



# Synthesis and structures of zirconium(IV) hydrogensulfato and carboxylato complexes with Kläui's oxygen tripodal ligand

Xiao-Yi Yi<sup>a,\*</sup>, Qian-Feng Zhang<sup>b</sup>, Ian D. Williams<sup>a</sup>, Wa-Hung Leung<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China

<sup>b</sup> Department of Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China

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## ABSTRACT

Interaction of  $[\text{L}_{\text{OEt}}\text{ZrF}_3]$  ( $\text{L}_{\text{OEt}}^- = [\text{Co}(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$ ) (**1**) with 3 equivalents of bis(trimethylsilyl) sulfate afforded the  $\text{Zr}^{\text{IV}}$  hydrogensulfato complex  $[(\text{L}_{\text{OEt}})_2\text{Zr}_2(\text{SO}_4)_2(\text{HSO}_4)_2]$  (**2**) that reacted with  $\text{Et}_3\text{N}$  to give  $[\text{Et}_3\text{NH}][\text{L}_{\text{OEt}}\text{Zr}(\text{H}_2\text{O})(\text{SO}_4)_2]$  (**3**). Treatment of complex **1** with 3 equivalents of trimethylsilyl acetate afforded  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OCOCH}_3)_3]$  (**4**), whereas that with 1 and 2 equivalents of trimethylsilyl trimethylsilyloxyacetate yielded  $[\text{L}_{\text{OEt}}\text{ZrF}(\text{OCOCH}_2\text{O})_2]$  (**5**) and  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OCOCH}_2\text{OH})(\text{OCOCH}_2\text{O})_2]$  (**6**), respectively. The crystal structures of complexes **2** and **6** have been determined.

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## 1. Introduction

Sulfated metal oxides and related inorganic solid acids have attracted much attention due to their applications in heterogeneous catalysis and organic synthesis [1–14]. Of particular interest is sulfated zirconia (SZ) that can catalyze isomerization of alkanes at relatively low temperatures [12–14]. In order to better understand the mechanisms of SZ-based catalysis, it is essential to elucidate the structures of SZ active sites at the molecular level. On the basis of spectroscopic and other evidence, several models including Zr-bound hydrogensulfate and hydroxyl species (a–f, Scheme 1) have been proposed for the acid sites of SZ [15–18]. Nevertheless, the issue as to how the sulfate/hydrogensulfate species interact with metal ions and mechanisms of organometallic reactions on SZ surfaces are not well understood. In an effort to model the active sites of SZ catalysts, we sought to synthesize molecular  $\text{Zr}^{\text{IV}}$  sulfato complexes containing the Kläui's oxygen tripodal ligand  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$  (denoted as  $\text{L}_{\text{OEt}}^-$  hereafter, Scheme 2) [19,20]. In a previous paper, we reported the isolation of a dinuclear  $\text{Zr}^{\text{IV}}$  sulfato complex,  $[(\text{L}_{\text{OEt}})_2\text{Zr}_2(\text{H}_2\text{O})(\kappa_2\text{-SO}_4)_2(\mu\text{-SO}_4)]$ , from  $\text{ZrCl}_4$  and  $\text{NaL}_{\text{OEt}}$  in sulfuric acid [21]. In the presence of  $\text{Ag}(\text{OTf})$ ,  $[(\text{L}_{\text{OEt}})_2\text{Zr}_2(\text{H}_2\text{O})(\kappa_2\text{-SO}_4)_2(\mu\text{-SO}_4)]$  rearranged to trinuclear  $[(\text{L}_{\text{OEt}})_3\text{Zr}_3(\text{H}_2\text{O})(\kappa_2\text{-SO}_4)_3(\mu_3\text{-SO}_4)]$  [OTf], demonstrating the flexible binding capability of the sulfato ligand [22]. In addition, we found that the fluoride ligands in  $[\text{L}_{\text{OEt}}\text{ZrF}_3]$  (**1**) can be removed easily by reacting with trimethylsilyl reagents. For example, treatment of complex **1** with trimethylsilyl perrhenate and triflate led to forma-

tion of  $[\text{L}_{\text{OEt}}\text{Zr}(\text{H}_2\text{O})(\text{ReO}_4)_3]$  and  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OTf})_3]$ , respectively [23]. This prompted us to synthesize aqua-free  $\text{Zr}^{\text{IV}}$  sulfato complexes from complex **1** and bis(trimethylsilyl) sulfate. In this paper, we report the isolation and solid-state structure of a dinuclear  $\text{Zr}^{\text{IV}}$  hydrogensulfato(sulfato) complex containing  $\text{L}_{\text{OEt}}^-$ . Also, the synthesis of  $\text{Zr}^{\text{IV}}$  carboxylato complexes from complex **1** and trimethylsilyl carboxylates will be described.

