Synthesis and Structure of a Bismuth(III)/Chromium(VI) Oxo Cluster Containing a $Bi_4Cr_4O_{12}$ Core

Guo-Cang Wang,[†] Xiao-Yi Yi,[‡] Ian D. Williams,[†] and Wa-Hung Leung[*,†]

[†]Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

[‡]School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, People's Republic of China

S *Supporting Information*

ABSTRACT: Bismuth(III) compounds containing the Kläui's oxygen tripodal ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-) have been synthesized, and their interactions with dichromate in aqueous media were studied. The treatment of $Bi_5O(OH)_9(NO_3)_4$ with NaL_{OEt} in water afforded $[L_{OEt}Bi(NO_3)_2]_2$ (**1**), whereas that of $BiCl_3$ with NaL_{OEt} in CH_2Cl_2 yielded $L_{OEt}BiCl_2$ (**2**). Chloride abstraction of **2** with AgX afforded $[L_{OEt}BiX_2]_2$ [X^- = triflate (OTf^-) (**3**), tosylate (OTs^-) (**4**)]. In aqueous solutions at pH > 4, **4** underwent ligand redistribution to give the bis(tripod) complex $[(L_{OEt})_2Bi(H_2O)][OTs]$ (**5**). The treatment of **4** with $Na_2Cr_2O_7$ in acetone/water afforded the Bi(III)/Cr(VI) oxo cluster $[(L_{OEt})_4Bi_4(\mu_3\text{-}CrO_4)_2(\mu_3\text{-}Cr_2O_7)_2]$ (**6**) containing a unique $Bi_4Cr_4O_{12}$ oxometallic core. Compound **6** oxidized benzyl alcohol to give ca. 6 equiv of benzaldehyde. The reaction between **2** and CrO_3 yielded $[L_{OEt}Bi(OCrO_2Cl)]_2(\mu\text{-}Cl)_2$ (**7**). The crystal structures of complexes **4−7** have been determined.
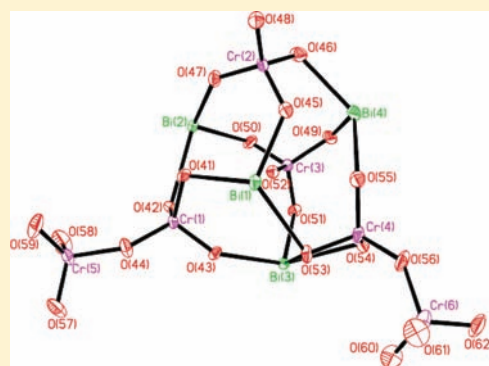
■ INTRODUCTION

Heterometallic oxo clusters and solid state materials containing bismuth are of interest due to their applications in materials science,[1] catalysis,[2,3] and medicine.[4,5] Heterobimetallic Bi(III) compounds have also been used as molecular precursors to advanced oxide materials.[6] Of industrial importance are $Bi_2O_3 \cdot MoO_3$ and related materials that are capable of catalyzing ammoxidation and oxidation of propylene.[6] Although the exact mechanism of the Bi/Mo-based ammoxidation is not fully understood, it is believed that a key step involves the transfer of an allylic hydrogen atom from propylene to the Bi—oxo or Bi—O—Mo group.[7] In this connection, much effort has been devoted to synthesize heterometallic Bi/Mo complexes with oxygen ligands as models of $Bi_2O_3 \cdot MoO_3$ catalysts.[7−12] A few soluble heterometallic Bi/Mo complexes containing covalent Mo^{VI}—O—$Bi^{III/V}$ linkages have been prepared and structurally characterized. The metal centers in these Mo—O—Bi complexes are stabilized by hydrocarbyl ligands such as allyl and cyclopentadienyl.[8,9]

Previously, we found that the π-donating tripodal ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ (denoted as L_{OEt}^- hereafter, Chart 1), commonly known as the Kläui's tripod ligand,[13] is capable of stabilizing early metal ions such as Ti^{4+}, Zr^{4+}, and Ce^{4+} in aqueous media.[14−16] In acidic aqueous solutions, $L_{OEt}Zr(NO_3)_3$ and $(L_{OEt})_2Ce(NO_3)_2$ undergo self-assembly with oxyanions to give heterometallic oxo clusters. For example, the reaction of $(L_{OEt})_2Ce(NO_3)_2$ with $(NH_4)_6[Mo_7O_{24}]$ in water afforded a Ce(IV) oxomolybdenum cluster, $H_4(L_{OEt})_6Ce_6Mo_9O_{38}$, which

