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Synthesis and crystal structure of the potassium ytterbium complex with triethylenetetraaminehexaacetic acid: $[K_3Yb(TTHA)(H_2O)_5]$

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Abstract—The title complex $[K_3Yb(TTHA)(H_2O)_5]$, where $TTHA^{6-}$ is triethylenetetraaminehexaacetic acid anion was synthesized in aqueous solution, and its crystal structure was determined by X-ray diffraction. In the complex, the ytterbium ion is coordinated by four nitrogen atoms and five carboxyl oxygen atoms of the same $TTHA^{6-}$ anion. The coordination number of the ytterbium ion is 9, and its coordination polyhedron can be described as a distorted monocapped square antiprism. Each $Yb(TTHA)^{3-}$ is further connected by K^+ ions through carboxyl groups of $TTHA^{6-}$ ion to form a three dimensional network structure. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: ytterbium complex; crystal structure; triethylenetetraaminehexaacetic acid.

Paramagnetic metal ion complexes are finding many applications in biomedicine, especially as bioconjugates for monoclonal antibody radioisotope labeling and as magnetic resonance imaging (MRI) agents [1,2]. Polyaminecarboxylic acids and their derivatives are very important chelating agents for metal ions, and diethylenetriaminepentaacetic acid (H_5DTPA) complex with gadolinium has been used as MRI agent in the NMR diagnosing of tumors [3,4]. Having similar coordination ability with H_5DTPA toward lanthanide ions, triethylenetetraaminehexaacetic acid (H_6TTHA) can also strongly chelate with lanthanide, and its complex with gadolinium may also be used as an image enhancing agent. Studies on lanthanide complex with H_6TTHA in solution have been carried out to determine the thermodynamic stability constants [5,6]. But crystallographic data on these complexes in the solid state has appeared only in one paper recently [7]. In this paper, we report the synthesis of an ytterbium complex with H_6TTHA and its crystal structure as determined by X-ray analysis.

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EXPERIMENTAL

Preparation

Ytterbium oxide(Yb_2O_3) and triethylenetetraaminehexaacetic acid(H_6TTHA) were mixed in 1:2 molar ratio in water. The mixed solution was refluxed for about 5 h with stirring. Then the solution was neutralized with KOH solution to about pH 6 and filtered. The filtrate was concentrated on a water bath, and the clear solution obtained was allowed to evaporate slowly at room temperature, yielding colorless crystals suitable for X-ray diffraction. The composition of the complex was deduced from the elemental analysis. Found: C, 25.1; H, 3.5; N, 6.1. Calc. for $K_3Yb(TTHA)(H_2O)_5$: C, 24.9; H, 3.9; N, 6.5%. This formula is approximately consistent with the result of diffraction analysis.

Table 1. Crystal data, details of data collection and refinement

Empirical formula	$K_3Yb(C_{18}H_{24}N_4O_{12})\cdot 5H_2O$
Color	Colorless
Crystal size (mm)	0.26 × 0.28 × 0.34
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.218(2)
b (Å)	12.489(1)
c (Å)	22.818(2)
β(°)	91.30(1)
V (Å^3)	2911.1(7)
Z	4
M	868.83
D_c(g cm^3)	1.982
Absorption coefficient (mm^{-1})	3.724
F(000)	1732
λ (Å) (Mo-K_α)	0.71073
Monochromator	Graphite
Scan type	$2\theta - \theta$
2θ range (°)	3.0–50.0
Scan speed (deg. min.)	6.00
Standard reflections	3/97
Index ranges h; k; l	−1–12; −1–14; −27–27
Reflections collected	6640
Independent reflections	5118(R_{int} = 6.39%)
Observed reflections	4556 ($F > 4.0\sigma(F)$)
Absorption correction	N/A
Quantity minimized	$\Sigma\omega(F_o\text{-}F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Number of parameters refined	388
Final R	0.0344
Final Rw	0.0494
Goodness-of-fit	1.67
Max., min. residual ρ(e Å^3)	0.91, −0.86

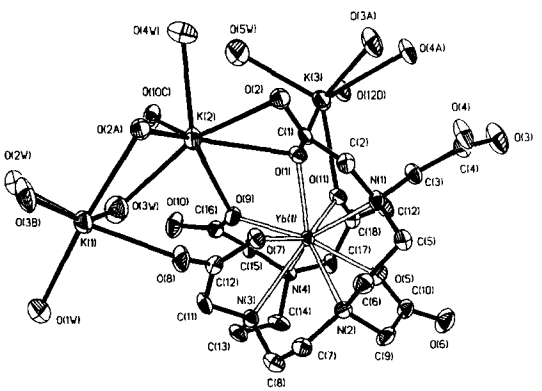

Fig. 1. Structure of $[K_3Yb(TTHA)(H_2O)_5]$.

