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Isolation and X-ray Structure of a Discrete Five-Coordinate Na(I) Complex Containing CpCoP(OMe)₂(=O)₃⁻ Ligands

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The anionic Cobalt(III)-based oxygen tripodal ligand L_{OEI} (L_{OEI} = [CpCo{P(=O)(OEt)₂}]⁻), developed by Kläui and co-workers, can form stable complexes with various transition metals.¹ La(III), Y(III) complexes of L_{OME} (L_{OME} = [CpCo{P(=O)(OMe)₂}]⁻) have been studied in order to compare with middle or late transition metal complexes containing the ligand in our laboratory.²⁻³ Also attempts to isolate Zr(L_{OME})₂Cl₂ from the feasible reaction of ZrCl₄ with 2 equivalent NaL_{OME} gave the formation of the unusual dimer in an unusual bridging fashion of tripodal ligands, (L)Zr(L)₂Zr(L) (L = CpCo{P(=O)(OMe)₂}]₂{P(=O)(OMe)(O)}₂,⁴ in which L_{OME} was modified by the labile chlorides at Zr(L_{OME})₂Cl₂ as an intermediate. Therefore, we tried to synthesize (L_{OME})₂Zr (amide), which would be an useful candidate for the catalyst of hydroamination of alkyne,⁵ by reaction of Zr(L_{OME})₂Cl₂ with excess amine. However, we isolated a discrete five-coordinate Na(I) complex containing L_{OME} instead of the desired product. In this paper we describe the crystal structure of the complex. Its structure is distinguishable from that of NaL_{OEI}, that is a trimeric aggregate with two water molecules.⁶

Experimental

All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature. All solvents were purified by standard methods and were freshly dried and distilled

prior to use. ZrCl₄ was purchased from Aldrich Co. and used as received, *tert*-Buthyl amine or diethylamine was dried over KOH and distilled under an argon atmosphere. L_{OME} was prepared by the literature method.⁷

¹H NMR spectra were obtained in CDCl₃ and referenced to internal deuterated solvent and recalculated relative to TMS on a Bruker AM-300 spectrometer. Elemental analyses were carried out by the Chemical Analysis Laboratory at Center for Scientific Instruments of Kyungpook National University.

Preparation of (L_{OME})₂Na·H₃NC(CH₃)₃·[H₃NC(CH₃)₃]Cl. To a mixture of ZrCl₄ (0.15 g, 0.6 mmol) and NaL_{OME} (0.50 g, 1.2 mmol) 50 mL of THF was introduced. The mixture was stirred for 2 days at room temperature to afford yellow solution and white precipitate, NaCl and then H₃NC(CH₃)₃ (0.307 g, 4.2 mmol) was added to the mixture solution. This mixture was stirred for 1 day at room temperature. Volatile materials were removed under reduced pressure. Extraction of the solid with benzene afforded a yellow solution. The solution was concentrated and left at room temperature to yield the yellow crystalline product (0.47 g, 70%).

Anal. Calcd for C₃₀H₇₀ClCo₂N₂NaO₁₈P₆: C, 32.49; H, 6.36. Found: C, 31.83; H, 6.34. ¹H NMR (C₆D₆): δ 5.13 (s, C₅H₅, 5H), δ 3.73 (m, (MeO)₂P(O)-, 18H), δ 1.40 (s, (Me₃C-, 9H), δ 8.91 (b, H₃N-, 3H).

X-ray crystallographic analysis. An X-ray quality single crystal, 0.45×0.40×0.35 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with MoK α radiation (λ =0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections (18°<2 θ <26°). Intensity data were collected with θ range of 2.37-25.37° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1h during data collection. 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 direct method and refined by full-matrix least-squares techniques on F² using SHELXS-86⁸ and SHELXL-93.⁹ All non-hydrogen atoms were refined by using anisotropic thermal factors except disordered C atoms of Cp rings, and all hydrogen atoms were positioned geometrically and refined using riding model. The final cycle of the refinement converged with R₁=0.055 and wR₂=0.129. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Relative bond distances and angles are tabulated in Table 2.