contains a $Ce_6Mo_9O_{38}$ oxometallic core.[16] As an extension of this study, we set out to synthesize heterometallic Bi(III)—O—M complexes by self-assembly of $L_{OEt}Bi^{2+}$ species with oxyanions, particularly those of group 6 metals, in aqueous media. Although L_{OEt}^- is known to form stable complexes with a range of main group and d- and f-block elements,[13] to our knowledge, $L_{OEt}Bi^{2+}$ compounds have not been isolated previously. Herein, we describe the synthesis of half-sandwich $L_{OEt}Bi^{2+}$ compounds and their interactions with chromate and dichromate in aqueous media. The isolation and crystal structure of the first Bi(III)/Cr(VI) cluster featuring a unique $Bi_4Cr_4O_{12}$ oxometallic core will be reported.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were carried out in the air. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400, 161.9, and 376.4 MHz for ^1H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H), H_3PO_4 (^{31}P), and $CF_3C_6H_5$ (^{19}F). Infrared (IR) spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, United Kingdom. $Bi_5O(OH)_9(NO_3)_4$ was purchased from Aldrich Ltd. The ligand NaL_{OEt} was synthesized according to a literature method.[17]

Synthesis of $[L_{OEt}Bi(NO_3)_2]_2$ (1). To a solution of $Bi_5O(OH)_9(NO_3)_4$ (73 mg, 0.05 mmol) in HNO_3 (1.32 M, 1.1 mL) was added a solution of

NaL_{OEt} (55.8 mg, 0.1 mmol) in acetone (0.6 mL). The mixture was stirred for 30 min at room temperature and filtered. The yellow solid was redissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals. Yield: 48.6 mg (56%). ^{1}H NMR (CDCl$_3$): δ 1.28 (t, 36H, CH$_3$), 4.08−4.16 (m, 24H, CH$_2$), 5.14 (s, 10H, Cp). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 121.8 (s). IR (KBr, cm^{-1}): 1384 [ν(NO$_3$)]. Anal. Calcd for $C_{17}H_{35}BiCoN_2O_{15}P_3$: C, 23.52 H, 4.06, N, 3.23. Found: C, 23.66; H, 4.06 N, 3.08.

Synthesis of $L_{OEt}BiCl_2$ (2). To a solution of BiCl$_3$ (31.5 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added NaL_{OEt} (55 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) at 0 °C under nitrogen. The mixture was stirred at room temperature overnight and filtered. The solvent was removed under reduced pressure, and the yellow residue was washed with hexane and Et$_2$O. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals. Yield: 46 mg (56%). ^{1}H NMR (CDCl$_3$): δ 1.28 (t, 18H, CH$_3$), 4.13−4.19 (m, 12H, CH$_2$), 5.12 (s, 5H, Cp). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 117.8 (s). Anal. Calcd for $C_{17}H_{35}BiCl_2CoO_9P_3$: C, 25.05; H, 4.33. Found: C, 24.79; H, 4.19.

Synthesis of $[L_{OEt}BiX_2]_2$ [X = OTf (3), OTs (4)]. To a solution of AgX (0.2 mmol) in MeCN (5 mL) was added a solution of 2 (82 mg, 0.1 mmol) in MeCN (5 mL) at 0 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered, and the solvent was removed under reduced pressure.

Chart 1
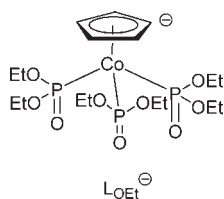
The residue was washed with Et$_2$O and recrystallized from CH_2Cl_2/Et$_2$O to give yellow crystals.

For 3. Yield: 23 mg (22%). ^{1}H NMR (CDCl$_3$): δ 1.29 (t, 18H, CH$_3$), 4.18 (m, 12H, CH$_2$), 5.16 (s, 5H, Cp). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 122.0 (s). ^{19}F {^{1}H} NMR (CDCl$_3$): δ −78.8 (s). Anal. Calcd for $C_{38}H_{70}Bi_2Co_2F_{12}O_{30}P_6S_4$: C, 21.89; H, 3.38; Found: C, 22.63; H, 3.60.

For 4. Yield: 60 mg (55%). ^{1}H NMR (CDCl$_3$): δ 1.26 (t, 18H, CH$_3$), 2.33 (s, 6H, CH$_3$), 4.14 (m, 12H, CH$_2$), 5.15 (s, 5H, Cp), 7.07 (d, 4H, J = 8.4 Hz, H$_m$ of p-tol), 7.75 (d, 4H, J = 8.4 Hz, H$_o$ of p-tol). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 121.9 (s). ^{1}H NMR (D$_2$O): δ 1.32 (t, 18H, CH$_3$), 2.40 (s, 6H, CH$_3$), 4.17 (m, 12H, CH$_2$), 5.41 (s, 5H, Cp), 7.37 (d, 4H, J = 7.8 Hz, H$_o$ of p-tol), 7.69 (d, 4H, J = 7.8 Hz, H$_m$ of p-tol). ^{31}P {^{1}H} NMR (D$_2$O): δ 124.9 (s). Anal. Calcd for $C_{62}H_{96}Bi_2Co_2O_{30}P_6S_4$: C, 34.30; H, 4.46. Found: C, 33.74; H, 4.49.

