

# Dimeric scandium(III) and monomeric lanthanide(III) complexes with perfluoropropane-1,3-disulfonates as counter anions for Lewis acid catalysis

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## Abstract

A novel scandium(III) complex with disulfonates as counter anions,  $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_2[\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_2$  (**5**), was prepared from scandium oxides ( $\text{Sc}_2\text{O}_3$ ) and perfluoropropane-1,3-disulfonic acid (**1**,  $\text{HO}_3\text{SCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ ). By X-ray analysis, **5** was found to be a  $\mu\text{-OH}$ -bridged dimeric structure bearing two perfluoropropane-1,3-disulfonates without bonding to scandium(III) centers. A series of lanthanide(III) complexes were also prepared from **1** and lanthanide oxides ( $\text{Ln}_2\text{O}_3$ ; Ln = La, Nd, Sm, and Gd). In sharp contrast to the dimeric scandium(III) complex, the corresponding lanthanide(III) complexes had monomeric structures. Interestingly, the dimeric scandium(III) complex, but not the monomeric lanthanide complexes, with perfluoropropane-1,3-disulfonates served as an efficient Lewis acid catalyst for the hydrolysis of esters.

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**Keywords:** Lanthanide; Lewis acid; Perfluoropropane-1,3-disulfonic acid; Scandium; X-ray analysis

## 1. Introduction

Perfluoroalkanesulfonate  $[\text{CF}_3(\text{CF}_2)_n\text{SO}_3^- (n \geq 0)]$  is an excellent counter anion and can enhance the Lewis acidity of a centered metal due to the strong electronegativity of fluorine [1]. Recently, considerable attention has been paid to scandium(III) and lanthanide(III) trifluoromethanesulfonate [2].  $\text{Sc}(\text{OTf})_3$  and  $\text{Ln}(\text{OTf})_3$  have been shown to be good catalysts for various organic reactions, such as the acylation reaction, aldol reaction, allylation reaction, Diels–Alder reaction, Friedel–Crafts reaction, Michael reaction, etc. [3,4]. However, perfluoroalkane- $\alpha,\omega$ -disulfonates  $[\text{O}_3\text{S}(\text{CF}_2)_n\text{SO}_3^- (n \geq 1)]$  have not been thoroughly studied, and the structures of the corresponding metal complexes and their catalytic activities are still unknown, except for the Li and K precursors [5]. Perfluoroalkane- $\alpha,\omega$ -disulfonates can also enhance of the Lewis acidity of

a centered metal, possibly by intramolecular chelation or supramolecular interaction [6]. We report here our investigation of the synthesis of scandium(III) and lanthanide(III) complexes with perfluoropropane-1,3-disulfonates. The resulting complexes are characterized by X-ray analyses and their activities were examined in the catalytic hydrolysis of esters.

## 2. Results and discussion

First, the synthesis of lanthanide(III) complexes bearing perfluoropropane-1,3-disulfonates was examined. A lanthanum (La) complex (**2**) bearing perfluoropropane-1,3-disulfonates was prepared by the established procedure for lanthanide(III) trifluoromethanesulfonate  $[\text{Ln}(\text{OTf})_3]$  [7,8]. A mixture of perfluoropropane-1,3-disulfonic acid (**1**) (1 equiv.) and  $\text{La}_2\text{O}_3$  (3 equiv.) in  $\text{H}_2\text{O}$  was heated at 100 °C for 2 h. After insoluble  $\text{La}_2\text{O}_3$  was removed from the resultant mixture, water in the eluate was removed at 200 °C for 2 h under 1–2 Torr, and **2** was obtained in

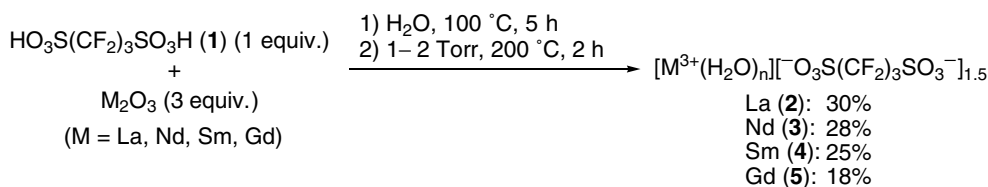
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30% yield (Scheme 1). The same procedure could be applied to other lanthanides (Nd, Sm, and Gd) and the corresponding complexes (**3–5**) were obtained in yields of 18–28%. These lanthanide(III) complexes are highly stable under open air conditions without hygroscopic or deliquescent characteristics. They were easily soluble in water, alcohols, and polar solvent such as acetonitrile, DMF, and DMSO but only slightly soluble in common organic solvents [9]. Fortunately, single crystals could be grown from water at room temperature, and thus X-ray analyses of these lanthanide(III) complexes (Nd, Sm, and Gd) could be carried out. By X-ray analyses, the lanthanide(III) complexes were found to be monomeric structures without either coordination of the disulfonates to a centered metal or an expected chelation with  $\alpha,\omega$ -disulfonates (Figs. 1–6) [10,11]. The obtained monomeric complexes with perfluoropropane-1,3-disulfonates were also aqua species, and the Nd(III) and Sm(III) complexes as light rare earth compounds showed 9-coordination while the Gd(III) complex as a heavy rare earth compound showed 8-coordination.

Interestingly, in **3–5** many hydrogen bonds were observed between the coordinating water ( $H_2O$ ) and disulfonates ( $SO_3$ ). Thus, the cations and anions in crystals **3–5** formed a complicated *polymeric* network through hydrogen bonds. That should be notable in  $\alpha,\omega$ -disulfonate anions having the linear structure (i.e.  $^-O_3SCF_3(CF_2)_3SO_3^-$ ) rather than *mono*-sulfonate (i.e.  $TfO^-$  or  $TsO^-$ ).