Results and Discussion

Reaction of ZrCl₄ with 2 equivalent NaL_{OME} in the THF at room temperature followed by addition of excess H₃NC(CH₃)₃, removal of precipitate and then evaporation of volatile material affords a yellow crystalline product. The ¹H NMR spectrum of the product exhibits the resonances of phosphonate methyl, Cp, and *tert*-buthyl groups. From the integrations of the peaks for Cp rings and *tert*-buthyl groups we found 1:1 ratio between the two groups. It was very wondering fact that two L_{OME} and two *tert*-buthyl amines were bound to Zr atom. Therefore, an X-ray crystal structure analysis was carried out. The crystal structure surprisingly shows Na(L_{OME})₂ H₃NC(CH₃)₃⁺ and co-crystallized [H₃NC(CH₃)₃]Cl

Table 1. Crystal data and structure refinement for $(\text{LOMe})_2\text{Na}\cdot\text{H}_3\text{NC}(\text{CH}_3)_3\cdot[\text{H}_3\text{NC}(\text{CH}_3)_3]\text{Cl}$

Empirical formula	$\text{C}_{30}\text{H}_{70}\text{ClCo}_2\text{N}_2\text{NaO}_{18}\text{P}_6$
Formula weight	1109.00
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P}2_1/\text{n}$
Unit cell dimensions	$a = 11.648(3)$ Å $b = 19.037(3)$ Å $c = 23.150(3)$ Å $\beta = 94.03(1)^\circ$
Volume	$5120(2)$ Å ³
Z	4
Density (calculated)	1.439 Mg/m ³
Absorption coefficient	0.960 mm ⁻¹
F(000)	2320
Crystal size	0.45 × 0.40 × 0.35 mm
Theta range for data collection	2.79 to 25.37 deg.
Index ranges	$-13 \leq h \leq 13$, $0 < k \leq 22$, $-27 \leq l \leq 0$
Reflections collected	5884
Independent reflections	5750 [R(int)=0.0196]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	5732/0/453
Goodness-of-fit on F ²	1.045
Final R indices [I > 2σ(I)]	$R_1 = 0.0554$, $wR_2 = 0.1292$
R indices (all data)	$R_1 = 0.0639$, $wR_2 = 0.1438$
Largest diff. peak and hole	0.802 and -0.339 e.Å ⁻³

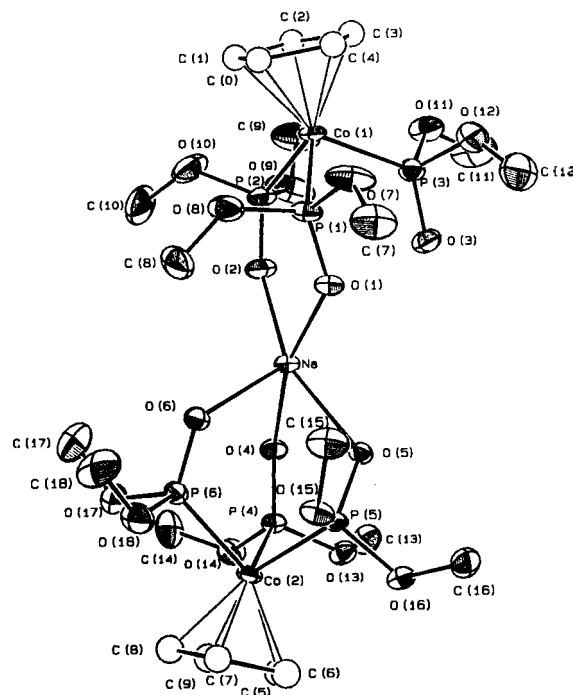
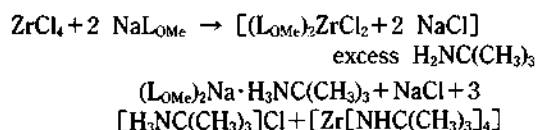
Table 2. Relevant Bond lengths [Å] and angles [°] for $[(\text{LOMe})_2\text{Na}]^+$