## 2. Experimental

### 2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 282.5 and 121.5 MHz for  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ , respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ),  $\text{CF}_3\text{C}_6\text{H}_5$  ( $^{19}\text{F}$ ) and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer.

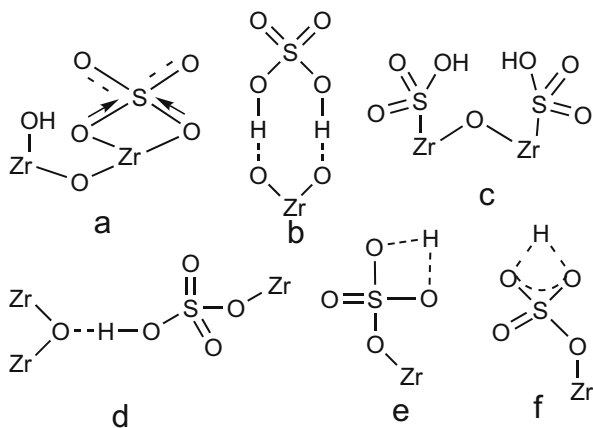
The complex  $[\text{L}_{\text{OEt}}\text{ZrF}_3]$  (**1**) was prepared as described elsewhere [21]. Bis(trimethylsilyl) sulfate and trimethylsilyl trimethylsilyloxyacetate were purchased from Aldrich Ltd. and used as received.

### 2.2. $[(\text{L}_{\text{OEt}})_2\text{Zr}_2(\text{SO}_4)_2(\text{HSO}_4)_2]$ (**2**)

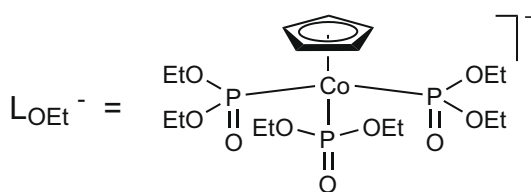
To a solution of bis(trimethylsilyl)sulfate (42 mg, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added complex **1** (40 mg, 0.058 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) under nitrogen at 0 °C. The mixture was warmed to room temperature at which it was stirred for 1.5 h. The volatiles were

\* Corresponding authors. Tel.: +852 2358 7360; fax: +852 2358 1594.

E-mail addresses: xyi@ust.hk (X.-Y. Yi), chleung@ust.hk (W.-H. Leung).



Scheme 1. Proposed models of SZ acid sites (Ref. [6]).



Scheme 2. Structure of Kläui's tripodal ligand  $L_{OEt}^-$ .

pumped off and the residue was washed with hexanes and then  $Et_2O$ . Recrystallization from THF/hexane gave yellow single crystals that were suitable for the X-ray diffraction study. Yield: 37 mg (78%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.30$  (t,  $J = 7.0$  Hz, 36H,  $CH_3$ ), 4.24 (m, 24H,  $OCH_2$ ), 5.14 (s, 10H,  $C_5H_5$ ), 7.79 (s, 2H,  $HSO_4$ ) ppm.  $^{31}P$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 122.5$  (s) ppm. Anal. Calc. for  $C_{34}H_{72}Co_2O_{34}P_6S_4Zr_2 \cdot 6H_2O$ : C, 23.4; H, 4.85. Found: C, 23.0; H, 4.82%.

### 2.3. $[Et_3NH][L_{OEt}Zr(H_2O)(SO_4)_2]$ (**3**)

To a solution of complex **2** (26.6 mg, 0.015 mmol) in THF was added 2 equivalents of  $Et_3N$ , and the reaction mixture was stirred at room temperature for 4 h. The volatiles were pumped off and the residue was washed with hexanes and  $Et_2O$ . Recrystallization from THF/hexane gave a yellow crystalline solid.  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.26$  (t,  $J = 7.0$  Hz, 18H,  $CH_3$ ), 1.33 (t,  $J = 7.0$  Hz, 9H,  $CH_3CH_2N$ ), 3.23 (m, 6H,  $CH_2$ ), 4.22 (m, 12H,  $OCH_2$ ), 5.09 (s, 5H,  $C_5H_5$ ), 9.62 (s, 1H,  $Et_3NH$ ) ppm.  $^{31}P$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 121.4$  (s) ppm. Anal. Calc. for  $C_{23}H_{53}CoO_{18}NP_3S_2Zr$ : C, 29.4; H, 5.69. Found: C, 28.8; H, 5.83%.