Synthesis of $[(L_{OEt})_2Bi(H_2O)][OTs]$ (5). To a solution of 4 (54.3 mg, 0.05 mmol) in Et$_2$O (5 mL) was added a solution of NaL_{OEt} (47.5 mg, 0.05 mmol) in Et$_2$O (5 mL) at room temperature, and the mixture was stirred for 2 h and filtered. The solvent was removed under reduced pressure. Recrystallization from Et$_2$O/hexane afforded yellow crystals. Yield: 40 mg (55%). ^{1}H NMR (CDCl$_3$): δ 1.27 (t, 36H, CH$_3$CH$_2$), 2.31 (s, 3H, CH$_3$), 4.06 (m, 24H, CH$_2$), 5.16 (s, 10H, Cp), 7.11 (d, J = 7.95 Hz, 2H, H$_o$ of p-tol), 7.87 (d, J = 7.95 Hz, 2H, H$_m$ of p-tol). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 117.9 (s). Anal. Calcd for $C_{41}H_{79}BiCo_2O_{22}P_6S$: C, 33.53; H, 5.42. Found: C, 33.32; H, 5.30.

Synthesis of $[(L_{OEt})_4Bi_4(\mu_3$-CrO$_4)_2(\mu_3$-Cr$_2O_7)_2]$ (6). To a solution of Na$_2$Cr$_2$O$_7$·2H$_2$O (24 mg, 0.0805 mmol) in water (0.6 mL) was added a solution of 4 (87 mg, 0.0805 mmol) in acetone (0.2 mL) dropwise, and the mixture was stirred at room temperature for 5 min. The orange precipitate was collected and air-dried. Recrystallization from CH_2Cl_2/hexane afforded single orange crystals. Yield: 45 mg (60%). ^{1}H NMR (CDCl$_3$): δ 1.30 (t, 18H, CH$_3$), 4.20 (m, 12H, CH$_2$), 5.17 (s, 5H, Cp). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 120.7 (s). Anal. Calcd for $C_{68}H_{140}Bi_4Co_4Cr_6O_{58}P_{12}$·1.5CH$_2Cl_2$: C, 22.15; H, 3.82. Found: C, 21.68; H, 3.81.

Table 1. Crystallographic Data and Experimental Details for Complexes 4−7

	4	5	6·1.5CH$_2$Cl$_2$	7
formula	$C_{62}H_{98}Bi_2$ $Co_2O_{30}P_6S_4$	$C_{41}H_{79}Bi$ $Co_2O_{22}P_6S$	$C_{68}H_{140}Bi_4Co_4Cr_6$ $O_{58}P_{12}$ 1.5CH$_2$Cl$_2$	$C_{34}H_{70}Bi_2Cl_4$ $Co_2Cr_2O_{24}P_6$
fw	2173.28	1468.76	3768.47	1830.34
T, K	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	13.7507(12)	12.3443(17)	24.764(3)	10.1999(3)
b, Å	21.5700(19)	22.456(3)	15.649(2)	24.3175(8)
c, Å	15.4649(13)	21.634(3)	33.997(5)	12.6501(4)
β, deg	115.7910(10)	102.993(2)	93.322(2)	97.930(3)
V, Å^3	4130.0(6)	5843.4(14)	13152(3)	3107.68(17)
Z	2	4	4	2
ρ_{calcd}, g cm^{-1}	1.748	1.670	1.903	1.956
$F(000)$	2168	2976	7356	1784
μ, mm^{-1}	4.937	3.837	6.583	6.897
no. of reflns	26914	36800	74775	17259
no. of indep reflns	7988	11431	25793	5949
R_{int}	0.0197	0.0459	0.1255	0.0596
GoF^a	1.040	1.029	1.004	1.057
R_1,^{b} wR_2^{c} [$I > 2\sigma(I)$]	0.0181, 0.0429	0.0355, 0.0793	0.0618, 0.1166	0.0665, 0.1402
R_1, wR_2 (all data)	0.0214, 0.0437	0.0571, 0.0845	0.1424, 0.1314	0.0900, 0.1508

^{a} GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. ^{b} $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $wR_2 = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$.