Na-O(6)	2.251(5)	Na-O(1)	2.272(5)
Na-O(2)	2.334(5)	Na-O(5)	2.351(4)
Na-O(4)	2.469(5)	O(1)-P(1)	1.477(4)
O(2)-P(2)	1.476(4)	O(3)-P(3)	1.476(5)
O(4)-P(4)	1.498(4)	O(5)-P(5)	1.495(4)
O(6)-P(6)	1.469(5)	Co(1)-P(1)	2.198(2)
Co(1)-P(2)	2.172(2)	Co(1)-P(3)	2.165(2)
P(1)-O(8)	1.593(6)	P(1)-O(7)	1.605(6)
P(2)-O(10)	1.586(7)	P(2)-O(9)	1.640(7)
P(3)-O(11)	1.622(5)	P(3)-O(12)	1.634(6)
Co(2)-P(4)	2.195(2)	Co(2)-P(5)	2.176(2)
Co(2)-P(6)	2.175(2)	P(4)-O(13)	1.600(5)
P(4)-O(14)	1.621(5)	P(5)-O(15)	1.610(5)
P(5)-O(16)	1.611(5)	P(6)-O(17)	1.608(6)
P(6)-O(18)	1.619(5)		
O(6)-Na-O(1)	106.0(2)	O(6)-Na-O(2)	116.4(2)
O(1)-Na-O(2)	82.9(2)	O(6)-Na-O(5)	87.6(2)
O(1)-Na-O(5)	91.4(2)	O(2)-Na-O(5)	156.0(2)
O(6)-Na-O(4)	84.0(2)	O(1)-Na-O(4)	165.9(2)
O(2)-Na-O(4)	101.8(2)	O(5)-Na-O(4)	78.9(2)
P(3)-Co(1)-P(1)	91.32(8)	P(2)-Co(1)-P(1)	92.65(7)
P(3)-Co(1)-P(2)	93.08(8)	P(6)-Co(2)-P(5)	90.6(1)
P(6)-Co(2)-P(4)	92.9(1)	P(5)-Co(2)-P(4)	92.7(1)

salt. An ORTEP drawing of the anion is shown in Figure 1.

The coordination geometry around Na atom is a highly distorted trigonal bipyramid through three oxygen atoms from one tripodal ligand and two oxygen atoms from the other tripodal ligand. O(2), O(4), O(5), and Na are found to be coplanar and with no atom displaced by more than 0.008 (3) Å from its best plane. O(1)-Na-O(4) as axis is 165.9(2)°, O(2)-Na-O(5), O(2)-Na-O(6), and O(5)-Na-O(6) are 156.0(2), 116.4(2), and 87.6(2)° respectively. Na-O distances are similar to those in $(\text{NaLOe})_3\cdot(\text{H}_2\text{O})_2^6$ and somewhat shorter than those of Na-O=C in Na salt of dipicolinic acid¹⁰ except Na-O(6) which is longer than others. O(3) atom is apart 3.78(5) Å from Na atom showing clearly not coordinating to Na. The distances between P and O atoms attached to the Na (1.476(4) to 1.498(4) Å), which are slightly longer than isolated P=O distance (1.45(6) Å) in tetrahedral phosphonate compounds,¹¹ are shorter than those between P and O atoms bound to the methyl groups (1.586(7) to 1.634(6) Å).

On the basis of experimental, spectroscopic, and crystallographic results, the overall reaction is tentatively proposed as following equation:

**Figure 1.** ORTEP Drawing of $[(\text{LOMe})_2\text{Na}]^+$ with 50% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity.

To our knowledge, this is the first example of discrete five-coordinate Na(I) complexes containing $\text{CpCo}[\text{P}(\text{OR})_2(\text{=O})]_3$ ligands. An interesting feature of the structure is that one tripodal ligand binds to Na ion as tridentate and another

one binds to that as bidentate. Otherwise, $[\text{Zr}(\text{LOMe})_2\text{Cl}_2]$ reacts with excess $\text{HN}(\text{Et})_2$ instead of $\text{H}_2\text{NC}(\text{CH}_3)_3$ in the presence of NaCl to afford $[(\text{LOMe})_2\text{Na}]^-[\text{H}_2\text{N}(\text{Et})_2]^+$ as the similar results¹² except the fact that alkylammonium chloride salt was co-crystallized.

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Supplementary Materials Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinate and isotropic displacement parameters (8 pages); table of observed and calculated structure factors (19 pages) are available from J. H. J.

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¹H NMR (C_6D_6): δ 5.17 (s, C_5H_5 , 5H), δ 3.74 (m, $(\text{MeO})_2\text{P}(\text{O})$, 18H), δ 2.74 (q, $-\text{H}_2\text{C}-\text{N}-$, 2H), δ 1.10 (t, $\text{H}_3\text{C}-$, 3H).

ERRATUM

Bull. Korean Chem. Soc. 1996, Vol. 17, No. 11, pp 985-987	
Error	Correction
Communication	Note