### 2.4. $[L_{OEt}Zr(OCOCH_3)_3]$ (**4**)

A mixture of complex **1** (242 mg, 0.35 mmol) and excess trimethylsilyl acetate (270  $\mu$ L, 1.7 mmol) in  $CH_2Cl_2$  (15 mL) was refluxed overnight. The volatiles were pumped off and the residue was extracted with hexane. Concentration and cooling at  $-18$  °C afforded a yellow crystalline solid. Yield: 144 mg (51%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.33$  (t,  $J = 7.0$  Hz, 18H,  $CH_3$ ), 1.42 (s, 9H,  $CH_3CO_2$ ), 4.41 (m, 12H,  $OCH_2$ ), 4.94 (s, 5H,  $C_5H_5$ ) ppm.  $^{31}P$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 118.1$  (s) ppm. IR (KBr,  $cm^{-1}$ ): 1680, 1649, 1607 [ $\nu(C=O)$ ]. Anal. Calc. for  $C_{23}H_{44}CoO_{15}P_3Zr \cdot 4H_2O \cdot CH_2Cl_2$ : C, 30.0; H, 5.67. Found: C, 29.7; H, 5.62%.

### 2.5. $[L_{OEt}ZrF(OCH_2CO_2)]_2$ (**5**)

An equimolar mixture of complex **1** (68 mg, 0.10 mmol) and trimethylsilyl trimethylsiloxyacetate (24  $\mu$ L, 0.10 mmol) in THF

(5 mL) was refluxed overnight. The volatiles were pumped off and the residue was washed with  $Et_2O$ . Recrystallization from THF/hexane afforded single crystals that were suitable for X-ray diffraction study. Yield: 40 mg (56%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.27$  (t,  $J = 7.0$  Hz, 18H,  $CH_3$ ), 1.28 (t,  $J = 7.0$  Hz, 18H,  $CH_3$ ), 1.63 (s, 4H,  $OCH_2CO_2$ ), 4.09 (m, 12H,  $OCH_2$ ), 4.18 (m, 12H,  $OCH_2$ ), 5.08 (s, 10H,  $C_5H_5$ ) ppm.  $^{31}P$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 119.9$  (s) ppm.  $^{19}F$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 69.3$  (s) ppm. IR (KBr,  $cm^{-1}$ ): 1671 [ $\nu(C=O)$ ]. Anal. Calc. for  $C_{38}H_{74}Co_2F_2O_{24}P_6Zr_2 \cdot 6H_2O$ : C, 29.5; H, 5.60. Found: C, 28.7; H, 5.38%.

### 2.6. $[L_{OEt}Zr(OCOCH_2OH)(OCOCH_2O)]_2$ (**6**)

A mixture of complex **1** (68 mg, 0.10 mmol) and 2 equivalents of trimethylsilyl trimethylsiloxyacetate in THF (5 mL) was refluxed overnight. The volatiles were pumped off and the residue was extracted with hexane. Cooling the filtrate at  $-18$  °C gave yellow crystals that were suitable for X-ray diffraction study. Yield: 35 mg (45%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.27$  (t,  $J = 7.0$  Hz, 36H,  $CH_3$ ), 2.30 (b, 2H, OH), 4.09 (m, 32H,  $CH_2$ ), 5.09 (s, 10H,  $C_5H_5$ ) ppm.  $^{31}P$  { $^1H$ } NMR ( $CDCl_3$ ):  $\delta = 121.0$  (s) ppm. IR (KBr,  $cm^{-1}$ ): 1658 [ $\nu(C=O)$ ]. Anal. Calc. for  $C_{42}H_{80}Co_2O_{30}P_6Zr_2 \cdot 2H_2O$ : C, 31.8; H, 5.33. Found: C, 31.5; H, 5.27%.

### 2.7. X-ray crystallography

Complexes **2** and **6** have been characterized by X-ray diffraction studies. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected frames were processed with the software SAINT [24]. Structures were solved by the direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [25]. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters and with suitable restraints. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement. Crystallographic data and experimental details for complexes **2** and **6** are listed in Table 1, and their selected bond lengths and angles in Tables 2 and 3, respectively. In complex **2**, the ethoxy groups of the  $L_{OEt}^-$  ligand

Table 1  
Crystallographic data and experimental details for **2** and **6**.

	<b>2</b>	<b>6</b>
Formula	$C_{70}H_{144}Cl_4Co_4O_{68}P_{12}S_8Zr_4$	$C_{42}H_{80}Co_2O_{30}P_6Zr_2$
Formula weight	3444.37	1551.18
<i>a</i> (Å)	35.042(2)	18.7047(14)
<i>b</i> (Å)	19.5902(13)	19.2268(14)
<i>c</i> (Å)	19.1000(12)	34.578(3)
$\alpha$ (°)	90	90
$\beta$ (°)	94.7790(10)	90.4180(10)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	13066.4(15)	12435.0(16)
<i>Z</i>	4	8
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
$\rho_{calc}$ [ $g\ cm^{-3}$ ]	1.751	1.657
<i>T</i> [K]	100(2)	100(2)
$\mu$ ( $mm^{-1}$ )	1.252	1.089
<i>F</i> (0 0 0)	7008	6368
Number of reflections	93 873	80 084
Number of independent reflections	22 292	20 002
$R_{int}$	0.0694	0.0464
$R_1, wR_2$ ( $I > 2.0\sigma(I)$ )	0.0934, 0.2016	0.0549, 0.1352
$R_1, wR_2$ (all data)	0.1359, 0.2192	0.0755, 0.1452
Goodness-of-fit (GOF) <sup>a</sup>	1.034	1.04

<sup>a</sup>  $GOF = [(\sum w|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$ .

