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Synthesis and Crystal Structure of Bis[(η^5-Cp)tris-(dimethylphosphito-P)cobalt-O,O',O''][acetylacetonato]Yttrium(III)

Kyung-Chae Kim, Yu-Chul Park, and Jong Hwa Jeong*

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea
Received March 15, 1997

Homoleptic β-diketonato complexes of yttrium have been extensively studied, which are useful precursors for Y123 superconducting material due to high vapor pressure.[1] However, heteroleptic yttrium complexes of β-diketonatonate are rare.[2] In our laboratory, yttrium complex containing O-donor tripodal ligands (L=CpCo[P(O)(OMe)$_2$]$_3$), L_2YCl, has been used to prepare an acetato complex of YL_2, in which the acetate ligand has been bound to yttrium ion in an isobidentate type to form four-membered ring.[3] This result implies the ligand L is bulk enough to prevent formation of polynuclear yttrium complex. Therefore, this fact has prompted us to investigate the chemical bonding behavior of acetylacetonato (acac) ligand toward YL_2 moiety since the ligand is more crowded than acetate and able to form six-membered ring. Here we wish to report the synthesis and X-ray structure of an acetylacetonato complex of YL_2.

Experimental

Solvents were purified by standard methods and were freshly dried and distilled prior to use. Potassium acetylacetonate hemihydrate was purchased from Aldrich Co. and dried using P_2O_5. NaL was prepared by the literature method.[4] All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature.

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ and referenced to the deuterated solvent (δ 7.14 ppm for ^{1}H, 77.0 ppm for ^{13}C) on a Bruker AM-300 spectrometer. FT-IR spectrum was obtained on a Bomen Michelson 100 spectrometer as KBr pellet. Chemical analyses were carried out by the Chemical Analysis Laboratory at Korea Basic Science Institute.

Preparation of L_2 (acac) Y. 20 mL of dry THF was introduced to a mixture of 0.49 g (1.0 mmol) of NaL and 0.10 g (0.5 mmol) of YCl_3. The mixture was stirred at room temperature for 24 h resulting yellow solution and precipitate. The solution was transferred to 0.07 g (0.5 mmol) of potassium acetylacetonate in 20 mL of THF. The resulting suspension was stirred at room temperature for 2 days and then the precipitate was filtered off. The filtrate was evaporated *in vacuo* to afford yellow solid. Recrystallization of the crude product from THF solution gives yellow crystals in 75% yield (0.4 g).
Analysis: Calcd. (%) C; 30.68, H; 5.46 Found (%) C; 30.52, H; 5.37.

^{1}H NMR ($CDCl_3$): δ 5.30 (s, -COCH=C-, 1H) δ 4.99 (s, $2C_5H_5$, 10H), δ 3.74 (m, $12H_3C$-O-P, 36H), δ 1.90 (s, H_3CCO-, 6H)

^{13}C NMR ($CDCl_3$): δ 186.2 (s, C=O), δ98.4 (s, CH=), δ 88.8 (s, C_5H_5), δ 51.3 (m, H_3COP), δ 27.3 (s, H_3C-)

IR (cm^{-1}): 2943 (m), 2837 (w), 1620 (m), 1513 (m), 1462 (w), 1263 (m), 1016 (vs)

X-ray crystallographic analysis. An X-ray quality single crystal, 0.30×0.30×0.50 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with Mo-Kα radiation (λ=0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections (10°<θ<13°). Intensity data were collected with θ range of 3.29-30.40° in ω/2θ scan mode. Three standard reflections (h k l = 5 −7 3; 5 7 6; −3 −2 8) were monitored every 1 hr during data collection, which was showing not significant variation. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with Ψ scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on F^2 using SHELXS-86[5] and SHELXL-93.[6] All non-hydrogen atoms were refined by using anisotropic thermal factors, and all hydrogen atoms were positioned geometrically using riding model with 1.2 times isotropic thermal factors of the attached non-hydrogen atoms. The final cycle of the refinement con-