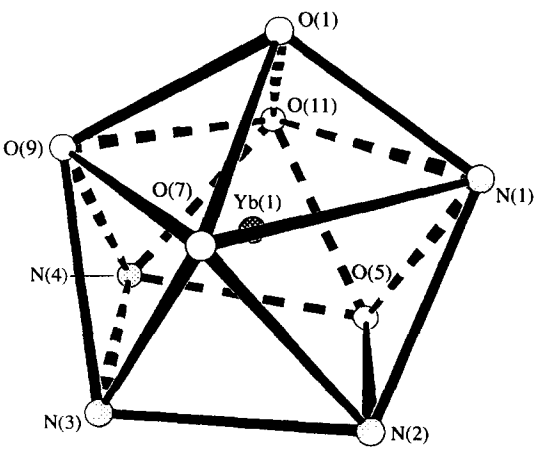

Fig. 2. Coordination polyhedron of $[K_3Yb(TTHA)(H_2O)_5]$.

IR spectra

IR spectra of the complex and free ligand were obtained from KBr pellet at 298 K using a Nicolet Magna-IR 750 spectrophotometer. Compared with the IR spectrum of free ligand, the ν_{as}(COO) band of complex is shifted 38 cm^{-1} to lower wavenumbers from 1642 cm^{-1}, the ν_s(COO) band of complex is shifted 4 cm^{-1} to higher wavenumbers from 1398 cm^{-1}. This shows that the carboxyl group of the ligand has been coordinated with metal ions [8,9]. A broad absorption band for ν(OH) appears at 3400 cm^{-1} after complexation, showing the presence of water molecules in the complex.

Crystal structure determination

A colorless crystal of the ytterbium compound with dimension 0.26 × 0.28 × 0.34 mm was mounted in a thin-walled capillary for structure determination. The reflection data were collected in the range 3.0–50.0° on a Siemens P4. 5188 independent reflections were collected, of which 4556 with $F > 4.0\sigma(F)$ were used for structure refinement. Intensities were not corrected for absorption. All calculations were performed using the Siemens SHELXTL P4/PC system. The structure was determined by direct methods and difference-Fourier synthesis, and then refined by full-matrix least-squares to the final R and Rw of 0.0344 and 0.0494, respectively. Crystal data, details of data collection and refinement are listed in Table 1.

RESULTS AND DISCUSSION

The crystal structure of the $[K_3Yb(TTHA)(H_2O)_5]$ complex and its coordination polyhedron are shown in Figs 1 and 2, respectively. Selected bond lengths and bond angles, are listed in Table 2.

In the complex, each Yb^{3+} ion is coordinated by four nitrogen atoms and five oxygen atoms from the five carboxyl groups of the same $TTHA^{6-}$ ion with coordination number nine, taking a monocapped square antiprism arrangement. The average bond lengths of Yb—N and Yb—O are 2.655 and 2.311 Å, respectively.

Each $Yb(TTHA)^{3-}$ is further connected with K^+ ions through carboxyl groups of $TTHA^{6-}$ ion serving as carboxyl bridges and oxygen bridges to form a three dimensional network structure (Fig. 3).

Recently, we reported the results [7] of crystallographic studies of lanthanum complex with triethylenetetraaminehexaacetic acid. Although both ytterbium and lanthanum complexes were obtained under the same conditions, they vary in composition and structure. In the latter $K[KLa(HTTHA)(H_2O)] \cdot 8H_2O$ complex, a proton of the triethylenetetraaminehexaacetic acid is not ionized; the

Table 2. Selected bond lengths (Å) and angles (°)