**Table 2**  
Selected bond lengths [Å] for complexes **2a**, **2b** and **2c**.

<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>
Zr(1)–O(21)	2.256(8)	Zr(3)–O(50)	2.213(6)	Zr(4)–O(70)	2.126(8)
Zr(1)–O(22)	2.258(9)	Zr(3)–O(52A)	2.224(6)	Zr(4)–O(73A)	2.087(7)
Zr(1)–O(25)	2.057(7)	Zr(3)–O(54)	2.321(5)	Zr(4)–O(74)	2.250(9)
Zr(1)–O(31)	2.178(8)	Zr(3)–O(54A)	2.284(5)	Zr(4)–O(75)	2.236(8)
Zr(2)–O(26)	2.065(8)	Zr(3)–O(55)	2.191(6)	S(7)–O(70)	1.452(8)
Zr(2)–O(33)	2.036(8)	S(5)–O(50)	1.469(6)	S(7)–O(71)	1.416(8)
S(1)–O(21)	1.471(8)	S(5)–O(51)	1.540(7)	S(7)–O(72)	1.474(9)
S(1)–O(22)	1.484(9)	S(5)–O(52)	1.463(6)	S(7)–O(73)	1.509(8)
S(2)–O(25)	1.497(8)	S(5)–O(53)	1.421(7)	S(8)–O(74)	1.492(10)
S(2)–O(26)	1.480(8)	S(6)–O(54)	1.528(6)	S(8)–O(75)	1.528(9)
S(2)–O(27)	1.413(8)	S(6)–O(55)	1.495(6)	S(8)–O(76)	1.497(11)
S(2)–O(28)	1.438(8)	S(6)–O(56)	1.466(7)	S(8)–O(77)	1.438(10)
S(3)–O(31)	1.464(8)	S(6)–O(57)	1.425(7)		
S(3)–O(32)	1.350(8)				
S(4)–O(33)	1.469(9)				
S(4)–O(34)	1.403(8)				
S(4)–O(35)	1.571(8)				
S(4)–O(36)	1.424(9)				

Symmetry operator: A =  $-x, -y + 1, -z$  (for **2b**);  $-x + 1, -y + 1, -z + 2$  (for **2c**).

**Table 3**  
Selected bond lengths [Å] and angles [°] for **6**.

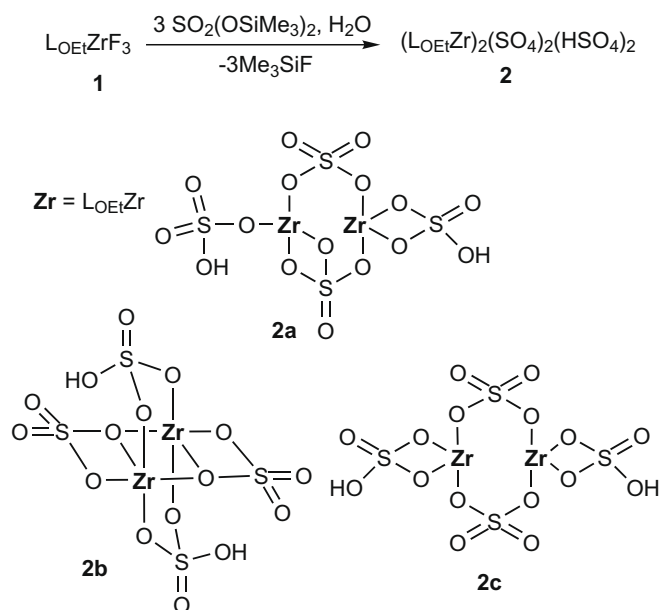
Zr(1)–O(10)	2.171(3)	Zr(2)–O(10)	2.126(4)
Zr(1)–O(11)	2.142(3)	Zr(2)–O(30)	2.176(3)
Zr(1)–O(13)	2.042(3)	Zr(2)–O(31)	2.151(3)
Zr(1)–O(30)	2.140(4)	Zr(2)–O(33)	2.046(3)
Zr(1)–Zr(2)	3.6304(7)		
O(30)–Zr(1)–O(10)	64.99(13)	O(10)–Zr(2)–O(30)	65.16(12)
Zr(1)–O(30)–Zr(2)	114.53(14)	Zr(2)–O(10)–Zr(1)	115.32(14)