Scheme 1. Syntheses of Bi(III)L$_{OEt}$ Compounds^a
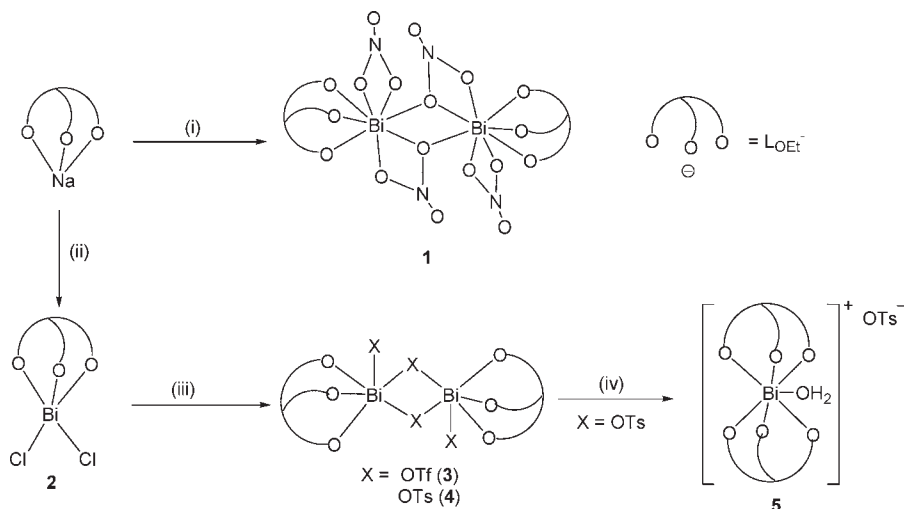
^{a} Reagents and conditions: (i) Bi$_5$O(OH)$_9$(NO$_3$)$_4$, 1.3 M HNO$_3$, acetone/H$_2$O, RT; (ii) BiCl$_3$, CH$_2$Cl$_2$/Et$_2$O, RT; (iii) AgOTf, MeCN, RT or AgOTs, MeCN, RT; (iv) NaL$_{OEt}$, Et$_2$O, RT.

Synthesis of [L$_{OEt}$Bi(OCrO$_2$Cl)]$_2$(μ-Cl)$_2$ (7). *Method A.* To a solution of Na$_2$Cr$_2$O$_7$·2H$_2$O (18.3 mg, 0.0613 mmol) in water (0.6 mL) was added **2** (50 mg, 0.0613 mmol) in acetone (0.2 mL), and the mixture was stirred at room temperature for 5 min. The yellow precipitate was collected and air-dried. Recrystallization from CH$_2$Cl$_2$/hexane afforded yellow crystals that were suitable for X-ray diffraction study. Yield: 22 mg (40%). ^{1}H NMR (CDCl$_3$): δ 1.29 (t, 18H, CH$_3$), 4.18 (m, 12H, CH$_2$), 5.15 (s, 5H, Cp). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 120.2 (s). Anal. Calcd for C$_{34}$H$_{70}$Bi$_2$Cl$_4$Co$_2$Cr$_2$O$_{24}$P$_6$: C, 22.31 H, 3.85; Found: C, 21.92; H, 3.64.

Method B. A mixture of CrO$_3$ (12 mg, 0.12 mmol) and **2** (50 mg, 0.061 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at room temperature for 2 h. The solvent was removed to give a yellow solid. Recrystallization from CH$_2$Cl$_2$/hexane afforded yellow crystals. Yield: 42 mg (75%).

X-Ray Crystallography. Crystallographic data and experimental details for compounds **4**–**7** are listed in Table 1. Data were collected at 173 K with ω and φ scans on a Bruker AXS SMART 1000 diffractometer using Mo Kα radiation (λ = 0.71073 Å) with Bruker SMART software. The absorption correction was based on the symmetry-equivalent reflections using the program SADABS. The space group determination was based on a check of the Laue symmetry and systematic absence and was confirmed using the structure solution. The structures were solved by direct methods with the SHELXS package, and refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method by using the SHELXL package program.[18,19] All non-hydrogen atoms were located from successive Fourier maps. Hydrogen atoms were calculated geometrically and were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms. In **6**, one of the tripod ligands (containing Co4) was found to be disordered. The ethoxy carbon atoms C86, C88, C89, and C90 are 75/25, 35/65, 60/40, and 60/40 disordered, respectively, whereas the other disordered atoms were refined with 0.5 occupancy each. In **7**, the oxygen atoms O3, O4, O5, and O6 and carbon atoms C16, C17, C18, and C20 of the ethoxy groups are 50/50 disordered.

