8배위 12면체 Y(tpb)₃(H₂O)₂ 착물의 합성과 구조

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Structural Characterization of the Eight-Coordinated Dodecahedral Y(tpb)₃(H₂O)₂

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요   약. 8배위 이트륨(III) 화합물 $Y(tpb)_3(H_2O)_2$을 합성하였고 X-선 회절법으로 구조를 규명하였다. 이 화합물은 12 면체의 구조를 가지며, 두 면(Y-O2-O1-O5-O6 and Y-O4-O3-O8-O7)사이의 각은 89.59°이다. 또한, O1-O5과 O3-O8 의 거리는 2.965 and 2.995 Å이며 O2-O6과 and O4-O7의 거리는 4.256 and 4.403 Å이다.

주제어: 이트륨, 12면체 구조, tpb 리간드

ABSTRACT. The eight coordinated yttrium(III) complex $Y(tpb)_3(H_2O)_2$ (Htpb=4,4,4-Trifluoro-1-phenyl-1,3-butane-dione) has been synthesized and structurally characterized by X-ray diffraction method. The coordination polyhedron of $Y(tpb)_3(H_2O)_2$ has a dodecahedron. The angle between two trapezia, Y-O2-O1-O5-O6 and Y-O4-O3-O8-O7, is 89.59°. The O1-O5 and O3-O8 distances are 2.965 and 2.995 Å whereas the O2-O6 and O4-O7 distances are 4.256 and 4.403 Å.

Keywords: Yttrium, dodecahedron, tpb β-diketonate ligand

INTRODUCTION

There are three important idealized structures for the eight coordinated metal complexes; the cube, the square antiprism, and the triangulated dodecahedron. The ground-state geometries for the eight coordinated d-metal complexes are mainly described by square antiprism or dodecahedron. Since the square antiprism and the dodecahedron alleviate the ligand-ligand repulsion, their energetic superiority over the cube is understandable.[1-7] There is little difference between the energies of the square antiprism, and the dodecahedron arrangement, unless other factors come into play.[8,9] The geometry of ZrMe₄(dmpe)₂ was determined as dodecahedral. The tantalum complex, TaCl₄(dmpe)₂, was shown to have a slightly distorted square-antiprismatic geometry. There are differences between the bonding geometry of the methyl and chloro-ligands in the two complexes and these differences are preferable to define the geometry of ZrMe₄(dmpe)₂ as dodecahedral. Two yttrium containing compounds, Y(hfa)₃(monoglyme) and [Y(hfa)₄]⁺, were shown to have a slighted distorted square-antiprismatic geometry.[10,11] This observation prompted us to study the comparison of the eight-coordinated yttrium environment when unsymmetric β-diketonate ligands such as tpb are coordinated to yttrium ion. We recently synthesized the eight coordinated Yttrium β-diketonate complex, Y(tpb)₃(H₂O)₂, that could be described a dodecahedral geometry.

EXPERIMENTAL

General procedures. All manipulations were performed under nitrogen atmosphere using Schlenk techniques. All solvents were dried by standard techniques. Yttrium oxide and Htpb were purchased from Aldrich and used as received.[12]

Preparation of Y(tpb)₃(H₂O)₂. To a ethyl alcohol solution of Htpb (0.648 g, 3 mmol) was added the sodium hydroxide solution (0.12 g, 3 mmol). This Natpb solution were added to Y(NO₃)(0.2749 g, 1 mmol) in a Schlenk flask. After stirring for 12 h the resulting product was filtered and washed with water. The crystals were gained by the crystallization of hexane/acetone. Yield: 0.685 g, 89%. mp: 125-127 °C. IR(KBr, cm^{-1}): 3660(w), 3459(w), 1616(s), 1577(m), 1535(m), 1492(w), 1469(w), 1319(m), 1292(s), 1249(w), 1187(m), 1141(s), 1079(w), 944(w), 775(w), 701(w), 632(w), 582(w), 520(w). ^{1}H NMR(500 MHz, acetone d⁶): δ 2.87(s, 4H, OH₂), 6.51(s, 3H, CH), 7.42(t, 6H, CH benzene), 7.54(t, 3H, CH benzene), 8.01(m, 6H, CH benzene). MS(FAB; m/z (fragment)): 735(Y(tpb)₃), 519(Y(tpb)₂), 304(Y(tpb)).