were found to be disordered. The sulfato oxygens O23, O24, O29 and O30 in **2a** were found to be 50:50 disordered. Complexes **3** and **5** also have been studied by X-ray diffraction. Their structures have not been refined satisfactorily due to poor crystal quality. Crystallographic data for complex **3**: monoclinic,  $C2/c$ ,  $a = 11.9105(17)$  Å,  $b = 20.1142(28)$  Å,  $c = 34.6208(48)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 98.728(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 8198(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_{\text{int}} = 0.1385$  refinement converged to  $R_1 = 0.0712$ ,  $wR_2 = 0.1165$ . Crystallographic data for complex **5**: monoclinic,  $P2_1/n$ ,  $a = 9.2735(17)$  Å,  $b = 15.5474(33)$  Å,  $c = 19.9076(45)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 94.78(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2860.2(10)$  Å<sup>3</sup>,  $Z = 2$ , refinement converged to  $R_1 = 0.1463$ ,  $wR_2 = 0.4108$ .

### 3. Results and discussion

#### 3.1. Hydrogensulfato compound

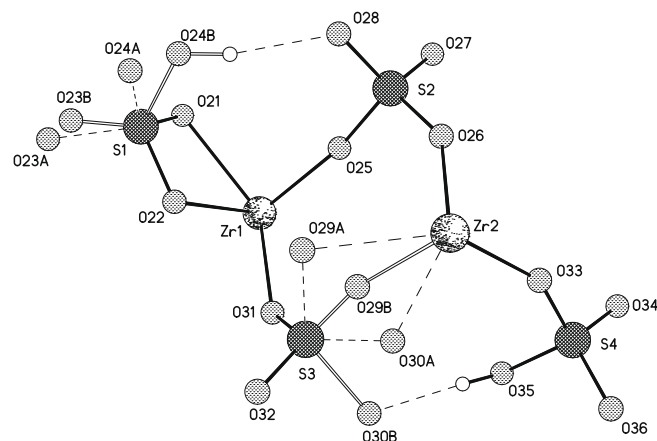
In an attempt to prepare aqua-free Zr<sup>IV</sup> sulfate compounds, the reaction of complex **1** with bis(trimethylsilyl) sulfate was studied. Treatment of complex **1** with 3 equivalents of bis(trimethylsilyl) sulfate in CH<sub>2</sub>Cl<sub>2</sub> afforded a moisture-sensitive yellow solid identified as [(L<sub>OEt</sub>)<sub>2</sub>Zr<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(HSO<sub>4</sub>)<sub>2</sub>] (**2**) (Scheme 3). The hydrogensulfato ligands in **2** were apparently produced by hydrolysis of bis(trimethylsilyl)sulfate with the moisture in the solvent and/or the starting material **1**. It may be noted that while Zr<sup>IV</sup>-bound hydrogensulfato species has been postulated as a possible acid site of SZ, complex **2**, to our knowledge, is the first isolated Zr<sup>IV</sup> hydrogensulfato compound characterized by X-ray crystallography. Complex **2** is soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, tetrahydrofuran (THF), and toluene, but insoluble in hexane and Et<sub>2</sub>O. Although X-ray crystallography revealed that in the solid-state complex **2** is composed of three different species with the same formula (*vide infra*), the <sup>1</sup>H and <sup>31</sup>P {<sup>1</sup>H} NMR spectra in CDCl<sub>3</sub> at room temperature show only one set of signals, suggesting that



**Scheme 3.** Synthesis of Zr<sup>IV</sup> hydrogensulfato complex.

the sulfato and hydrogensulfato ligands are highly fluxional in solutions. The <sup>1</sup>H NMR spectrum displays a singlet at  $\delta = 5.14$  ppm due to the Cp protons of the L<sub>OEt</sub><sup>-</sup> ligands along with a singlet at  $\delta = 7.79$  ppm assignable to the HSO<sub>4</sub><sup>-</sup> ligands. Consistent with this assignment, addition of Et<sub>3</sub>N to complex **2** in CDCl<sub>3</sub> resulted in the disappearance of the resonance at  $\delta = 7.79$  ppm and the formation a new signal at  $\delta = 9.62$  ppm attributable to Et<sub>3</sub>NH<sup>+</sup>.

