Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Heptaaquatetra-μ_3-hydroxy-hexa-μ_2-L-leucine-(L-leucine)tetraytterbium(III) tetrachlorozinc(II) trichlorohydroxyzinc(II) tetrachloride octahydrate

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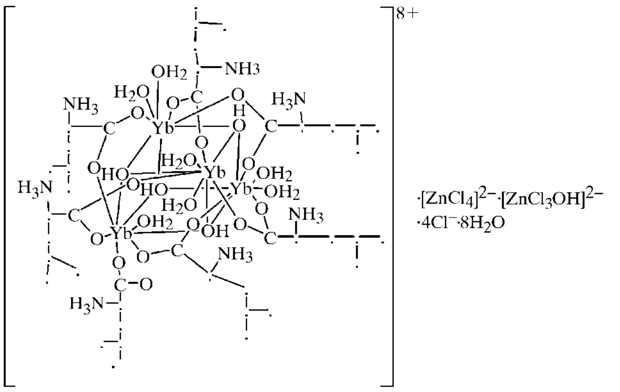
Received 9 December 2003
Accepted 28 January 2004
Online 28 February 2004

The title bimetallic compound, $[Yb_4(\mu_3\text{-}OH)_4(C_6H_{13}NO_2)_7(H_2O)_7][ZnCl_4][ZnCl_3(OH)]Cl_4\cdot 8H_2O$, was synthesized at near physiological pH (6.0). The compound exhibits some novel structural features, including an asymmetric $[Yb_4(\mu_3\text{-}OH)_4(\text{L-leucine})_7(H_2O)_7]^{8+}$ complex cation in which four OH groups act as bridging ligands, linking four Yb^{3+} cations into a Yb_4O_4 structural unit. Each pair of adjacent Yb^{3+} ions is further bridged by one carboxy group from a leucine ligand. Water molecules and a monodentate leucine ligand also coordinate to Yb^{3+} ions, completing their eight-coordinate square-antiprismatic coordination. The $Yb_4(\mu_3\text{-}OH)_4(\text{L-leucine})_7(H_2O)_7]^{8+}$ cation, the $[ZnCl_4]^{2-}$, $[ZnCl_3OH]^{2-}$ and Cl^- anions, and the lattice water molecules are linked *via* hydrogen bonds.

Comment

Because lanthanides are widely used, for example, as spectroscopic probes in studies of biological systems and as microfertilizers in Chinese agriculture, more and more rare earth metals are entering into the environment and human body *via* the food chain and other routes (Brittain *et al.*, 1976; Evans, 1990; Ni, 1995), and many investigations have therefore been undertaken into the biological effects of lanthanides. As a biological trace metal, zinc is an essential component of many proteins, playing important structural and catalytic roles (Karlin *et al.*, 1991; Berg & Shi, 1996; Karlin & Zhu, 1997). Potential effects of lanthanide ions on biological systems are related to the interactions of lanthanide ions with biological trace metal ions and biological ligands, such as amino acids. Therefore, the study of the coordination chemistry of lanthanide ions, biological trace metal ions and amino acids has implications for the biochemistry of lanthanides. Much effort has already been expended on studying the structures and properties of metal complexes of amino acids (Dalosto *et al.*, 1999). In recent years, some lanthanide complexes with amino acids have been synthesized at near physiological pH (6.0–6.5), by controlling the hydrolysis or alcoholysis of metal ions with the aid of supporting ligands and auxiliary ligands (Blake *et al.*, 1994; Abbati *et al.*, 1998; Wang *et al.*, 1999, 2001; Ma *et al.*, 2000; Wang & Selby, 2002). However, studies of bimetallic compounds of lanthanide ions and biological trace metal ions with amino acids have rarely been reported. In the present work, we describe the synthesis, at near physiological pH, of the bimetallic title compound, (I). The crystal structure of (I) has been studied by X-ray diffraction analysis for the first time, showing that this compound has a novel and complex structure.



(I)

Compound (I) is composed of a discrete tetranuclear $[Yb_4(\mu_3\text{-}OH)_4(Leu)_7(H_2O)_7]^{8+}$ cation, $[ZnCl_4]^{2-}$, $[ZnCl_3OH]^{2-}$ and Cl^- anions, and lattice water molecules, none of which exhibit crystallographically imposed symmetry (Fig. 1). The tetranuclear cation contains a Yb_4O_4 structural unit that can be regarded as a distorted cube, in which O atoms from four bridging OH^- groups are also considered as vertices of the polyhedron. Each Yb_3 triangular face is capped by a triply bridging hydroxy ligand, with Yb—O bond lengths in the range 2.232 (13)–2.377 (12) Å (Table 1). Each pair of adjacent Yb^{3+} ions is also bridged by one carboxy group of a leucine ligand [mean $Yb-O_{carboxy}$ = 2.292 (12) Å]. In this case, all the Yb^{3+} ions have eight-coordinate square-antiprismatic coordination [eight-coordinate rare earth ions are common (Ni, 1995)], with atoms Yb1, Yb2 and Yb4 each surrounded by three OH^- groups, three carboxy O atoms and two water molecules. In contrast, atom Yb3 is surrounded by three OH^- groups, four carboxy O atoms and one water molecule.

