DALTON
FULL PAPER

Syntheses and characterization of mixed acetylacetonate–catecholate complexes of zirconium, $[Zr_3(acac)_4(cat)_4(MeOH)_2]$, $[Zr(acac)_2(DBcat)]_2$ (H_2DBcat = 3,5-di-*tert*-butylcatechol) and $[Zr_4(\mu_4\text{-}O)(acac)_4(DBcat)_3(OMe)_4(MeOH)]$

Yun Chi,[*a] **Jing-Wen Lan,**[a] **Wei-Li Ching,**[a] **Shie-Ming Peng**[b] **and Gene-Hsiang Lee**[b]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China. E-mail: ychi@mx.nthu.edu.tw*
[b] *Department of Chemistry and Instrumentation Center, National Taiwan University, Taipei 10764, Taiwan, Republic of China*

Received 5th April 2000, Accepted 6th July 2000
Published on the Web 8th August 2000

Reactions of the acetylacetonate complex $[Zr(acac)_4]$ with catechols have been investigated. Two crystalline complexes $[Zr_3(acac)_4(cat)_4(MeOH)_2]$ **1** and $[Zr(acac)_2(DBcat)]_2$ **2** (H_2DBcat = 3,5-di-*tert*-butylcatechol) are isolated from the respective reactions in toluene, and their solid-state structures established by X-ray diffraction studies. Complex **2** consists of an edge-shared capped trigonal prismatic structure involving two symmetry related $[Zr(acac)_2(DBcat)]$ units, while **1** is best visualized as a Zr_3 complex, possessing two $[Zr(acac)_2(cat)(MeOH)]$ units linked to the central $[Zr(cat)_2]$ fragment *via* four bridging catecholate ligands. Their reactivity was investigated; treatment of **2** with a trace amount of water in a solution of methanol and CH_2Cl_2 gave a Zr_4 oxo complex $[Zr_4(\mu_4\text{-}O)(acac)_4(DBcat)_3(OMe)_4(MeOH)]$ **3**.

There is a considerable current interest in developing the chemistry of zirconium alkoxides, aryl oxides and their derivative complexes so as to provide better source reagents for the generation of zirconium dioxide ZrO_2 or other zirconium-containing oxide materials,[1] such as lead zirconium titanate $Pb(Zr,Ti)O_3$[2] or lanthanide doped zirconia.[3] Several synthetic routes to these zirconium oxides have been investigated, including sol–gel methods, hydrothermal synthesis, physical vapor deposition (sputtering or laser ablation) and chemical vapor deposition.[4] The success of these methodologies heavily relied on understanding of the basic physical and chemical properties of the zirconium source reagents, such as the relative volatility, chemical reactivity in the gas phase, solution state, or even in the presence of protic solvents such as alcohol and water.

The precursors typically used for such investigations include metal β-diketonates such as $[Zr(acac)_4]$ and $[Zr(tmhd)_4]$[5] tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate, or various alkoxide complexes such as $Zr(OBu^n)_4$, $[Zr_2(OPr^i)_8(HOPr^i)_2]$ and $[Zr_2(OPr^i)_6(tmhd)_2]$.[6] Their chemical and physical properties differ greatly; for example, the alkoxide and aryl oxide complexes are highly sensitive towards moisture, so that the use of these reagents needs special attention to avoid hydrolytic decomposition. On the other hand, diketonate complexes, $[Zr(acac)_4]$ and $[Zr(tmhd)_4]$, tend to be inert towards various chemical reagents at lower temperature and an elevated temperature is required for converting them into the final oxide products.

In efforts to search for new and better source reagents that can be converted into the oxide ceramics as well as to examine the fundamental co-ordination chemistry of zirconium diketonate and alkoxide complexes, we have studied the reactivity of $Zr(acac)_4$ with catechol (H_2cat) and 3,5-di-*tert*-butylcatechol (H_2DBcat). The catechols are attractive starting materials since they are easy to access, inexpensive, highly soluble in hydrocarbon solvents, and have the ability to form stable metal complexes by chelation.[7] In addition, the catechol molecule has the potential to release two protons during formation of a metal complex, giving stable dianionic forms such as cat^{2-} or $DBcat^{2-}$. This indicates that catecholate is able to replace two equivalent diketonate ligands based on the principle of charge balance; thus, upon addition of one catecholate ligand, it reduces the total co-ordination number by two at Zr, making the product complex more reactive and possessing a greater tendency to form strongly associated aggregates.

Experimental

General information and materials

$[Zr(acac)_4]$ was purchased from Strem Chemical, while catechol and 3,5-di-*tert*-butylcatechol were from Aldrich Chemical Co. Solvents were reagent grade dried over appropriate drying agents before use. As all products are highly air-sensitive, the manipulation of compounds was carried under an inert atmosphere such as nitrogen. ^1H NMR spectra were recorded on a Bruker AMX-400 instrument. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of $[Zr(acac)_4]$ with catechol

A toluene (35 mL) solution of $[Zr(acac)_4]$ (3.0 g, 6.16 mmol) and catechol (0.9 g, 8.2 mmol) was heated at reflux for 4 h, during which the solution changed from colorless to yellow. After cooling to room temperature, evaporation of the solvent *in vacuo* produced a light yellow oily residue. Recrystallization from a homogeneous mixture of CH_2Cl_2 and MeOH at room temperature afforded the yellow crystalline solid $[Zr_3(acac)_4(cat)_4(MeOH)_2]$ **1** (1.58 g, 1.13 mmol, 55%). ^1H NMR (400 MHz, methanol-d_4, 298 K): δ 6.95–6.93 (m, 4 H), 6.85–6.82 (m, 4 H), 6.62 (br, 8 H) and 2.22 (br, 18 H). Calc. for $C_{46}H_{50}O_{18}Zr_3$: C, 47.52; H, 4.30. Found: C, 46.74; H, 4.13%.