Next, we prepared a scandium(III) complex with perfluoropropane-1,3-disulfonates from scandium oxide ( $Sc_2O_3$ ) by the same convenient procedures that were used for lanthanide oxides (Scheme 2) [7,8]. The corresponding white powdery compound,  $[Sc(\mu-OH)(H_2O)_5]_2[O_3S(CF_2)_3SO_3]_2$  (**6**), was obtained in 52% yield and the structure was confirmed by X-ray analysis (Figs. 7 and 8). In sharp contrast to lanthanide(III) complexes, a dimeric Sc(III) structure was observed, in which  $\mu-OH$  moieties were bridged between two Sc(III) centers [12–14]. Therefore, the formal charge is 2+ in each of the Sc(III) centers. Moreover, a very rare coordination number of 7 for a  $Sc(III)^{2+}$  center was found in **6** [15]. The plane of  $[Sc-(\mu-O)]_2$  and the penta-



Scheme 1. Preparation of monomeric lanthanide(III) complexes with perfluoropropane-1,3-disulfonates.

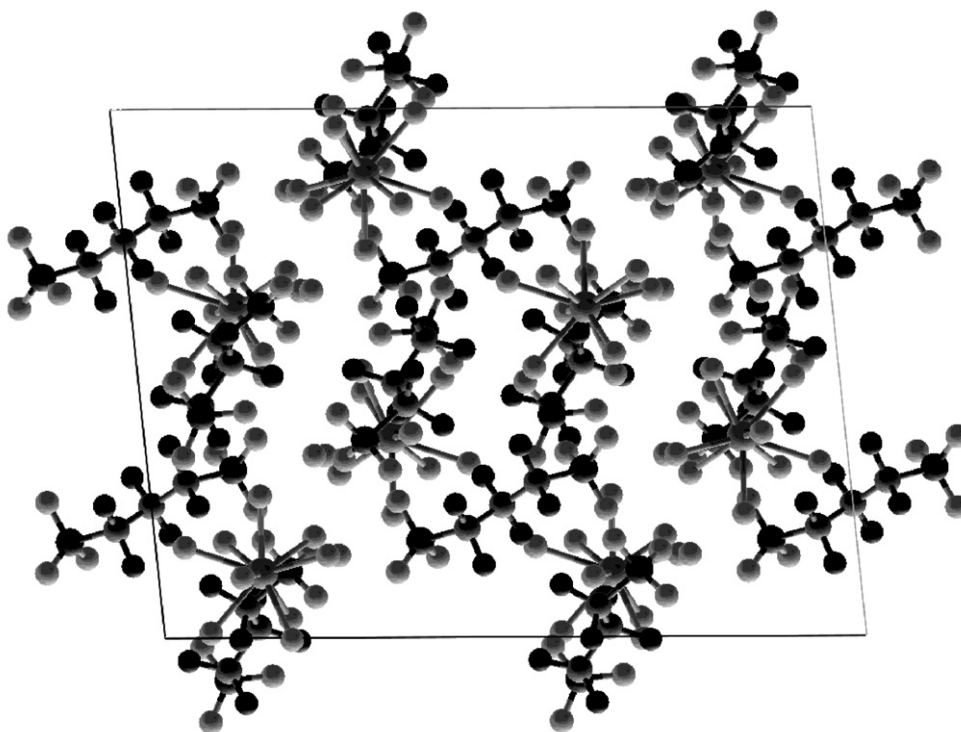


Fig. 1. Unit cell structure of neodymium(III) with perfluoropropane-1,3-disulfonates (**3**).

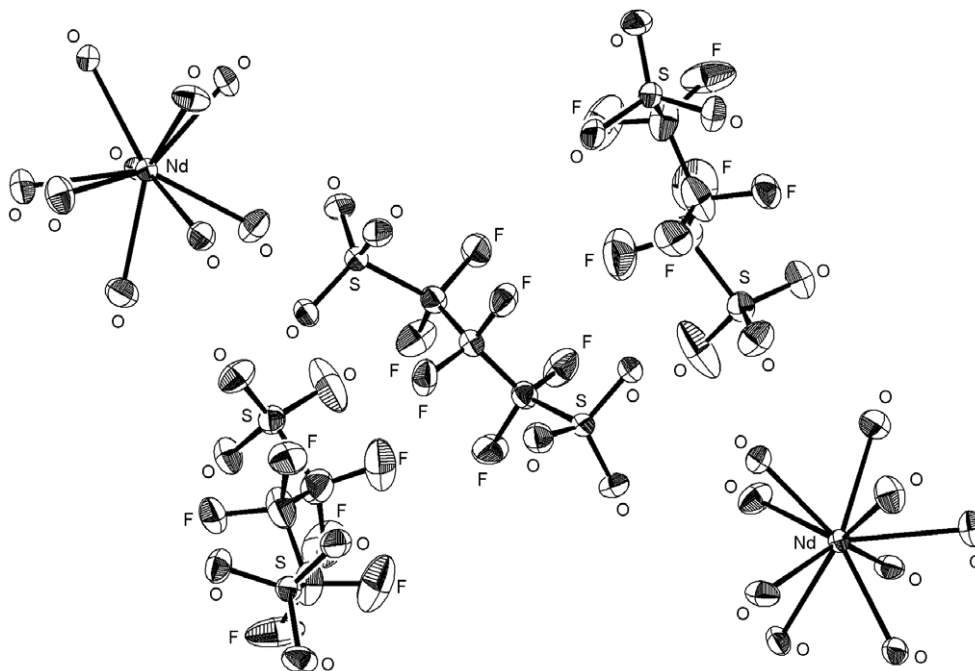


Fig. 2. ORTEP drawing of monomeric neodymium(III) with perfluoropropane-1,3-disulfonates (3). (Hydrogen atoms and free water molecules are omitted for clarity.)