Complex **2** crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit was found to contain three different species, **2a**, **2b** and **2c** (Scheme 3), which have the same molecular formula. Complex **2a** (Fig. 1) is composed of one [L<sub>OEt</sub>Zr(κ<sub>2</sub>-HSO<sub>4</sub>)]<sup>2+</sup> moiety and one [L<sub>OEt</sub>Zr(κ<sub>1</sub>-HSO<sub>4</sub>)]<sup>2+</sup> moiety that are bridged by one μ<sub>2</sub>-sulfato-O,O' ligand and one μ<sub>2</sub>-sulfato-O,O',O'' ligand. The Zr–O bond in [Zr(κ<sub>1</sub>-HSO<sub>4</sub>)]<sup>3+</sup> species (2.036(8) Å) is significantly shorter than those in [Zr(κ<sub>2</sub>-HSO<sub>4</sub>)]<sup>3+</sup> species (av. 2.257 Å). The average of Zr–O(SO<sub>4</sub>) distance is 2.061 Å. The Zr1–Zr2 distance is 4.979(8) Å. Intramolecular hydrogen bonds between the S–OH groups and S=O groups of the sulfate ligands were observed. The O24B...O28 and O35...O30B distances are 2.671(5) and 2.606(7) Å, respectively, and the O24B–H–O28 and O35–H–O30B angles are 165.95(9) and 167.95(7)°, respectively.



**Fig. 1.** Molecular structures of complex **2a**. The L<sub>OEt</sub><sup>-</sup> ligands are omitted for clarity.

Complex **2b** (Fig. 2) consists of two symmetry-related  $[\text{L}_{\text{OEt}}\text{Zr}]^{3+}$  fragments linked by two  $\mu_2$ -sulfato- $O,O',O''$  and two  $\mu_2$ -hydrogen-sulfato- $O,O'$  ligands. The  $\mu_2$ -sulfato- $O,O',O''$  ligands bind to Zr in an unsymmetrical fashion [Zr3–O54, 2.321(5) Å; Zr3–O55, 2.191(6) Å]. The Zr–O distances for the  $\mu_2$ -hydrogensulfato- $O,O'$  ligands (av. 2.219 Å) are longer than those in **2a** (av. 2.061 Å). The Zr3–Zr3A distance is 3.893 Å. The S–OH distance (1.547(7) Å) of the hydrogensulfato ligand is similar to that in  $[\text{Ag}(\text{PPh}_3)_2(\text{HSO}_4)]$  (1.538(3) Å) [26] and significantly longer than those of S=O terminal bonds (av. 1.457 Å). Intramolecular hydrogen bonds between the S–OH groups and S=O groups of the sulfate ligands were found. The O51...O56A distance is 2.559(6) Å and the O51–H–O56A angle is 174.56(8)°.

Complex **2c** (Fig. 3) consists of two symmetry-related  $[\text{L}_{\text{OEt}}\text{Zr}(\kappa_2\text{-HSO}_4)]^+$  moieties linked by two  $\mu_2$ -sulfato- $O,O'$  ligands. The hydrogensulfato ligand binds to Zr in a symmetrical, bidentate fashion (Zr4–O74, 2.250(9) Å; Zr4–O75, 2.236(8) Å). The average of Zr–O distances for the hydrogensulfato and  $\mu_2$ -sulfato ligands in **2c** (2.243 and 2.107 Å, respectively) are similar to those in **2a** (2.257 and 2.061 Å, respectively). The Zr4–Zr4A distance of 5.167(6) Å is longer than those in **2a** and **2b**. Intramolecular hydrogen bond involving an S–O group of the hydrogensulfato ligand and a terminal S=O group of the sulfato ligand was observed. The O76...O72A

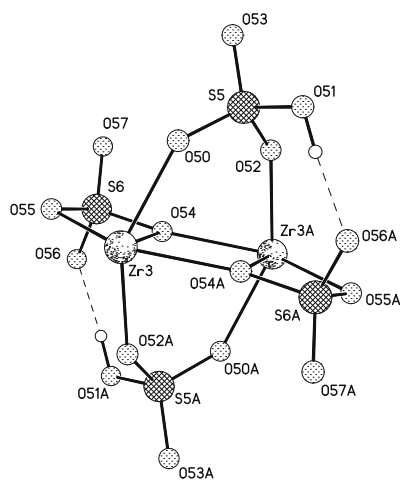


Fig. 2. Molecular structures of complex **2b**. The  $\text{L}_{\text{OEt}}^-$  ligands are omitted for clarity.

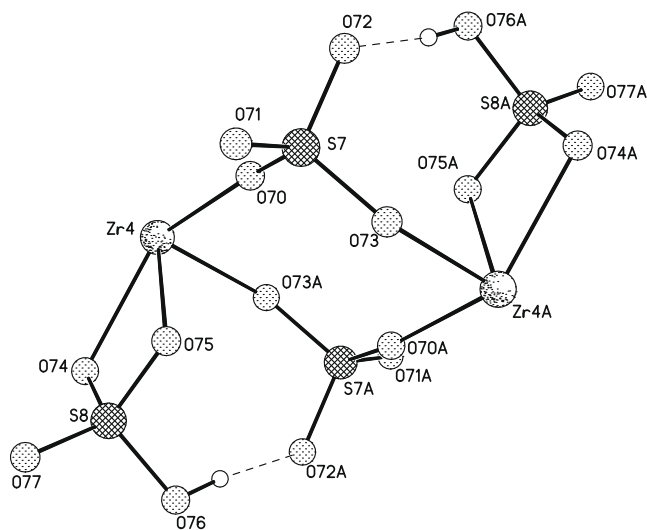


Fig. 3. Molecular structures of complex **2c**. The  $\text{L}_{\text{OEt}}^-$  ligands are omitted for clarity.