Table 1. Crystal data and structure refinement for L_2 (acac) Y

Empirical formula	$C_27H_{53}Co_2O_{20}P_6Y$
Formula weight	1090.28
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a=11.408(3) Å α=71.21(2)°
	b=12.633(2) Å β=88.14(2)°
	c=17.470(5) Å γ=67.56(2)°
Volume	2191.3(9) $Å^3$
Z	2
Density (calculated)	1.652 Mg/m^3
Absorption coefficient	2.352 mm^{-1}
F(000)	1116
Crystal size	0.30×0.30×0.50 mm
Theta range for data collection	3.29 to 30.40°
Index ranges	$-16\leq h\leq 14$, $-17\leq k\leq 0$, $-24\leq l\leq 23$
Reflections collected	11641
Observed reflections	6188
Absorption correction range	62.45-99.88%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6170/0/505
Goodness-of-fit on F^2	1.075
Final R indices [I>2σ(I)]	R_1=0.0669, wR_2=0.1158
R indices (all data)	R_1=0.0905, wR_2=0.1328
Largest diff. peak and hole	0.853 and -0.909 $e.Å^3$

$R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w=1/[\sigma2(Fo^2)+(0.0433*P)^2+5.60*P]$ where $P = (Max.(Fo^2, 0)+2*Fc^2)/3$

verged with R_1=0.067 and wR_2=0.116. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles are presented in Table 2.

Results and Discussion

Prepared [L_2YCl] from the reaction of YCl_3 with 2 equivalent NaL reacts with potassium acetylacetonate to yield the title compound.

$$YCl_3 + 2\ NaL \xrightarrow[-2NaCl]{} [L_2YCl] \xrightarrow[-KCl]{+K\ (acac)} L_2\ (acac)\ Y$$

The ^1H NMR spectrum of the compound shows a singlet at 5.30 ppm for -COCH=C-(1H), a singlet at 4.99 ppm for 2 Cp rings (10H), a multiplet at 3.74 ppm for H_3C-O-P (36H), and a singlet at 1.90 ppm for H_3CCO-(6H). The ^{13}C NMR spectrum reveals singlets at 186.2, 98.4, and 27.3 ppm for C=O, -CH= and H_3C- at the acac ligand and a singlet at 88. 8 for C_5H_5), a multiplet at 51.3 ppm for H_3COP at the tripodal ligands. Since these data illustrated uncertain structural information, X-ray crystal structure determination has been carried out. Figure 1 shows an ORTEP[7] drawing with atomic labeling scheme of the compound. The coordination polyhedrons around the yttrium presented in Figure 2 is nearly a square antiprism consisting of O(1), O(2), O(3), O (4), O(5), O(6) via two tripodal groups and O(19), O(20)