The seven leucine ligands exhibit two different bonding modes with respect to the Yb^{3+} ions, six of these leucine molecules being bidentate ligands and one being monodentate. The $Yb3-O_{carboxy}$ (the O atom is from the monodentate leucine molecule) bond length [2.470 (10) Å] is approximately equal to the mean Yb—O*W* bond length [2.460 (4) Å], and therefore the monodentate leucine molecule bound to atom Yb3 can be considered to have replaced a water ligand. As a leucine molecule is larger than a water molecule, the steric effect introduces asymmetry into the structure. For example, the Yb1···Yb3, Yb2···Yb3 and Yb3···Yb4 distances [3.8035 (15), 3.6882 (15) and 3.6905 (15) Å, respectively] are longer than those between

DOI: 10.1107/S0108270104002264

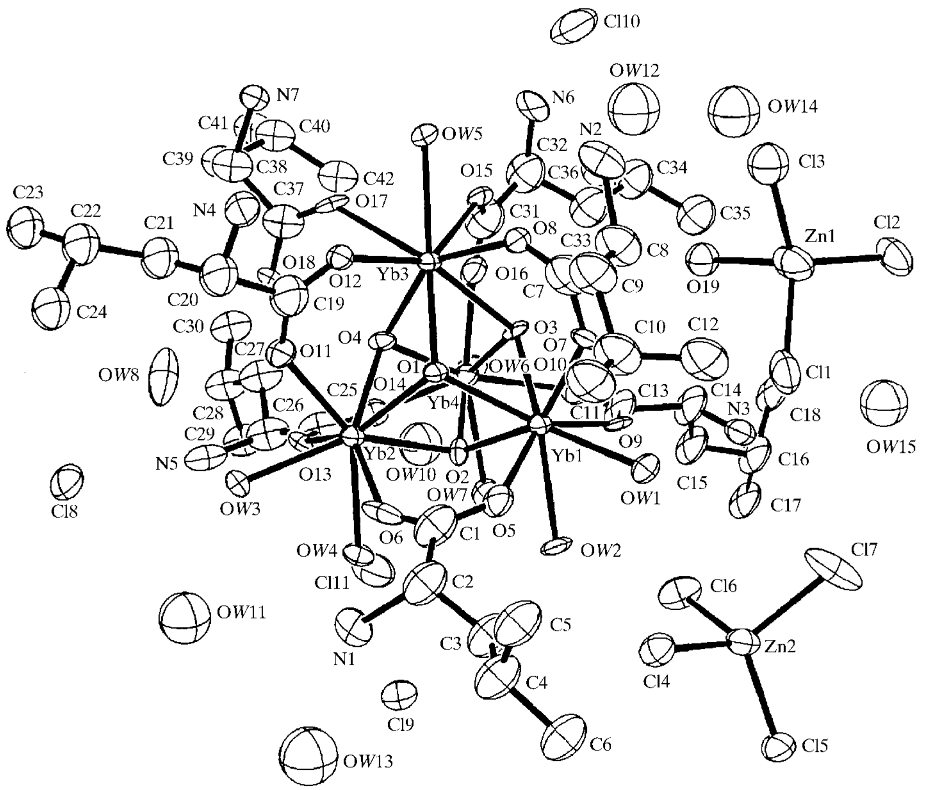


Figure 1

A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

other Yb^{3+} ions [3.6414 (14)–3.6875 (15) Å]. Since the tetrameric cation is based on a Yb_4 trigonal pyramid, this unit is also an irregular tetrahedron. Similar $Ln_4(OH)_4$ core motifs have been reported (Wang *et al.*, 1999, 2001; Ma *et al.*, 2000; Wang & Selby, 2002). However, the bonding modes of amino acid ligands and the geometry of the Ln_4O_4 core motif are different from those of Yb_4O_4. Thus, the Yb_4O_4 unit exhibits some novel characteristics and is the first example of a Yb_4O_4 cluster (Ni, 1995). Nevertheless, the $[Ln_4(OH)_4]^{8+}$ cluster core appears to be a stable structural entity and is expected to serve as a building block for more complex structures.