X-ray crystal analysis. Crystallographic parameters and information related to data collection and structural refinements for the complex are given in *Table* 1. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical φ-scan method. The struc-

Table 1. Crystal data and structure refinement for Y(tpb)₃(H₂O)₂

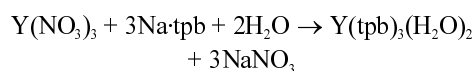| formula	$Y_1C_{30}H_{18}F_9O_8$
T(K)	290
Space group	Orthorhombic P2₁2₁2₁
a, Å	10.709(3)
b, Åþ	13.122(4)
c, Å	22.782(6)
V, Å³	3201.4(15)
Z	4
ρ_{calcd}, g/cm⁻³	1.590
no. of indep rflns	8013
no. of params	434
GOF on F²	0.966
final R indices [I>2σ(I)]	R1 = 0.0562, wR2 = 0.1297
R indices (all data)	R1 = 0.1385, wR2 = 0.1814

Table 2. The least-squares plane data of two geometries for Y(tpb)₃(H₂O)₂

	dodecahedron		square antiprism	
	plane 1	plane 2	plane 1	plane 2
Y	0.0228	0.0076	-1.2537	1.3215
O1	0.0140		-0.2247	
O2	-0.0201		0.2220	
O3		-0.0015	-0.2227	
O4		-0.0025	0.2254	
O5	-0.0213			0.2351
O6	0.0045			-0.2451
O7		-0.0029		-0.2373
O8		-0.0006		0.2472
ave.	0.0178	0.0039	0.2237	0.2412

ture was solved by the Patterson method and refined by full-matrix least squares techniques(SHELXL-97).[13,14] All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were idealized, assigned isotropic thermal parameters [Uiso(H)=1.2 Ueq(C)] and allowed to ride on the parent carbon atoms. All calculations were carried out on the personal computer with use of the SHELXL-97 programs.

RESULTS AND DISCUSSION

Y(tpb)₃(H₂O)₂ complex was obtained by the reaction of Y(NO₃)₃ with sodium salt of tpb in ethyl alcohol solution. Suitable crystals were harvested by the hexane/acetone solution.

$$Y(NO_3)_3 + 3Na\cdot tpb + 2H_2O \rightarrow Y(tpb)_3(H_2O)_2 + 3NaNO_3$$

The molecular structure of Y(tpb)₃(H₂O)₂ is shown in *Fig.* 1, with the CF₃ groups of the tpb anionic ligand omitted for clarity. Yttrium ions bind to eight oxygen atoms, contributed by three bidentate tpb ligands and two water molecules.

The ground-state geometries for the eight coordinated metal complexes are mainly described by square antiprism or dodecahedral. One criterion of the geometry assignment is the planarity of the five-atom group. The planarity of the two five-atom groups is seen in *Table* 2. The planarity of the dodecahedron, Y-O1-O2-O5-O6 and Y-O3-O4-O7-O8, is
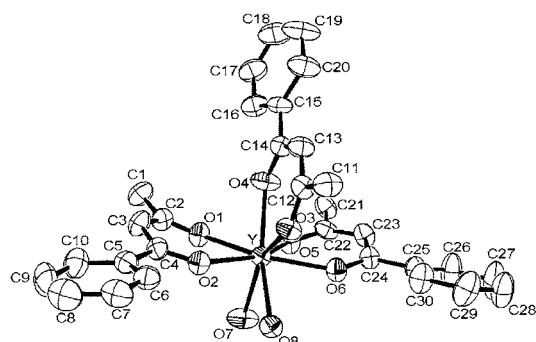
Fig. 1. ORTEP drawing of the crystal structure of Y(tpb)₃(H₂O)₂ showing the atomic labelling and thermal ellipsoidal at 50% level.

Fig. 2. The coordination of dodecahedron of Y(tpb)₃(H₂O)₂. a) Yttrium environment, b) Two interpenetrating planar trapezia.

Fig. 3. The length of the polyhedron edges.

better fitted than that of the square antiprism, Y-O1-O2-O3-O4 and Y-O5-O6-O7-O8. The average deviation from the least-squares plane of the square antiprism is about 0.24 Å while that of the dodecahedron is about 0.01 Å. Based on the planarity, the coordination polyhedron of Y(tpb)₃(H₂O)₂ can be described as a dodecahedron.

An alternative useful way of viewing the dodecahedron is to consider it as two interpenetrating planar trapezia, which are at right angles to each other. The angle between two trapezia, Y-O1-O2-O5-O6 and Y-O3-O4-O7-O8, is 89.59°. Therefore, based on the planarity and the angle between two trapezia, the coordination polyhedron of Y(tpb)₃(H₂O)₂ should be described as a dodecahedron.

In dodecahedron, one set of four atoms is necessarily different from the other set of four donor atoms.[1] The four A atoms constitute a tetrahedron that has been elongated along the fourfold inversion axis. The set of B atoms form a tetrahedron that has been squashed along the same axis, creating a puckered square interposed between the two pairs of A atoms.