Table 2. Selected bond distances (Å) and angles (°) for L_2 (acac) Y

Y-O(1)	2.373(5)	Y-O(2)	2.362(5)
Y-O(3)	2.315(5)	Y-O(4)	2.368(4)
Y-O(5)	2.371(5)	Y-O(6)	2.336(5)
Y-O(19)	2.338(5)	Y-O(20)	2.319(5)
Co(1)-P(1)	2.164(2)	Co(1)-P(2)	2.156(2)
Co(1)-P(3)	2.184(2)	Co(2)-P(4)	2.157(2)
Co(2)-P(5)	2.167(2)	Co(2)-P(6)	2.170(2)
O(1)-P(1)	1.497(5)	O(2)-P(2)	1.492(5)
O(3)-P(3)	1.502(5)	O(4)-P(4)	1.486(5)
O(5)-P(5)	1.494(5)	O(6)-P(6)	1.483(5)
P(1)-O(7)	1.604(6)	P(1)-O(8)	1.609(6)
P(2)-O(10)	1.588(6)	P(2)-O(9)	1.600(6)
P(3)-O(11)	1.604(6)	P(3)-O(12)	1.604(6)
P(4)-O(14)	1.611(5)	P(4)-O(13)	1.619(6)
P(5)-O(15)	1.599(6)	P(5)-O(16)	1.613(6)
P(6)-O(17)	1.600(6)	P(6)-O(18)	1.611(5)
O(3)-Y-O(20)	77.0(2)	O(3)-Y-O(6)	141.8(2)
O(20)-Y-O(6)	139.5(2)	O(3)-Y-O(19)	140.9(2)
O(20)-Y-O(19)	75.9(2)	O(6)-Y-O(19)	73.7(2)
O(3)-Y-O(2)	75.5(2)	O(20)-Y-O(2)	75.6(2)
O(6)-Y-O(2)	117.7(2)	O(19)-Y-O(2)	70.9(2)
O(3)-Y-O(4)	116.9(2)	O(20)-Y-O(4)	70.3(2)
O(6)-Y-O(4)	78.1(2)	O(19)-Y-O(4)	79.1(2)
O(2)-Y-O(4)	138.9(2)	O(3)-Y-O(5)	76.3(2)
O(20)-Y-O(5)	116.1(2)	O(6)-Y-O(5)	75.7(2)
O(19)-Y-O(5)	141.7(2)	O(2)-Y-O(5)	145.7(2)
O(4)-Y-O(5)	72.4(2)	O(3)-Y-O(1)	75.9(2)
O(20)-Y-O(1)	143.8(2)	O(6)-Y-O(1)	74.0(2)
O(19)-Y-O(1)	112.6(2)	O(2)-Y-O(1)	74.8(2)
O(4)-Y-O(1)	144.5(2)	O(5)-Y-O(1)	79.8(2)
P(2)-Co(1)-P(1)	88.51(9)	P(2)-Co(1)-P(3)	90.89(9)
P(1)-Co(1)-P(3)	92.44(9)	P(4)-Co(2)-P(5)	89.03(9)
P(5)-Co(2)-P(6)	91.44(9)	P(4)-Co(2)-P(6)	90.00(9)
C(19)-O(19)-Y	132.7(5)	C(21)-O(20)-Y	133.7(5)
O(19)-C(19)-C(20)	125.2(8)	O(19)-C(19)-C(23)	115.8(8)
C(20)-C(19)-C(23)	119.0(8)	C(21)-C(20)-C(19)	125.8(8)
O(20)-C(21)-C(20)	125.9(8)	O(20)-C(21)-C(22)	116.6(8)
C(20)-C(21)-C(22)	117.5(8)		

from the acac ligand although a heteroleptic complex. Four atoms of O(1), O(2), O(19), and O(6) are almost in the plane also four atoms of O(3), O(5), O(4), and O(20) are nearly coplanar. The distances of latera are 2.698(7) to 2.895(7) Å and the angles of eight conners are 87.0(2) 0 to 93.3(2)°. The twist angle of two squares is 46.9(2)°. Distances of Y-O(1), Y-O(2), Y-O(3), Y-O(4), Y-O(5), Y-O(6), Y-O(19), and Y-O(20) are 2.373(5), 2.362(5), 2.315(5), 2.368(4), 2.371(5), 2.336(5), 2.338(5), and 2.319(5) Å, respectively. All Y-O distances are nearly not distinguishable whether they are those between yttrium and oxygen atoms of L or acac. This feature is different from that in L_2 (acetato) Y, in which lengths between yttrium and oxygen atoms of L are shorter than those of acetate ligand.[3] This means that the negative charge at L is fully delocalized as if the charge at acac is not localized. Distances of P-O(1), P-O(2), P-O(3), P-O(4), P-O(5), and P-O(6) are 1.497(5), 1.492(5), 1.502(5), 1.486(5), 1.494(5), and 1.483(5) Å. The