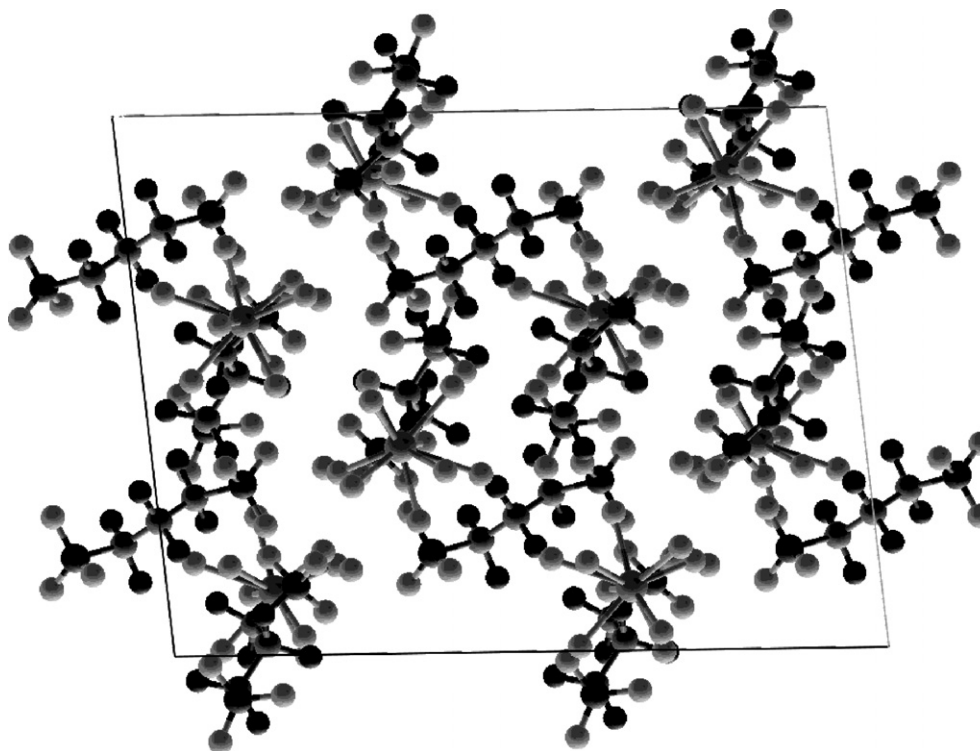


Fig. 3. Unit cell structure of samarium(III) with perfluoropropane-1,3-disulfonates (4).

nal plane of Sc(III) were not the same, and the dihedral angle was  $24.2\text{--}25.9^\circ$  [12]. The major distance or angles were  $2.060\text{--}2.084 \text{ \AA}$  for Sc-( $\mu$ -O),  $3.396\text{--}3.429 \text{ \AA}$  for Sc-Sc with no obvious interactions each other,  $68.75\text{--}69.92^\circ$  for Sc-( $\mu$ -O)-Sc, and  $110.08\text{--}111.25^\circ$  for ( $\mu$ -O)-Sc-( $\mu$ -O).

The shortest distance between  $\text{SO}_3$  and a Sc(III) center was  $4.093 \text{ \AA}$ , which indicated that perfluoropropane-1,3-disulfonates act as non-coordinating anions in 6. However, many hydrogen bonds were observed between the coordinating water ( $\text{H}_2\text{O}$ ) and disulfonates ( $\text{SO}_3$ ) in  $1.96\text{--}$

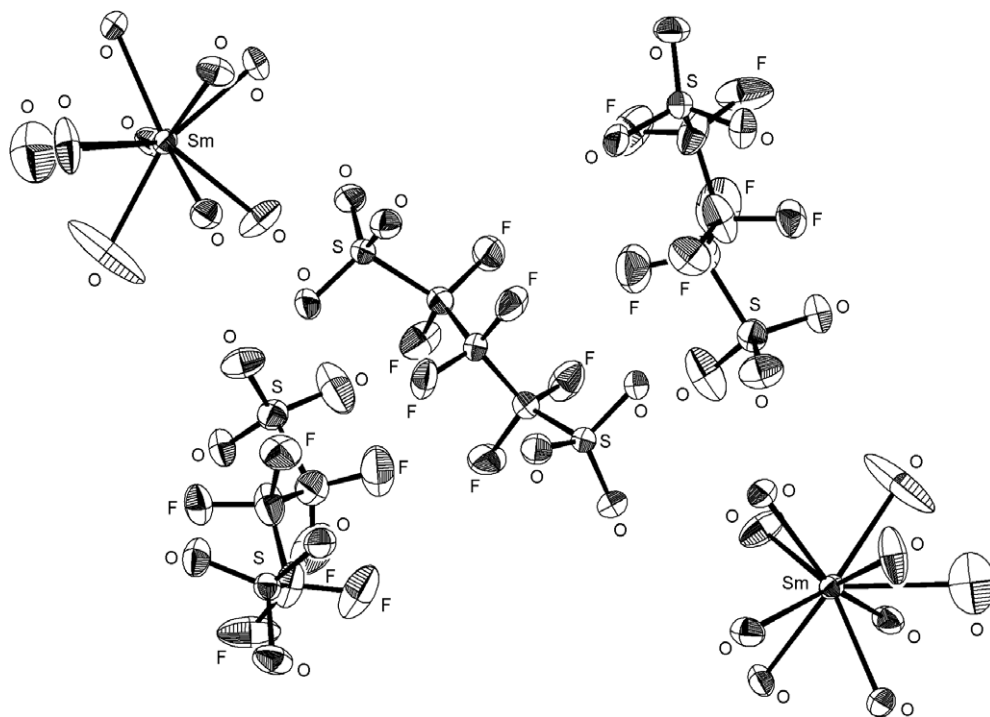


Fig. 4. ORTEP drawing of monomeric samarium(III) with perfluoropropane-1,3-disulfonates (**4**). (Hydrogen atoms and free water molecules are omitted for clarity.)