In the Y-O1-O2-O5-O6 plane, the oxygen atoms, O2 and O6, near to the phenyl group occupy B sites and the oxygen atoms, O1 and O5, near to the CF₃ group occupy the A sites of the trapezia. In the Y-O3-O4-O7-O8 plane, the O4 atom near to the phenyl group and O7 of the water molecule occupy B sites and the O3 and O8 atoms occupy the A sites
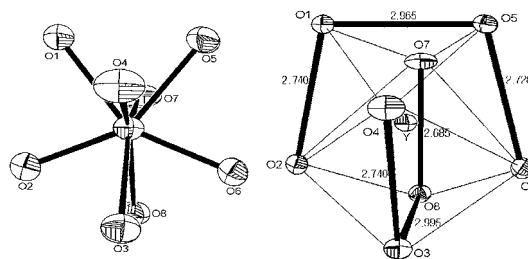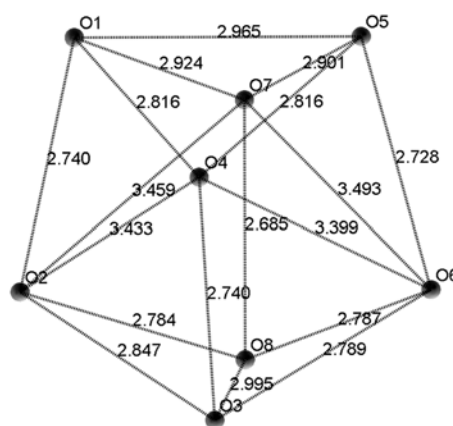
of the trapezia.

The O1-O5 and O3-O8 distances which are distances between A sites are 2.965 and 2.995 Å, respectively. However, the O-O distances between B sites which are O2-O6 and O4-O7, are 4.256 and 4.403 Å, respectively. In addition, the O4-Y-O7 angle including B sites, 142°, are wider than the O3-Y-O8 angle including A sites, 77°.

Two yttrium containing compounds, Y(hfa)₃ (monoglyme) and [Y(hfa)₄]⁺, were shown to have a slighted distorted square-antiprismatic geometry. However, as mentioned, the geometry of Y(tpb)₃(H₂O)₂ was determined as dodecahedral. What is the main factor to effect the geometry of the eight-coordinated complex? The characteristic aspect of bidentate tpb ligand has two different substituents, -CF₃ and phenyl. Usually, ligands having two different substituents are located in a trans position.[15] In the Y-O1-O2-O5-O6 plane of the Y(tpb)₃(H₂O)₂, two

Table 3. The average bond distances of Y-O and polyhedron edges

bond type	Y-O		O-O				
			a	m		g	b
	Y-O1	Y-O2	O1-O5	O1-O2	O2-O3	O1-O4	O2-O4
	Y-O3	Y-O4	O3-O8	O3-O4	O2-O8	O1-O7	O2-O7
	Y-O5	Y-O6		O5-O6	O6-O3	O5-O4	O6-O4
	Y-O7	Y-O8		O7-O8	O6-O8	O5-O7	O6-O7
average distance(Å)	2.34(6)		2.82(9)				3.45(4)

phenyl rings of the tpb ligands are located in a cis position. The oxygen atoms, O2 and O6, near to the phenyl group of the tpb chelating ligand are located (B) sites of the trapezia which are more open space. This structural factor might come into play for the structural determination of the Y(tpb)$_3$(H$_2$O)$_2$ as the dodecahedron. Further, the bond distances of Y-O$_{CF3}$ is from 2.345 to 2.408Å, and the bond distances of Y-O$_{ben}$ is from 2.248 to 2.289Å. This difference is quite related with dodecahedron structure.

The detailed geometry of the dodecahedron has alternatively been described in terms of the length of the polyhedral edges a, b, m, and g. For a hard-sphere model, for all metal-ligand distances of unity, a = m = g = 1.20, but b = 1.50.

Table 3 shows the average metal-ligand distance, the average a, m and g distance, and the average b distance of the Y(tpb)$_3$(H$_2$O)$_2$ complex.

In the Y(tpb)$_3$(H$_2$O)$_2$ complex, the average Y-O distance is 2.34(6)Å, the average a, m and g distance is 2.82(9)Å, and the average b distance is 3.45(4)Å. For the average yttrium-oxygen distance of unity, the average of a, m and g is 1.21 and the average of b is 1.47. These are quite close to ideal values which are 1.20 and 1.50.

Supplementary Data. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data centre (Deposition No. CCDC-606913). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+441223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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