■ RESULTS AND DISCUSSION

L$_{OEt}$BiX$_2$-type Complexes. The syntheses of L$_{OEt}$BiX$_2$-type compounds are summarized in Scheme 1. The treatment of Bi$_5$O(OH)$_9$(NO$_3$)$_4$ with 1 equiv of NaL$_{OEt}$ in water afforded a yellow precipitate characterized as the dinitrate compound [L$_{OEt}$Bi(NO$_3$)$_2$]$_2$ (**1**). A preliminary X-ray diffraction study confirmed that **1** is a dinuclear compound consisting of two symmetry-related [Bi(L$_{OEt}$)(κ^2-NO$_3$)]$^+$ fragments linked together by two nitrate ligands. Unlike L$_{OEt}$M(NO$_3$)$_3$ (M = Ti, Zr), **1** is insoluble in water, possibly because the nitrate ligands do not dissociate in water easily. Therefore, we sought to synthesize L$_{OEt}$Bi(III) compounds containing weakly coordinating triflate and tosylate ligands, which are expected to have higher solubility in water.

The treatment of BiCl$_3$ with 1 equiv of NaL$_{OEt}$ in CH$_2$Cl$_2$ afforded the dichloride compound L$_{OEt}$BiCl$_2$ (**2**). Chloride abstraction of **2** with AgX gave dimeric [L$_{OEt}$BiX$_2$]$_2$ (X = OTf (**3**) or OTs (**4**)). While **4** is soluble in both organic solvents and acidic aqueous solutions, **3** is only soluble in organic solvents such as CH$_2$Cl$_2$. In aqueous solutions at pH > 4, **4** undergoes ligand redistribution to give the bis(tripod) compound [(L$_{OEt}$)$_2$Bi(H$_2$O)][OTs] (**5**), which can also be prepared in good yield by the reaction of **4** with 1 equiv of NaL$_{OEt}$. The solid-state structure of **4** featuring two symmetry-related [L$_{OEt}$Bi(OTs)]$^+$ fragments bridged by two μ-O,O′ tosylate ligands is shown in Figure 1. The Bi–O(L$_{OEt}$) distances are in the range of 2.1604(13)–2.2182(15) Å. The Bi–O distance for the terminal tosylate ligands [2.4691(17) Å] is shorter than those of the bridged ones [2.5487(16) and 2.6226(16) Å]. The structure of **5** consisting of a seven-coordinated Bi atom is shown in Figure 2. The Bi–O(L$_{OEt}$) distances in **5** [2.226(3)–2.594(3) Å] are obviously longer than those in **4** [2.1604(13)–2.2182(15) Å]. One Bi–O(L$_{OEt}$) bond, Bi(1)–O(9) [2.594(3) Å], which is close to the aqua ligand, is significantly longer than others possibly because of steric effects.

Bi(III) Chromate Compounds. Attempts have been made to synthesize heterometallic Bi(III)/Mo(VI) oxo clusters by the reaction of L$_{OEt}$Bi^{2+} with molybdate under various conditions. In organic solvents such as CH$_2$Cl$_2$ and MeCN, the reaction of **2**, **3**, or **4** with [n-Bu$_4$N][MoO$_4$] resulted in the transfer of the tripod ligand from Bi(III) to Mo(VI) and the formation of the reported compound [L$_{OEt}$Mo(O)$_2$(μ-O)]$_2$.[16] The reaction of **4** with Na$_2$MoO$_4$ in water (pH ∼ 5) led to the isolation of **5**. Therefore,
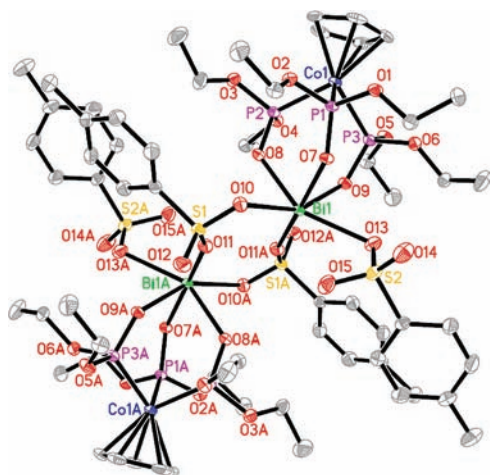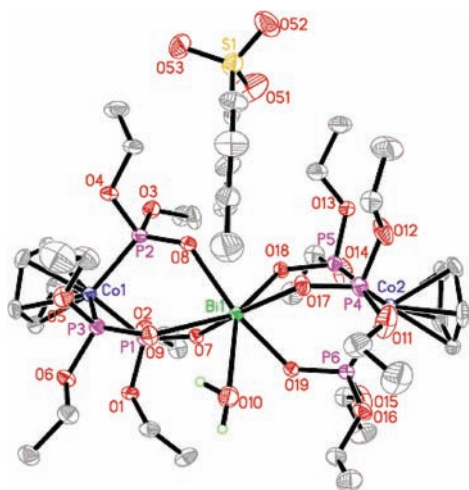
Figure 1. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): Bi(1)−O(7) 2.1604(13), Bi(1)−O(9) 2.2086(15), Bi(1)−O(8) 2.2182(15), Bi(1)−O(13) 2.4691(17), Bi(1)−O(10) 2.5487(16), Bi(1)−O(11)A 2.6226(16). Symmetry code: A = −x + 1, −y + 1, −z + 1.