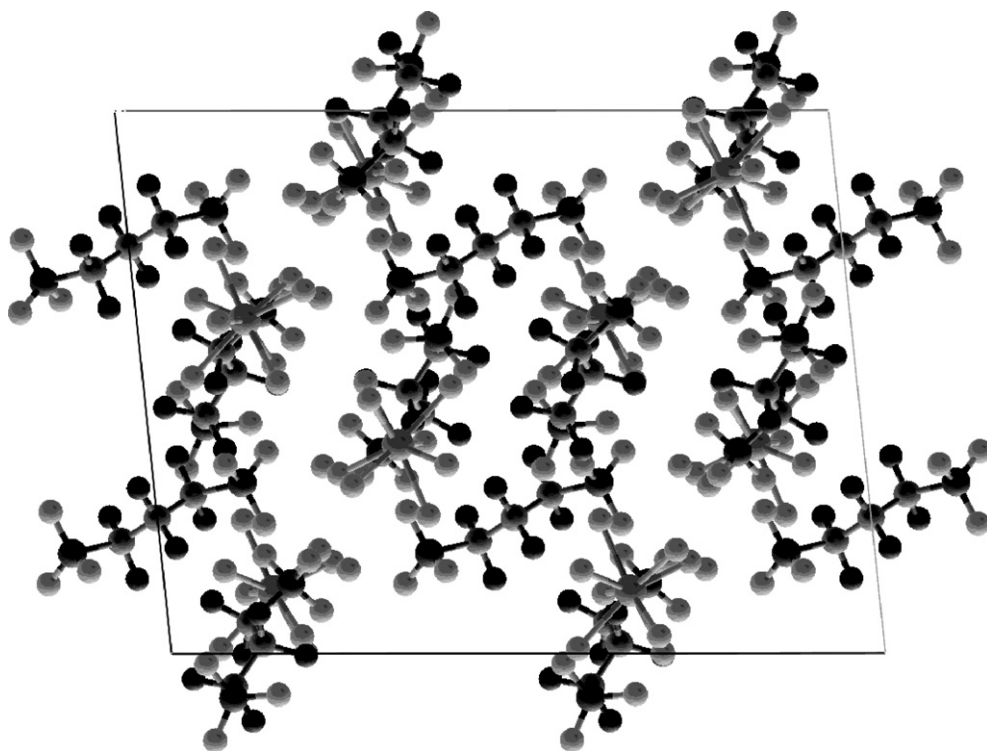


Fig. 5. Unit cell structure of gadolinium(III) with perfluoropropane-1,3-disulfonates (**5**).

2.16 Å. Thus, the cations and anions in crystal **6** also formed a *polymeric* network through hydrogen bonds, which should be notable in linear  $\alpha,\omega$ -disulfonate anions.

Partially due to this polymeric nature, the dimeric Sc(III) complex **6** is easy to handle and completely stable toward air and moisture since it is not hygroscopic.

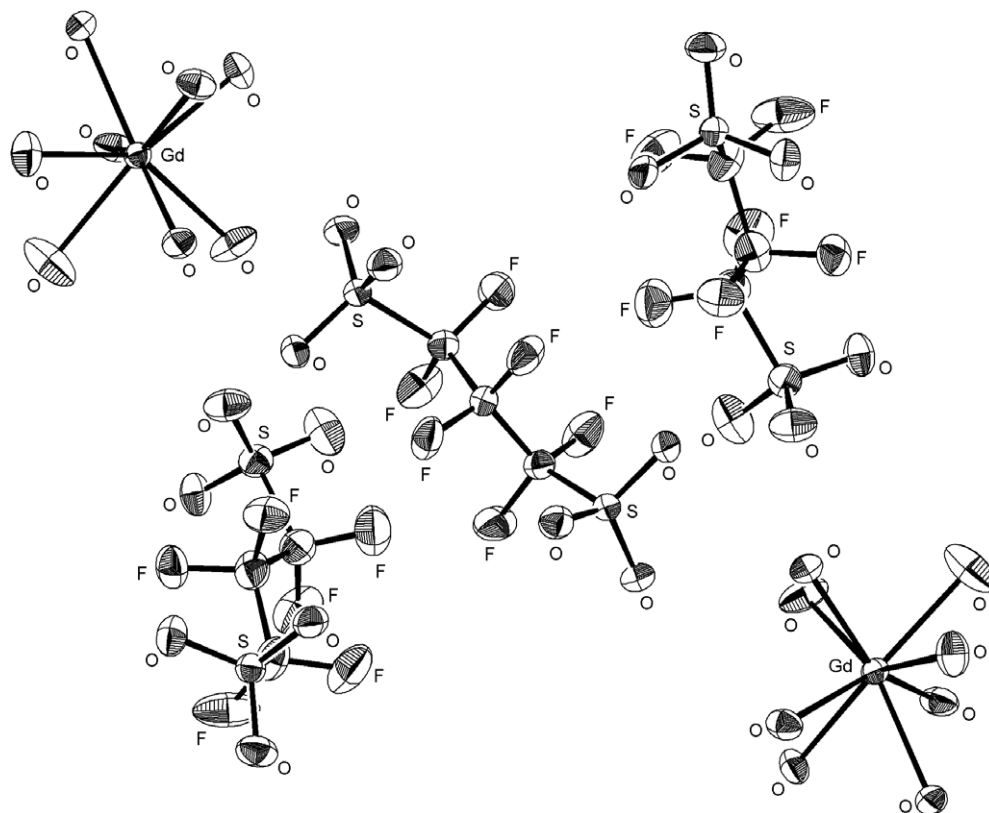
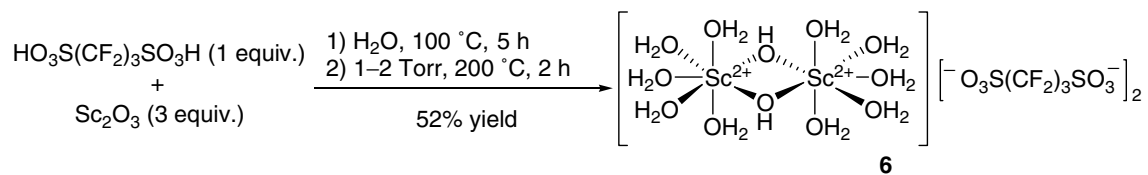


Fig. 6. ORTEP drawing of monomeric gadolinium(III) with perfluoropropane-1,3-disulfonates (5). (Hydrogen atoms and free water molecules are omitted for clarity.)