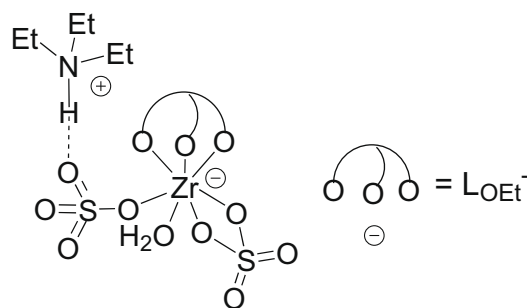
distance and O76–H–O72A angle are 2.447(4) Å and 173.88(6)°, respectively.

An attempt has been made to prepare an anionic Zr sulfato compounds by deprotonation of complex **2** with bases. Treatment of **2** with 2 equivalents of  $\text{Et}_3\text{N}$  in THF gave yellow crystals characterized as  $[\text{Et}_3\text{NH}][\text{L}_{\text{OEt}}\text{Zr}(\text{H}_2\text{O})(\text{SO}_4)_2]$  (**3**). The aqua ligand in **3** was presumably derived from the moisture of solvent. A preliminary X-ray diffraction study revealed that **3** is a 7-coordinated  $\text{Zr}^{\text{IV}}$  complex with one aqua, one  $\kappa_2$ -sulfato and one  $\kappa_1$ -sulfato ligand. The  $\text{Et}_3\text{NH}^+$  is the hydrogen donor to the terminal O atom in  $\kappa_1$ -sulfato ligand (Scheme 4). Unfortunately, the structure has not been refined satisfactorily due to poor quality of the crystal. The  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$  displays a singlet at  $\delta = 9.62$  ppm that is assigned to  $\text{Et}_3\text{NH}^+$ . Attempts to exchange the H-bonded  $\text{Et}_3\text{NH}^+$  cation in complex **3** with non-coordinating cations such as  $n\text{Bu}_4\text{N}^+$  or  $\text{PPh}_4^+$  were unsuccessful.

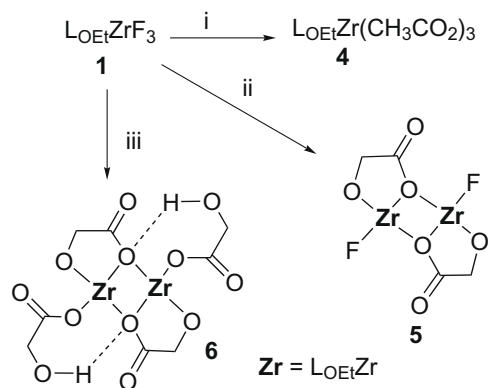
### 3.2. Carboxylato compounds

The success in isolation of complex **2** led us to synthesize  $\text{Zr}^{\text{IV}}$  carboxylato compounds by reaction of **1** with trimethylsilyl carboxylates (Scheme 5). Treatment of **2** with trimethylsilyl acetate afforded yellow crystals characterized the tris(acetato) complex  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OCOCH}_3)_3]$  (**4**). It may be noted that for the reaction of  $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{F}_3]$  and  $\text{Me}_3\text{SiOCOCF}_3$  in refluxing toluene, only the bis(acetato) complex  $[\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{F}(\text{OCOCF}_3)_2\}_2]$  was isolated regardless of the molar ratio of the starting materials used [27]. Complex **4** is soluble in common organic solvents including hexane. It is air sensitive in both the solid-state and solutions. We have not been able to obtain single crystals of complex **4** for structure determination. The  $^1\text{H}$  NMR spectrum of complex **4** in  $\text{CDCl}_3$  displays a singlet at  $\delta = 1.42$  ppm that is assigned to methyl protons of the magnetically equivalent acetate ligands. The IR spectrum (KBr) shows three strong C=O bands at 1680, 1649 and 1607  $\text{cm}^{-1}$ . Treatment of **1** with 1 equivalents of trimethylsilyl trimethylsilyloxyacetate at reflux afforded dinuclear  $[\text{L}_{\text{OEt}}\text{ZrF}(\text{OCOCH}_2\text{O}_2)]_2$  (**5**). The  $^{19}\text{F}$  NMR spectrum of complex **5** displays a singlet at  $\delta = 69.3$  ppm due to the fluoride ligand that is more downfield than that for **1** ( $\delta = 56.1$  ppm). A preliminary X-ray diffraction study confirmed that **5** is a dinuclear  $\text{Zr}^{\text{IV}}$  complex containing two  $\mu_2$ -O(carboxy),O'(alkoxy)  $[\text{OCOCH}_2\text{O}_2]^{2-}$  and two terminal fluoride ligands. Unfortunately, the structure has not been refined satisfactorily due to poor quality of the crystal.