Yb(1)—O(1)	2.342(4)	Yb(1)—O(5)	2.279(4)
Yb(1)—O(7)	2.264(4)	Yb(1)—O(9)	2.304(4)
Yb(1)—O(11)	2.365(4)	Yb(1)—N(1)	2.644(4)
Yb(1)—N(2)	2.721(5)	Yb(1)—N(3)	2.686(5)
Yb(1)—N(4)	2.568(4)	K(1)—O(2A)	2.738(5)
K(1)—O(3B)	2.633(5)	K(1)—O(8)	2.601(5)
K(1)—O(1w)	2.737(6)	K(1)—O(2w)	2.833(5)
K(1)—O(3w)	2.893(5)	K(2)—O(1)	2.843(4)
K(2)—O(2A)	2.840(4)	K(2)—O(9)	2.847(4)
K(2)—O(10C)	2.780(5)	K(2)—O(3w)	2.878(5)
K(2)—O(4w)	2.783(6)	K(2)—O(2)	2.835(4)
K(3)—O(1)	2.871(4)	K(3)—O(4A)	2.760(5)
K(3)—O(11)	2.732(5)	K(3)—O(12D)	2.861(4)
K(3)—O(3B)	2.789(5)	K(3)—O(5w)	2.778(7)

O(1)—Yb(1)—O(5)	127.1(1)	O(1)—Yb(1)—O(7)	75.4(1)
O(1)—Yb(1)—O(9)	72.8(1)	O(1)—Yb(1)—O(11)	73.9(1)
O(1)—Yb(1)—N(1)	64.7(1)	O(1)—Yb(1)—N(2)	124.1(1)
O(1)—Yb(1)—N(3)	134.9(1)	O(1)—Yb(1)—N(4)	123.6(1)
O(5)—Yb(1)—O(7)	136.4(1)	O(5)—Yb(1)—O(9)	142.4(1)
O(5)—Yb(1)—O(11)	73.0(1)	O(5)—Yb(1)—N(1)	77.9(1)
O(5)—Yb(1)—N(2)	65.2(1)	O(5)—Yb(1)—N(3)	97.6(2)
O(5)—Yb(1)—N(4)	75.3(1)	O(7)—Yb(1)—O(9)	75.0(1)
O(7)—Yb(1)—O(11)	147.5(2)	O(7)—Yb(1)—N(1)	82.4(1)
O(7)—Yb(1)—N(2)	71.3(1)	O(7)—Yb(1)—N(3)	66.7(1)
O(7)—Yb(1)—N(4)	127.2(1)	O(9)—Yb(1)—O(11)	85.8(1)
O(9)—Yb(1)—N(1)	135.6(1)	O(9)—Yb(1)—N(2)	135.1(1)
O(9)—Yb(1)—N(3)	74.3(1)	O(9)—Yb(1)—N(4)	67.6(1)
O(11)—Yb(1)—N(1)	94.1(1)	O(11)—Yb(1)—N(2)	136.9(1)
O(11)—Yb(1)—N(3)	132.9(1)	O(11)—Yb(1)—N(4)	64.8(1)
N(1)—Yb(1)—N(2)	67.4(1)	N(1)—Yb(1)—N(3)	129.8(1)
N(1)—Yb(1)—N(4)	149.7(1)	N(2)—Yb(1)—N(3)	65.6(1)
N(2)—Yb(1)—N(4)	112.3(2)	N(3)—Yb(1)—N(4)	68.2(1)

Symmetry operation: $A = 1 - x, 1 - y, -z$; $B = x, 1 + y, z$; $C = -x, 1 - y, -z$; $D = -x, -y, -z$.

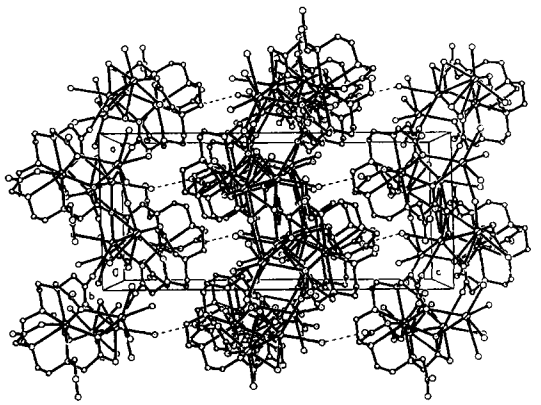

Fig. 3. Arrangement of $[K_3Yb(TTHA)(H_2O)_5]$ in unit cell.

coordination number of La^{3+} ion is ten, forming a bicapped square antiprism, and the crystal is composed of one dimensional chain.

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