1985). An IR spectral study showed that the lanthanide ion in tetrakis(ethylenediamine) complexes of lanthanide salts can be either eight-coordinate  $\{[Ln(en)]_4^{3+}(X^-)_3\}$  or nine-coordinate  $\{[Ln(en)_4X]^{2+}(X^-)_2\}$  depending on ion size and the coordinating power of the anion (Forsberg & Moeller, 1969). The Y—N distances of 2.488 (4)–

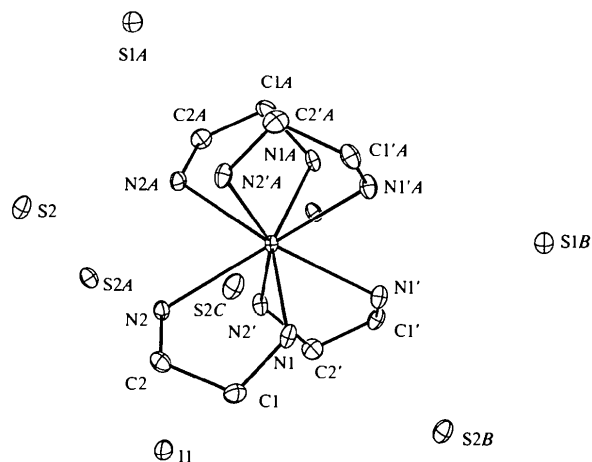


Fig. 1. Displacement ellipsoid drawing (20% probability) of the title compound. H atoms have been omitted for clarity and the nine nearest symmetry-related S or I atoms are shown. Sites labeled as I1, S1A and S1B are partially occupied by both I and S.