Scheme 2. Preparation of dimeric ( $\mu$ -OH)Sc(III) complex with perfluoropropane-1,3-disulfonates (6).

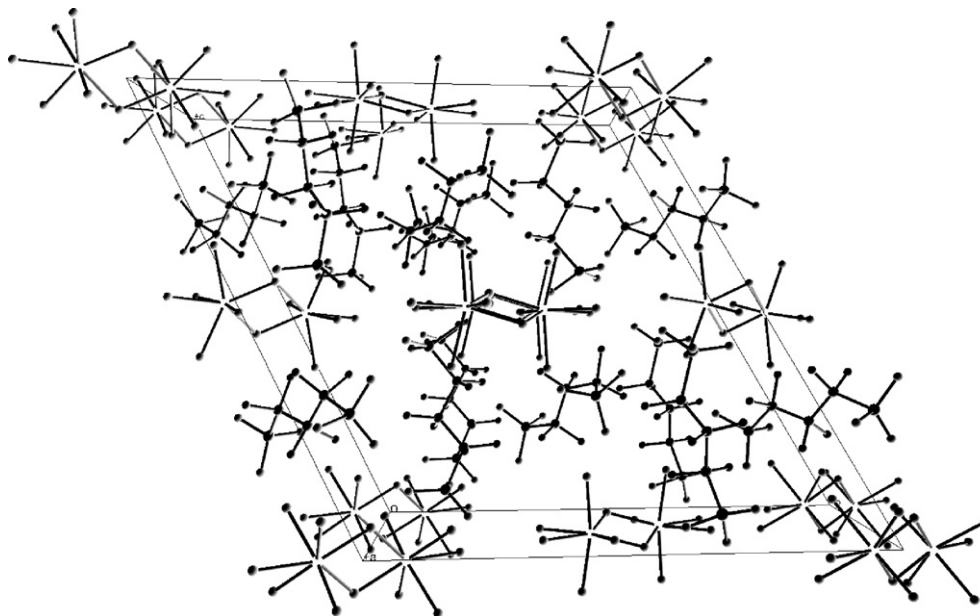


Fig. 7. Unit cell structure of scandium(III) with perfluoropropane-1,3-disulfonates (6).

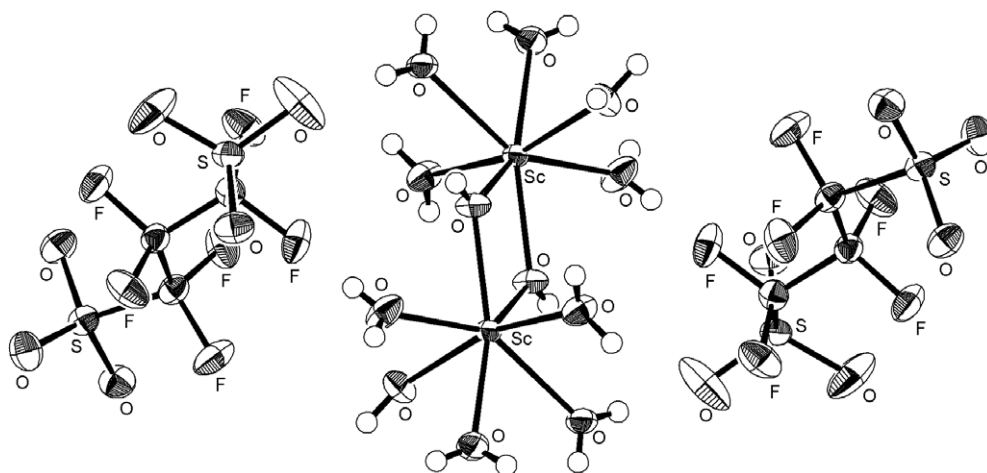
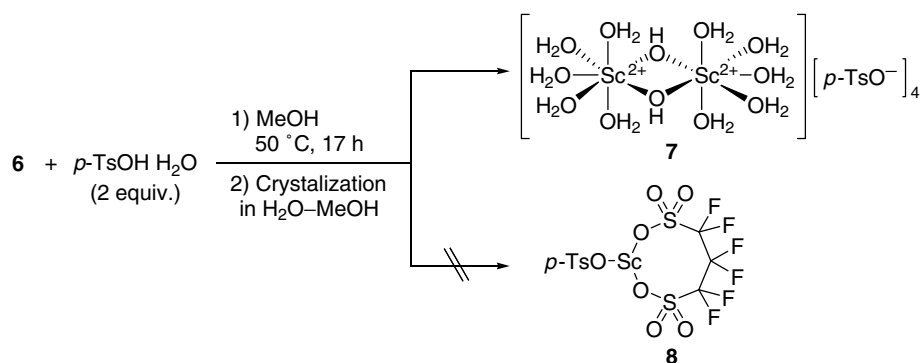


Fig. 8. ORTEP drawing of dimeric ( $\mu$ -OH)Sc(III) complex with perfluoropropane-1,3-disulfonates (**6**).



Scheme 3. Preparation of dimeric ( $\mu$ -OH)Sc(III) complex **7** by anion exchange reaction.

Interestingly, exchange of counter anions from perfluoropropane-1,3-disulfonates to *p*-toluenesulfonate ( $p$ -TsO<sup>-</sup>), instead of generating an expected monomeric complex **8**, occurred in a mixture of **6** (1 equiv.),  $p$ -TsOH · H<sub>2</sub>O (2 equiv.), and MeOH at 50 °C for 17 h (Scheme 3). The corresponding complex **7** bearing the coordinating water molecules had almost the same dimeric cation moiety to **6**. This exchange behavior was unusual because the strong acid (i.e. **1**) was released and the weak acid anion (i.e.  $p$ -TsOH) was paired with Sc(III) cations. The distance between SO<sub>3</sub> and a Sc(III) center in **7** was 4.28–4.37 Å, which was longer than that of **6**, with no obvious interactions with each other [16]. However, hydrogen bonds between the coordinating water molecules or the crystalline water molecules (H<sub>2</sub>O) and sulfonates (SO<sub>3</sub>) in **7** were observed in 1.87–2.07 Å, which was even shorter than that of **6**. Notably, the supramolecular interaction, which could be shown in **3–6** by the polymeric network through the linear *di*-sulfonates, disappeared in **7** bearing *mono*-sulfonate,

while weak  $\pi$ - $\pi$  interactions (3.78–4.00 Å) were observed among aromatic rings of TsO<sup>-</sup> moieties.