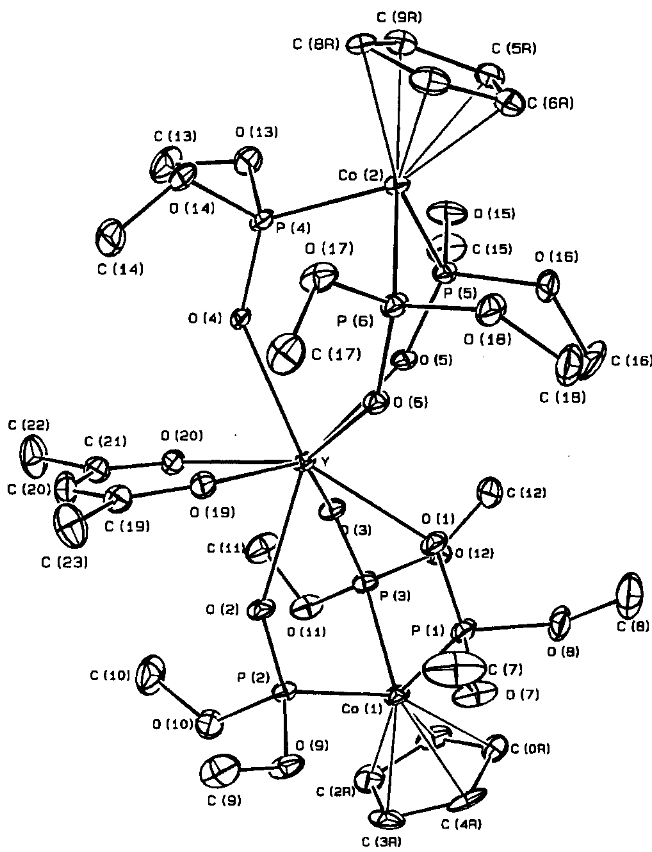

Figure 1. ORTEP drawing of 40% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity.

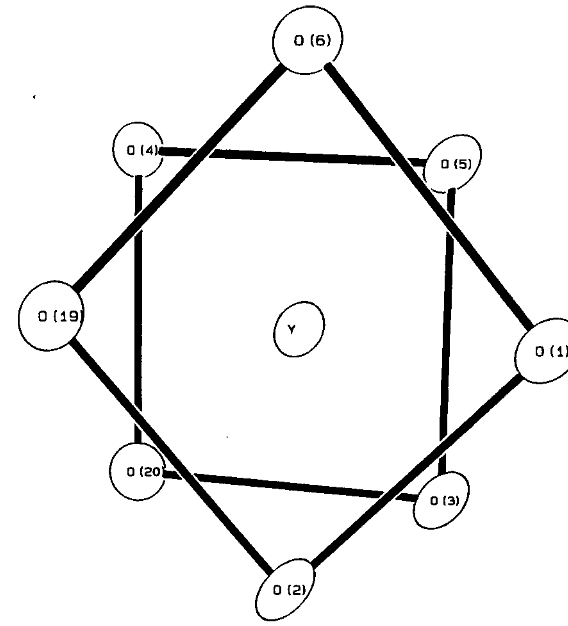

Figure 2. ORTEP drawing of the molecule showing the coordination ployhedron around the yttrium. O(1)-O(2) 2.876(7), O(1)-O(6) 2.834(7), O(2)-O(19) 2.725(7), O(19)-O(6) 2.804(7), O(3)-O(20) 2.883(7), O(20)-O(4) 2.698(7), O(4)-O(5) 2.798(7), O(5)-O(3) 2.895(7). O(2)-O(1)-O(6) 89.5(2), O(1)-O(2)-O(19) 88.8(2), O(2)-O(19)-O(6) 93.3(2), O(19-O(6)-O(1) 88.1(2), O(5)-O(3)-O(20) 87.0(2), O(3)-O(20)-O(4) 91.2(2), O(20)-O(4)-O(5) 92.8(2), O(4)-O(5)-O(3) 89.0(2).

mean distance between P and O attached yttrium atom is 1.492(6) Å, which is somewhat longer than P=O distance (1.46(5) Å)[8], suggesting that Y-O bonds have partial double bond character.

Acknowledgment. This research has been supported financially by the Korea Science and Engineering Foundation and Basic Science Research Institute Program of Ministry of Education in Korea.

Supplementary Material Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms (2 pages), bond distances and angles (3 pages), anisotropic displacement parameters (2 pages), hydrogen coordinate and isotropic displacement parameters (2 pages), and observed and calculated structure factors (19 pages) are available from J. H. J..

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