Compound 1 is assembled *via* hydrogen bonding (Fig. 2 and Table 2). Zinc forms two tetrahedral complex anions, namely $[ZnCl_4]^{2-}$ and $[ZnCl_3OH]^{2-}$, with Cl^- and OH^- ions, which respectively provide four and three hydrogen-bond acceptors. In addition to both coordinated and lattice water molecules, Cl^- ions are involved in forming hydrogen bonds. As the leucine molecules exist in zwitterionic form, with the amino groups protonated and the carboxy groups deprotonated, each protonated amino group has three H-atom donors available to form hydrogen bonds. Two Cl atoms from the $[ZnCl_3OH]^{2-}$ ion form hydrogen bonds with two amino groups [N···Cl = 3.15 (2)–3.426 (18) Å], while the third forms a hydrogen bond with a coordinated water molecule [O*W*15···Cl2 = 3.157 (15) Å]; the OH^- group does not participate in hydrogen bonding. Three of the Cl atoms of the $[ZnCl_4]^{2-}$ ion form hydrogen bonds with an amino group [N···Cl = 3.187 (15)–3.426 (18) Å] and one forms a weaker hydrogen bond with a coordinated water molecule [O*W*6···Cl5 = 3.256 (19) Å]. Both free Cl^- ions and lattice water molecules form hydrogen bonds with amino groups, and lattice water molecules also form hydrogen bonds with free Cl^- ions. In the crystal structure, the $[ZnCl_4]^{2-}$, $[ZnCl_3OH]^{2-}$ and Cl^- ions and lattice water molecules occupy cavities between the $[Yb_4(\mu_3\text{-}OH)_4(Leu)_7(H_2O)_7]^{8+}$ cations. Hydro-

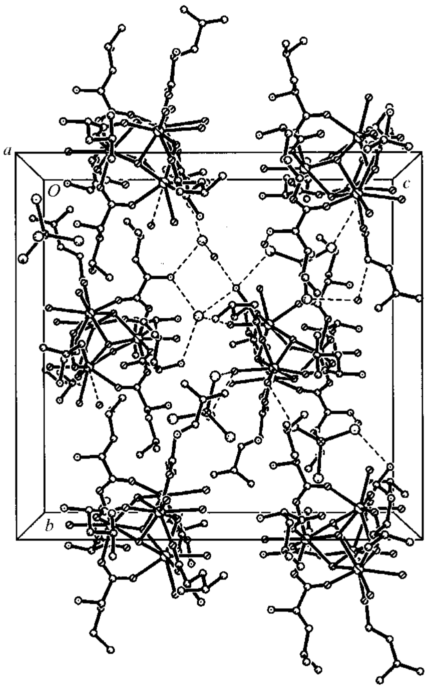


Figure 2

The arrangement of the structural components of (I) in the unit cell; the $[ZnCl_4]^{2-}$, $[ZnCl_3OH]^{2-}$ and Cl^- ions, and the lattice water molecules, occupy cavities between the $[Yb_4(\mu_3\text{-}OH)_4(Leu)_7(H_2O)_7]^{8+}$ cations.

gen bonds direct the associations of host and guest units into a three-dimensional network.

Experimental

$YbCl_3$ (0.335 g, 1.20 mmol), $ZnCl_2$ (0.164 g, 1.20 mmol) and L-leucine (0.159 g, 1.20 mmol) were mixed in aqueous solution. The pH of the resulting solution was adjusted to ~6.0 by slow addition of several millilitres of 0.1 *M* NaOH, with heating and stirring. The precipitate formed by partial hydrolysis of $YbCl_3$ was filtered off and the filtrate concentrated by slow evaporation at room temperature, yielding colorless prismatic crystals (yield 60% based on L-leucine) after several weeks.

Crystal data

$[Yb_4(OH)_4(C_6H_{13}NO_2)_7(H_2O)_7][ZnCl_4][ZnCl_3(OH)]Cl_4\cdot 8H_2O$
$M_r = 2486.35$
Orthorhombic, $P2_12_12_1$
$a = 18.171$ (4) Å
$b = 22.130$ (5) Å
$c = 23.251$ (7) Å
$V = 9349$ (4) Å^3
$Z = 4$
$D_x = 1.766$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 5.2$–$11.4°$
$\mu = 4.85$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.50 × 0.42 × 0.38 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Siemens, 1994)
$T_{\min} = 0.440$, $T_{\max} = 0.586$
10 699 measured reflections
10 247 independent reflections
5857 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 21$
$k = -1 \rightarrow 26$
$l = -1 \rightarrow 27$
3 standard reflections every 197 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.100$
$S = 1.06$
10 247 reflections
669 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -0.93$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.013 (15), 385 Friedel pairs

Table 1
Selected interatomic distances (Å).