To evaluate the activity of the prepared catalysts, catalytic hydrolysis of methyl benzoate at 100 °C in 1,4-dioxane–H<sub>2</sub>O (*v/v* = 2/1) was examined using lanthanide(III) and scandium(III) complexes with perfluoropropane-1,3-disulfonates (**2–6**). 10 mol% of lanthanide(III) complexes with perfluoropropane-1,3-disulfonates (**2–5**) had low reactivity and gave the product in only 13–25% yield over 44 h (Table 1, entries 1–4). Obviously, these results were inferior to those with the corresponding Ln(OTf)<sub>3</sub> (Ln = La, Nd, Sm, and Gd) in the hydrolysis of methyl benzoate (brackets in entries 1–4). However, the reaction proceeded smoothly with 5 mol% of dimeric Sc(III)<sup>2+</sup> complex **6**, and the product, benzoic acid, was obtained in 96% yield over 36 h (entry 5). Therefore, the catalytic activity of the dimeric Sc(III)<sup>2+</sup> complex **6** was never inferior to that of Sc(III)<sup>3+</sup>(<sup>-</sup>OTf)<sub>3</sub> which gave the product in 97% yield over 36 h (bracket in entry 5). Hydrolysis of ethyl benzoate with 5 mol% of **6** also proceeded smoothly (entry 6). The key to promoting the reaction even with the Sc(III)<sup>2+</sup> complex



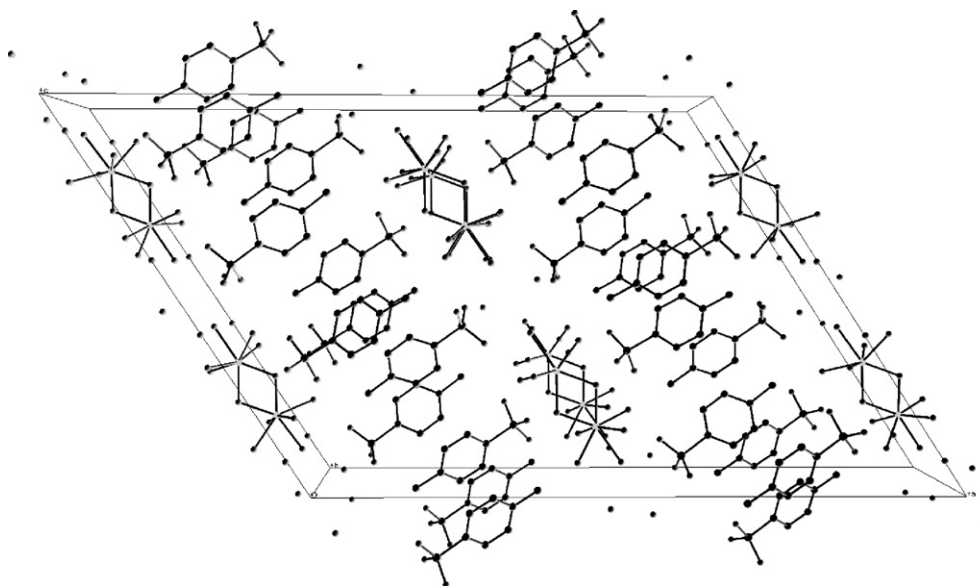
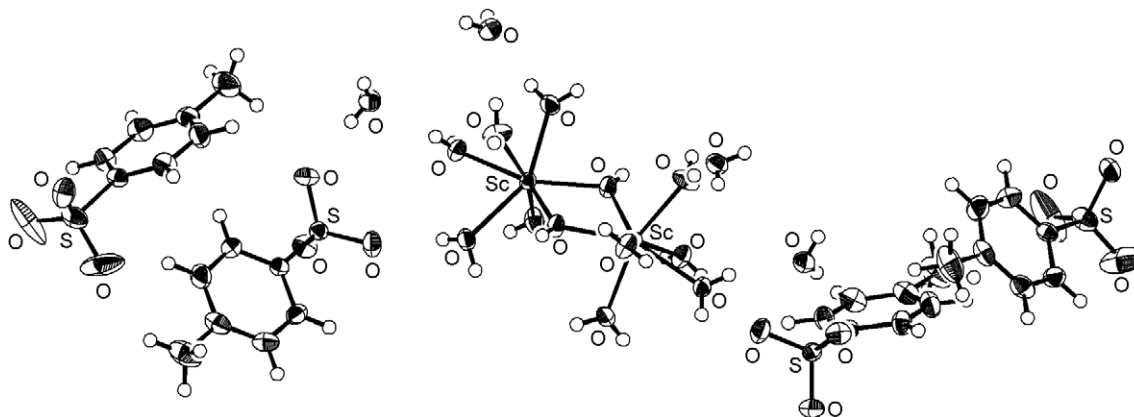
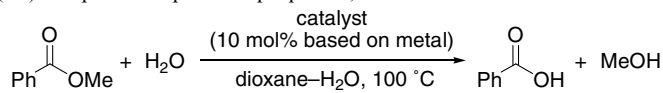
Fig. 9. Unit cell structure of scandium(III) with *p*-toluenesulfonate (7).Fig. 10. ORTEP drawing of dimeric ( $\mu$ -OH)Sc(III) complex with *p*-toluenesulfonate (7).