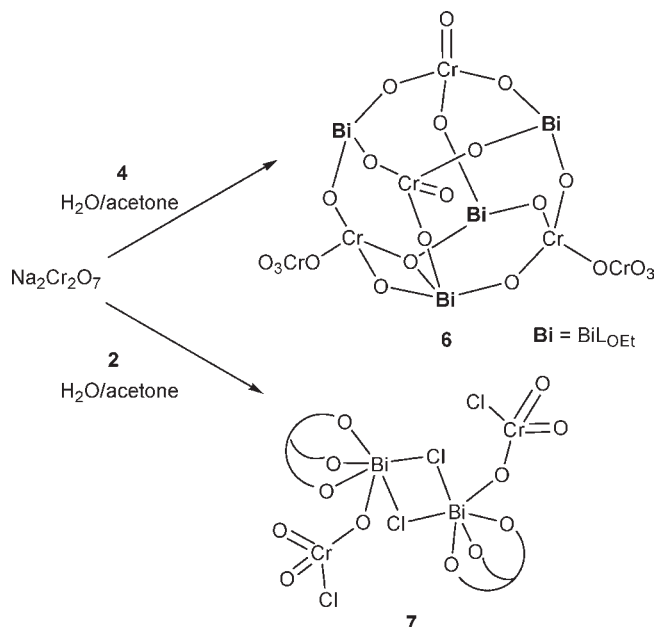**Scheme 2. Syntheses of Bi(III) Chromate(VI) Compounds**

$Bi = BiL_{OEt}$

Figure 2. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): Bi(1)−O(17) 2.399(3), Bi(1)−O(18) 2.226(3), Bi(1)−O(19) 2.291(3), Bi(1)−O(7) 2.240(3), Bi(1)−O(8) 2.332(3), Bi(1)−O(9) 2.594(3), Bi(1)−O(10) 2.835(4).

it appears that under nonacidic conditions, the conversion of **4** to **5** is more facile than the formation of L_{OEt}Bi(III) molybdate compounds. Acidification of an aqueous solution of Na_2MoO_4 with 1 M HCl(aq) (to ca. pH 3), followed by the addition of **4**, led to formation of a precipitate. Extraction with CH_2Cl_2 followed by recrystallization from CH_2Cl_2/hexane afforded yellow crystals identified as $[L_{OEt}Mo(O)_2(\mu\text{-}O)]_2$. The remaining yellow residue is virtually insoluble in all organic solvents including *N,N*-dimethylformamide and dimethylsulfoxide. The IR spectrum of this insoluble yellow solid did not show any signals due to the L_{OEt}^- ligand, suggesting that it is probably a ligand-free Bi/Mo oxide. No further attempt was made to characterize this insoluble yellow solid.

We next turned our attention to L_{OEt}Bi(III) chromate compounds. Similar to molybdate, Na_2CrO_4 in water (pH > 8)

reacted with **4** to afford **5**. On the other hand, the reaction of **4** with more acidic $Na_2Cr_2O_7$ (pH ∼ 3.5) resulted in the formation of an orange precipitate. Recrystallization from CH_2Cl_2/hexane afforded orange crystals that were characterized as the Bi(III)/Cr(VI) oxo cluster $[(L_{OEt})_4Bi_4(\mu_3\text{-}CrO_3)_2(\mu_3\text{-}Cr_2O_7)_2]$ (**6**, see Scheme 2). Crystalline **6** was found to be contaminated with CrO_3 that could be separated by repeated recrystallization from CH_2Cl_2/hexane. We were not able to assign the Cr−O stretch of **6** due to overlap with the intense P=O bands of the L_{OEt}^- ligands in the IR spectrum. Although **6** was found to consist of four different types of BiL_{OEt} moieties in the solid state (vide infra), the ^{1}H and ^{31}P {^{1}H} NMR spectra in CDCl$_3$ exhibited only a set of resonances for the L_{OEt}^- ligands, indicating that the molecule is fluxional in solution. Compound **6** is a stoichiometric oxidant for alcohols. For example, the reaction of **6** with benzyl alcohol under nitrogen afforded ca. 6 equiv of benzaldehyde and an unidentified paramagnetic inorganic species. However, attempts to use **6** as a catalyst for catalytic oxidation of benzyl alcohol with terminal oxidants such as dioxygen and *tert*-butyl-hydroperoxide failed.