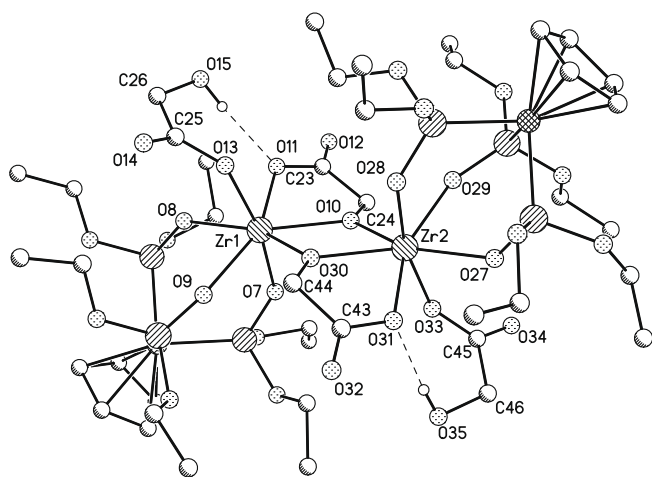
In order to remove all the fluoride ligands in complex **1**, excess trimethylsilyl trimethylsilyloxyacetate was used. Thus, treatment of complex **1** with 2 equivalents of trimethylsilyl trimethylsilyloxyacetate in THF at reflux afforded  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OCOCH}_2\text{OH})(\text{OCOCH}_2\text{O}_2)]_2$  (**6**). No  $^{19}\text{F}$  signal was found for complex **6**, indicating all the fluoride ligands in **1** have been substituted. X-ray crystallography confirmed that **6** is a dinuclear complex consisting of two  $[\text{L}_{\text{OEt}}\text{Zr}(\text{OCOCH}_2\text{OH})]^{2+}$  fragments linked together by two  $[\text{OCOCH}_2\text{O}_2]^{2-}$  ligands



Scheme 4. Structure of **3**.



**Scheme 5.** Syntheses of Zr<sup>IV</sup> carboxylato complexes. Reagents: (i) 3 equivalents of Me<sub>3</sub>SiOCOCH<sub>3</sub>, (ii) 1 equivalent of Me<sub>3</sub>SiOCH<sub>2</sub>CO<sub>2</sub>SiMe<sub>3</sub>, (iii) 2 equivalents of Me<sub>3</sub>SiOCH<sub>2</sub>CO<sub>2</sub>SiMe<sub>3</sub>.



**Fig. 4.** Structure of complex **6**. Hydrogen atoms were omitted for clarity.

(Fig. 4). Similar to complex **5**, the bridged [OCOCH<sub>2</sub>O]<sup>2-</sup> ligands bind to the two Zr in a  $\mu_2$ -O(carboxy),O'(alkoxy) mode. The unidentate hydroxyacetate ligand binds to Zr via the carboxylate group with the hydroxyl group H-bonded to the oxygen of the bridged carboxylate group. The Zr<sub>2</sub>O<sub>2</sub> four-membered ring is planar with a total bond angle of 360.1(8)°. The Zr–O(terminal carboxylate) distances (av. 2.044 Å) are shorter than the Zr–O(bridged carboxylate) distances (av. 2.153 Å), which are comparable to those of Zr–O(alkoxy) (av. 2.147 Å). The Zr1–Zr2 distance is 3.630(9) Å.

#### 4. Conclusions

In summary, we have synthesized and structurally characterized a Zr<sup>IV</sup> hydrogensulfato complex by reaction of [L<sub>OEt</sub>ZrF<sub>3</sub>] with bis(trimethylsilyl) sulfate. X-ray crystallography revealed that the

hydrogensulfato ligand binds to Zr<sup>IV</sup> in various modes, namely hydrogensulfato-O, hydrogensulfato-O,O',  $\mu_2$ -hydrogensulfato-O,O'. Such binding modes of the hydrogensulfato ligand may play a role in sulfated zirconia-based catalysis. In addition, [L<sub>OEt</sub>ZrF<sub>3</sub>] reacted with trimethylsilyl trimethylsilyloxyacetate to give Zr<sup>IV</sup> alkoxy(carboxylate) complexes, demonstrating that [L<sub>OEt</sub>ZrF<sub>3</sub>] can serve as a good starting material for Zr–L<sub>OEt</sub> complexes containing Zr–O bonds.

#### 5. Supplementary material

CCDC 724606 and 724607 contain the supplementary crystallographic data for complexes **2** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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