Table 1

Catalytic hydrolysis with Ln(III) or Sc(III) complex with perfluoropropane-1,3-disulfonates



Entry	Catalyst	Time (h)	Yield (%) <sup>a</sup>
1	[La(H <sub>2</sub> O) <sub>9</sub> ][O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>1.5</sub> (2)	44	13 [44] <sup>b</sup>
2	[Nd(H <sub>2</sub> O) <sub>9</sub> ][O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>1.5</sub> (3)	44	16 [32] <sup>b</sup>
3	[Sm(H <sub>2</sub> O) <sub>9</sub> ][O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>1.5</sub> (4)	44	18 [62] <sup>b</sup>
4	[Gd(H <sub>2</sub> O) <sub>8</sub> ][O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>1.5</sub> (5)	44	25 [43] <sup>b</sup>
5	[Sc( $\mu$ -OH)(H <sub>2</sub> O) <sub>5</sub> ] <sub>2</sub> [O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub> (6)	36	96 [97] <sup>b</sup>
6 <sup>c</sup>	[Sc( $\mu$ -OH)(H <sub>2</sub> O) <sub>5</sub> ] <sub>2</sub> [O <sub>3</sub> S(CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub> (6)	36	95 [98] <sup>b</sup>

<sup>a</sup> Isolated yield of benzoic acid.<sup>b</sup> Ln(OTf)<sub>3</sub> or Sc(OTf)<sub>3</sub> was used in place of 2–6.<sup>c</sup> Ethyl benzoate was used instead of methyl benzoate.

was probably the well-ordered dimeric structure of **6** with a total formula charge of +4, which might cause attractive interaction with a carbonyl moiety of the ester.

### 3. Conclusion

Novel scandium(III) and lanthanide(III) complexes with perfluoropropane-1,3-disulfonate as counter anions were synthesized for the first time [18]. By X-ray analysis, the corresponding scandium(III) complex,  $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_2[\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_2$  (**6**), was found to be a  $\mu\text{-OH}$ -bridged dimeric structure without bonding between the Sc(III) centers and perfluoropropane-1,3-disulfonates. In sharp contrast, a series of lanthanide(III) complexes had monomeric structures. The dimeric scandium(III) complex (**6**), but not monomeric lanthanide complexes, with perfluoropropane-1,3-disulfonates was a good Lewis acid catalyst for the hydrolysis of esters.

### 4. Experimental

#### 4.1. Preparation of perfluoropropane-1,3-disulfonates (**1**)

Potassium perfluoropropane-1,3-disulfonate  $[\text{K}(\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3\text{K})]$  (5.0 g, 12.9 mmol) dissolved in 10 mL of water were passed through a cation exchange column ( $\approx 100 \text{ cm}^3$ , Amberlite<sup>®</sup> IR-120H ion-exchange resin, Aldrich). The column was washed until neutral, and water was removed from the eluate. Remaining solid was dried *in vacuo* (1–2 Torr) at room temperature for 120 h (4.0 g, >99%). <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>OD)  $\delta$  –118.3 (2F), –113.1 (4F). IR(neat) 3519, 3457, 1657, 1308, 1240, 1146, 1091, 1047  $\text{cm}^{-1}$ . HRMS(FAB) calcd for  $\text{C}_3\text{HF}_6\text{O}_6\text{S}_2[\text{M-H}]^-$  310.9119, found 310.9121.

#### 4.2. Preparation of monomeric lanthanide(III) complex (**2–5**) bearing perfluoropropane-1,3-disulfonates as counter anions

Lanthanide(III) complexes (La, Nd, Sm, and Gd) with perfluoropropane-1,3-disulfonate could be prepared in 18–30% yields by the same procedure for the dinuclear Sc(III) complex (**6**).

##### 4.2.1. $[\text{La}(\text{H}_2\text{O})_n][\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_{1.5}$ (**2**)

<sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>OD)  $\delta$  –117.5 (2F), –111.8 (4F). IR(KBr) 3855, 1618, 1265, 1158, 1138, 1071, 1044, 848  $\text{cm}^{-1}$ .

##### 4.2.2. $[\text{Nd}(\text{H}_2\text{O})_9][\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_{1.5}$ (**3**)

X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods and expanded using Fourier techniques [17]. The single crystal of **3** was grown from H<sub>2</sub>O at room temperature for 24 h under open air condition. Formula  $\text{C}_9\text{H}_{40}\text{F}_{18}\text{Nd}_2\text{O}_{38}\text{S}_6$ , colorless, crystal

dimensions  $0.20 \times 0.10 \times 0.10 \text{ mm}^3$ , monoclinic, space group  $C2/c$  (#15),  $a = 22.140(5) \text{ \AA}$ ,  $b = 13.158(5) \text{ \AA}$ ,  $c = 16.760(5) \text{ \AA}$ ,  $\beta = 95.747(5)^\circ$ ,  $V = 4858(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 2.159 \text{ g cm}^{-3}$ ,  $F(000) = 3104$ ,  $\mu = 2.543 \text{ mm}^{-1}$ ,  $T = 223 \text{ K}$ . 6743 reflections collected, 5168 independent reflections with  $I > 2\sigma(I)$  ( $2\theta_{\text{max}} = 29.18^\circ$ ), and 412 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically.  $R_1 = 0.0461$  and  $wR_2 = 0.1208$ . GOF = 1.025. <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>OD)  $\delta$  –119.2 (2F), –114.1 (4F). IR(KBr) 3389, 1619, 1266, 1158, 1123, 1071, 1045, 848  $\text{cm}^{-1}$ .