Yb1—Yb2	3.6414 (14)	Yb3—O3	2.339 (10)
Yb1—Yb3	3.8035 (15)	Yb3—O4	2.296 (12)
Yb1—Yb4	3.6849 (16)	Yb3—O8	2.313 (13)
Yb2—Yb3	3.6882 (15)	Yb3—O12	2.262 (11)
Yb2—Yb4	3.6875 (15)	Yb3—O15	2.366 (13)
Yb3—Yb4	3.6905 (15)	Yb3—O17	2.465 (12)
Yb1—O1	2.316 (12)	Yb3—O*W*5	2.470 (10)
Yb1—O2	2.310 (12)	Yb4—O2	2.240 (12)
Yb1—O3	2.332 (12)	Yb4—O3	2.314 (13)
Yb1—O5	2.294 (13)	Yb4—O4	2.295 (11)
Yb1—O7	2.241 (13)	Yb4—O10	2.286 (13)
Yb1—O9	2.247 (14)	Yb4—O14	2.269 (14)
Yb1—O*W*1	2.428 (13)	Yb4—O16	2.232 (13)
Yb1—O*W*2	2.500 (11)	Yb4—O*W*6	2.319 (15)
Yb2—O1	2.355 (11)	Yb4—O*W*7	2.648 (12)
Yb2—O2	2.342 (11)	Zn1—Cl1	2.220 (8)
Yb2—O4	2.327 (11)	Zn1—Cl2	2.261 (7)
Yb2—O6	2.301 (14)	Zn1—Cl3	2.215 (16)
Yb2—O11	2.347 (11)	Zn1—O19	2.296 (16)
Yb2—O13	2.315 (13)	Zn2—Cl4	2.315 (7)
Yb2—O*W*3	2.413 (12)	Zn2—Cl5	2.201 (6)
Yb2—O*W*4	2.477 (10)	Zn2—Cl6	2.309 (8)
Yb3—O1	2.377 (12)	Zn2—Cl7	2.252 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl9	0.89	2.78	3.261 (19)	115
N1—H1*A*···O*W*13	0.89	2.46	2.82 (3)	105
N1—H1*B*···O6	0.89	2.13	2.63 (2)	115
N1—H1*C*···O*W*13	0.89	2.39	2.82 (3)	110
N1—H1*C*···Cl3$^{\rm i}$	0.89	2.39	3.15 (2)	144
N2—H2*A*···Cl10	0.89	2.64	3.24 (2)	126
N2—H2*B*···O*W*14	0.89	2.11	2.89 (3)	146
N2—H2*C*···Cl11$^{\rm ii}$	0.89	2.52	3.35 (2)	156
N3—H3*C*···O9	0.89	2.00	2.55 (2)	119
N3—H3*D*···O*W*15	0.89	2.12	2.89 (3)	144
N3—H3*E*···Cl6	0.89	2.80	3.426 (18)	128
N4—H4*A*···O*W*9$^{\rm ii}$	0.89	2.06	2.92 (2)	162
N4—H4*B*···O*W*15$^{\rm i}$	0.89	2.50	3.35 (3)	161
N4—H4*C*···Cl7$^{\rm i}$	0.89	2.77	3.426 (18)	131
N5—H5*D*···Cl10$^{\rm iii}$	0.89	2.42	3.302 (18)	172
N5—H5*E*···Cl8	0.89	2.45	3.255 (18)	151
N5—H5*F*···O*W*8	0.89	2.07	2.95 (3)	168
N6—H6*D*···O*W*12	0.89	2.36	2.74 (3)	106
N6—H6*D*···Cl8$^{\rm iv}$	0.89	2.67	3.213 (17)	120
N6—H6*E*···O*W*12	0.89	2.37	2.74 (3)	105
N6—H6*E*···O15	0.89	2.04	2.57 (2)	116
N6—H6*F*···Cl9$^{\rm ii}$	0.89	2.62	3.187 (15)	122
N7—H7*A*···O*W*9$^{\rm ii}$	0.89	2.11	2.99 (2)	173
N7—H7*B*···Cl4$^{\rm ii}$	0.89	2.46	3.334 (17)	168
N7—H7*C*···Cl9$^{\rm ii}$	0.89	2.44	3.271 (17)	156

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

Atom Cl3 is disordered over two equal positions. H atoms of the amino acid ligands were placed at calculated positions, but water H atoms were not located. H atoms were treated using a riding model, with N—H distances of 0.89 Å, and C—H distances of 0.98, 0.97 and 0.96 Å for methine, methylene and methyl groups, respectively [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$].

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

The authors acknowledge financial support from the Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and the National Natural Science Foundation of China (project No. 29971029)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1556). Services for accessing these data are described at the back of the journal.

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