Figure 3 shows the structure of the $Bi_4Cr_4O_{16}$ oxometallic core in **6**, which is derived from four $[BiL_{OEt}]^{2+}$, two μ_3-$Cr_2O_7^{2-}$, and two μ_3-CrO_4^{2-} moieties. To our knowledge, **6** is the first example of a molecular Bi(III) chromate(VI) cluster, although solid-state bismuth chromium oxide materials are well documented.[20] The chromate and dichromate anions usually bind to main group, transition, and lanthanide elements to form dinuclear compounds or polymeric materials.[21] Heteropolychromates with the general formula $[XCr_nO_{3n+4}]^{3-}$ (X = As, P) have also been studied.[21,22] Compared with the molybdenum and tungsten congeners, polyoxochromate clusters are rare apparently because of the tetrahedral geometry of Cr(VI). Heterometallic chromate(VI) and dichromate(VI) complexes usually contain μ_2-CrO_4^{2-} and μ_2-$Cr_2O_7^{2-}$ ligands.[21] Compound **6** is a rare example of a heterometallic Cr−oxo cluster featuring μ_3-chromate and μ_3-dichromate ligands, although Sn(IV) chromate(VI) polymers with μ_3- and μ_4-CrO_4^{2-} ligands have

been isolated.[23−25] In **6**, three of the Bi atoms are six-coordinated, while the remaining one is seven-coordinated. The Bi−O(L_{OEt}) and Bi−O(Cr) distances are in the range of 2.178(7)−2.309(7) and 2.318(7)−2.758(7) Å, respectively. The Cr−O distances in **6** are summarized in Scheme 3. The Cr−O(Bi) distances of the CrO_4^{2-} ligands [1.615(6)−1.657(7) Å] are similar to those of the $Cr_2O_7^{2-}$ ligands [1.632(7)−1.698(7) Å] and obviously longer than the terminal Cr=O ones [1.577(8)−1.638(7) Å]. The Cr−O−Cr bridges in the $Cr_2O_7^{2-}$ ligands are not symmetric [Cr−O(CrO₃), 1.703(4) and 1.722(8) Å; O_3Cr−O(Cr), 1.824(8) and 1.834(8) Å]. This is in contrast with the free dichromate anion that contains an essentially symmetrical Cr−O−Cr bridge [1.77(1) Å].[26] Therefore, two resonance forms, **A** and **B** (Scheme 4), may be used to describe the bonding of the dichromate ligands in **6**. In resonance form **B**, **6** can be described as a neutral $[(L_{OEt})_4Bi_4(\mu_3\text{-}CrO_4)_4]$ cluster that binds to two external CrO_3 moieties via Cr=O→CrO_3 interactions.

An attempt has been made to prepare Bi(III) chromate compounds starting from **2**, which is expected to have a lower tendency to form $(L_{OEt})_2Bi^+$ compounds. The treatment of **2** in acetone with $Na_2Cr_2O_7 \cdot 2H_2O$ in water afforded the dinuclear chlorochromate(VI) complex $[L_{OEt}Bi(OCrO_2Cl)]_2$-(μ-Cl)$_2$ (**7**) in 40% yield. The formation of **7** possibly involves the conversion of $Cr_2O_7^{2-}$ into CrO_3Cl^- (possibly by Bi−Cl), which subsequently binds to Bi(III). Alternatively, **7** could be

isolated in higher yield (70%) by the reaction of **2** with CrO_3 in CH_2Cl_2, which may be viewed as insertion of CrO_3 into the Bi−Cl bond.

Figure 4 shows the structure of **7**, which consists of two symmetry-related $[L_{OEt}Bi(OCrO_2Cl)]$ fragments bridged by two chlorides. The geometry around Bi is pseudo-octahedral, whereas that around Cr is pseudo-tetrahedral. The $[CrO_3Cl]^-$ ligand binds to Bi via an oxo group. The Bi−O(L_{OEt}) [2.160(7)−2.238(8) Å] and Bi−O(Cr) [2.604(9) Å] distances in **7** compare well with those in **6**. Unlike **6**, the terminal Cr=O [1.581(12) and 1.595(11) Å] and bridged Cr−O(Bi) [1.594(10) Å] distances in **7** are similar. The Bi−O−Cr unit is bent with an angle of 111.7(5)°. The chloride binds to the two Bi atoms unsymmetrically with Bi−Cl distances of 2.726(3) and 2.983(3) Å.