##### 4.2.3. $[\text{Sm}(\text{H}_2\text{O})_9][\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_{1.5}$ (**4**)

The single crystal of **4** was grown from H<sub>2</sub>O at room temperature for 24 h under open air condition. Formula  $\text{C}_9\text{H}_{40}\text{F}_{18}\text{O}_{38}\text{S}_6\text{Sm}_2$ , colorless, crystal dimensions  $0.30 \times 0.10 \times 0.10 \text{ mm}^3$ , monoclinic, space group  $C2/c$  (#15),  $a = 22.042(3) \text{ \AA}$ ,  $b = 13.0652(19) \text{ \AA}$ ,  $c = 16.784(3) \text{ \AA}$ ,  $\beta = 95.851(3)^\circ$ ,  $V = 4808.4(12) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 2.198 \text{ g cm}^{-3}$ ,  $F(000) = 3120$ ,  $\mu = 2.852 \text{ mm}^{-1}$ ,  $T = 223 \text{ K}$ . 6389 reflections collected, 5607 independent reflections with  $I > 2\sigma(I)$  ( $2\theta_{\text{max}} = 29.14^\circ$ ), and 330 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically.  $R_1 = 0.0479$  and  $wR_2 = 0.1374$ . GOF = 1.051. <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>OD)  $\delta$  –118.1 (2F), –112.5 (4F). IR(KBr) 3389, 1620, 1266, 1158, 1138, 1071, 1045, 987  $\text{cm}^{-1}$ .

##### 4.2.4. $[\text{Gd}(\text{H}_2\text{O})_8][\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_{1.5}$ (**5**)

The single crystal of **5** was grown from H<sub>2</sub>O at room temperature for 24 h under open air condition. Formula  $\text{C}_9\text{H}_{36}\text{F}_{18}\text{Gd}_2\text{O}_{38}\text{S}_6$ , colorless, crystal dimensions  $0.40 \times 0.30 \times 0.30 \text{ mm}^3$ , monoclinic, space group  $C2/c$  (#15),  $a = 22.002(6) \text{ \AA}$ ,  $b = 13.063(4) \text{ \AA}$ ,  $c = 16.818(5) \text{ \AA}$ ,  $\beta = 95.931(5)^\circ$ ,  $V = 4808(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 2.168 \text{ g cm}^{-3}$ ,  $F(000) = 3056$ ,  $\mu = 3.163 \text{ mm}^{-1}$ ,  $T = 223 \text{ K}$ . 6339 reflections collected, 5780 independent reflections with  $I > 2\sigma(I)$  ( $2\theta_{\text{max}} = 29.09^\circ$ ), and 393 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically.  $R_1 = 0.0360$  and  $wR_2 = 0.1033$ . GOF = 1.069. IR(KBr) 3388, 1620, 1265, 1158, 1138, 1045, 848  $\text{cm}^{-1}$ .

#### 4.3. $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_2[\text{O}_3\text{S}(\text{CF}_2)_3\text{SO}_3]_2$ (**6**)

Sc<sub>2</sub>O<sub>3</sub> (1.41 g, 10.23 mmol) was added to a aqueous solution of perfluoropropane-1,3-disulfonic acid (1.065 g, 3.41 mmol) ( $\approx 50\%$  v/v), and the mixture was heated at 100 °C for 5 h. After filtration through a pad of Celite<sup>®</sup> to remove the powdery unreacted Sc<sub>2</sub>O<sub>3</sub>, the water was evaporated under reduced pressure. The resulting white powder was dried by heating *in vacuo* (1–2 Torr) at 200 °C for 2 h (0.828 g, 52.5%). The single crystal of **5** was grown from H<sub>2</sub>O at room temperature for 24 h under open air condition. Formula  $\text{C}_{12}\text{H}_{44}\text{F}_{24}\text{O}_{48}\text{S}_8\text{Sc}_4$ , colorless, crystal dimensions  $0.40 \times 0.20 \times 0.15 \text{ mm}^3$ , monoclinic, space group  $P\bar{1}$  (#2),  $a = 9.7075(14) \text{ \AA}$ ,  $b = 18.542(3) \text{ \AA}$ ,



$c = 19.352(3) \text{ \AA}$ ,  $\alpha = 116.268(2)^\circ$ ,  $\beta = 101.677(3)^\circ$ ,  $\gamma = 95.814(3)^\circ$ ,  $V = 2985.9(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 2.056 \text{ g cm}^{-3}$ ,  $F(000) = 1856$ ,  $\mu = 0.901 \text{ mm}^{-1}$ ,  $T = 223 \text{ K}$ . 15290 reflections collected, 12266 independent reflections with  $I > 2\sigma(I)$  ( $2\theta_{\text{max}} = 29.21^\circ$ ), and 1162 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically.  $R_1 = 0.0413$  and  $wR_2 = 0.1020$ . GOF = 1.035.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$   $-118.1$  (2F),  $-112.8$  (4F). IR(KBr) 3855, 1618, 1266, 1158, 1045,  $848 \text{ cm}^{-1}$ .

#### 4.4. $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_2(\text{p-TsO})_4$ (7)

The single crystal of **7** was grown from a mixture of **6** (20.0 mg, 0.0216 mmol),  $\text{TsOH} \cdot \text{H}_2\text{O}$  (8.1 mg, 0.0432 mmol), and  $\text{H}_2\text{O}$ –MeOH at room temperature under open air condition. Formula  $\text{C}_{14}\text{H}_{29}\text{O}_{14}\text{S}_2\text{Sc}$ , colorless, crystal dimensions  $0.20 \times 0.15 \times 0.15 \text{ mm}^3$ , monoclinic, space group  $C2/c$  (#15),  $a = 32.536(3) \text{ \AA}$ ,  $b = 7.4093(8) \text{ \AA}$ ,  $c = 23.538(2) \text{ \AA}$ ,  $\beta = 123.277(2)^\circ$ ,  $V = 4744.0(9) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_{\text{calc}} = 1.485 \text{ g cm}^{-3}$ ,  $F(000) = 2224$ ,  $\mu = 0.549 \text{ mm}^{-1}$ ,  $T = 223 \text{ K}$ . 6303 reflections collected, 5140 independent reflections with  $I > 2\sigma(I)$  ( $2\theta_{\text{max}} = 29.15^\circ$ ), and 342 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically.  $R_1 = 0.0398$  and  $wR_2 = 0.1004$ . GOF = 1.040.

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#### Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary publication nos. for complexes **3–7** are CCDC-297410, CCDC-297411, CCDC-297412, CCDC-297413 and CCDC-298148, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.057.

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