Scheme 4. Two Resonance Forms of the $Cr_2O_7^{2-}$ Ligands in 6
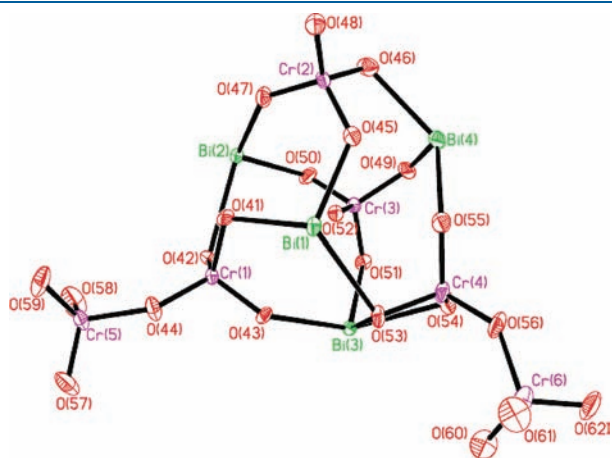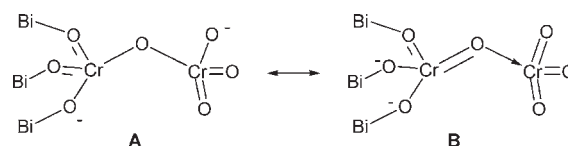
Figure 3. Oxometallic core structure of **6**. The L_{OEt}^- ligands are omitted for clarity. The ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Bi−O(L_{OEt}) 2.178(7)−2.309(7), Bi−O(Cr) 2.318(7)−2.758(7), Cr−O(Bi) 1.615(6)−1.698(7), Cr−O$_t$ 1.577(8)−1.638(7); Cr−O−Bi 95.9(3)−136.0(4), Cr−O−Cr′ 143.2(5) and 138.8(5).
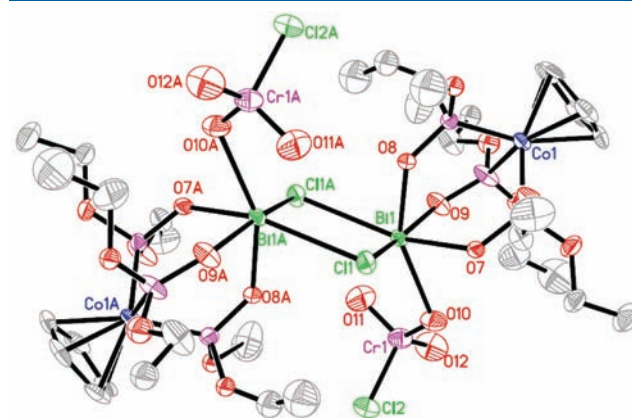
Figure 4. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Bi(1)−O(8) 2.160(7), Bi(1)−O(7) 2.180(7), Bi(1)−O(9) 2.238(8), Bi(1)−O(10) 2.604(9), Bi(1)−Cl(1) 2.726(3), Bi(1)−Cl(1)A 2.983(3), Cr(1)−O(11) 1.581(12), Cr(1)−O(10) 1.594(10), Cr(1)−O(12) 1.595(11), Cr(1)−Cl(2) 2.159(5); Cr(1)−O(10)−Bi(1) 111.7(5), Cl1−Bi1−Cl1A 83.46(7), Bi1−Cl1−Bi1A 96.54(7). Symmetry code: A = −x + 2, −y, −z + 1.

Scheme 3. Cr−O Bond Distances (Å) in 6
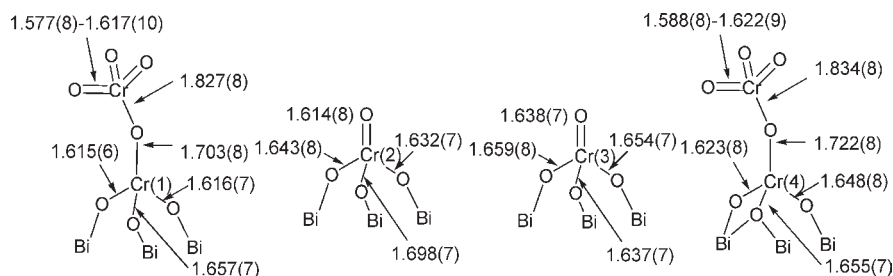
■ CONCLUSIONS

In summary, we have synthesized half-sandwich Bi(III)-L$_{OEt}$ compounds by the reaction of NaL$_{OEt}$ and Bi(III) salts. [Bi(L$_{OEt}$)(OTs)$_2$]$_2$ (**4**) is stable in acidic aqueous solution and can serve as a precursor to heterometallic Bi(III) oxo clusters. For example, the interaction of **4** with Na$_2$Cr$_2$O$_7$ in acetone/water afforded the first Bi(III)/Cr(VI) oxo cluster containing a unique Bi$_4$Cr$_4$O$_{12}$ oxometallic core. The synthesis of heterometallic Bi(III) compounds/clusters containing other transition metals and the study of their reactivity are underway.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information.** Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **4**—**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: chleung@ust.hk.

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