DOI: 10.1039/b002705g

Reaction of $[Zr(acac)_4]$ with H_2DBcat

A toluene (35 mL) solution of $[Zr(acac)_4]$ (2.0 g, 4.1 mmol) and 3,5-di-*tert*-butylcatechol (1.0 g, 4.5 mmol) was heated at reflux for 4 h. Then the solution was cooled to room temperature, and the solvent evaporated *in vacuo* to produce an oily residue. Recrystallization from a mixed solution of CH_2Cl_2 and hexane at room temperature afforded the light yellow crystalline solid $[Zr_2(acac)_4(DBcat)_2]$ **2** (0.94 g, 0.82 mmol, 45%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.11 (d, $J_{HH} = 2.0$, 2 H), 6.69 (d, $J_{HH} = 2.0$ Hz, 2 H), 5.63 (s, 4 H, CH), 1.89 (s, 24 H, 8 Me), 1.26 (s, 18 H, 2 Bu^t) and 1.24 (s, 18 H, 2 Bu^t). Calc. for $C_{24}H_{34}O_6Zr$: C, 56.55; H, 5.67. Found: C, 56.23; H, 5.78%.

Reaction of $[Zr_2(acac)_4(DBcat)_2]$ with methanol and water

Complex $[Zr_2(acac)_4(DBcat)_2]$ **2** (0.94 g, 0.82 mmol) was dissolved in a mixed solution of CH_2Cl_2 (4 mL), CH_3OH (2 mL) and a trace amount of water (10 μL) by gentle heating. Keeping this solution at room temperature led to the formation of a new compound $[Zr_4(\mu_4\text{-}O)(acac)_4(DBcat)_3(OMe)_4(MeOH)]$ **3** (0.73 g, 0.38 mmol, 90%) as light yellow needles. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.54 (d, $J_{HH} = 2.0$, 3 H), 6.16 (d, $J_{HH} = 2.0$ Hz, 3 H), 5.85 (s, 4 H, CH), 3.78 (s, 15 H, OMe), 2.03 (s, 24 H, 8 Me), 1.24 (s, 27 H, 4 Bu^t) and 1.13 (s, 27 H, 4 Bu^t). Calc. for $C_{73}H_{122}Cl_6O_{23}Zr_4$: C, 45.07; H, 6.32. Found: C, 44.91; H, 6.18%.

X-Ray crystallography

Single crystal X-ray diffraction data were measured on a Nonius CAD-4 (**2**, **3**) or Bruker SMART CCD diffractometer (**1**) using Mo-Kα radiation $\lambda = 0.7107$ Å. On the CCD diffractometer the data collection was executed using the SMART program.[15] Crystal decay was monitored by repeating the data collection for the initial 50 frames and at the end of the experiment. Cell refinement and data reduction were made by using the SAINT program.[15] The structure was solved by the direct method using the SHELXTL/PC program.[16] Anisotropic displacement parameters were used for all non-hydrogen atoms, while the hydrogen atoms were given fixed isotropic displacement parameters.

Crystallographic refinement parameters of compounds **1**, **2** and **3** are summarized in Table 1; selected bond distances and angles are presented in Tables 2, 3 and 4, respectively.

CCDC reference number 186/2081.

See http://www.rsc.org/suppdata/dt/b0/b002705g/ for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization

The readily available zirconium precursor $[Zr(acac)_4]$ reacts with catechol in toluene over a period of 4 h at reflux to form a pale yellow solution. Upon recrystallization from a mixture of CH_2Cl_2 and MeOH, complex **1** is obtained in moderate yield according to eqn. (1).

$$3\,[Zr(acac)_4] + 4\,H_2cat + 2\,MeOH \longrightarrow [Zr_3(acac)_4(cat)_4(MeOH)_2]\ \mathbf{1} + 8\,Hacac \qquad (1)$$

The yield of reaction was optimized by using 1.33 equivalents of catechol after knowing the molecular formula of product **1**. The ^1H NMR spectrum of **1** in CD_2Cl_2 or even in CD_3OD is not structurally significant, showing two broad signals in the area for aromatic protons of the catecholate ligand (δ 6.95–6.62) and for CH_3 groups of the acac ligand (δ 2.22). The broadened NMR signals suggest the occurrence of a ligand rearrangement process in solution, which is probably induced by dissociation of the co-ordinated methanol, making the Zr_3 complex unsaturated and increasing the ligand mobility. In addition to these broadened signals, a set of weak signals at δ 3.53 and 2.37 with approximate ratio of 1 : 6 were observed, which are identical to those of the free acetylacetone molecule. The most logical explanation is that complex **1** is relatively unstable in solution and can release some of its acac ligand into solution through slow hydrolysis during measurement of the NMR spectrum. A variable temperature NMR study was carried out in an attempt to investigate the solution fluxionality. However, no obvious change in line shape was observed for all signals in the temperature range −50 to 50 °C, suggesting that the catecholate and the acac ligands are in exchange at an intermediate rate on the NMR timescale.

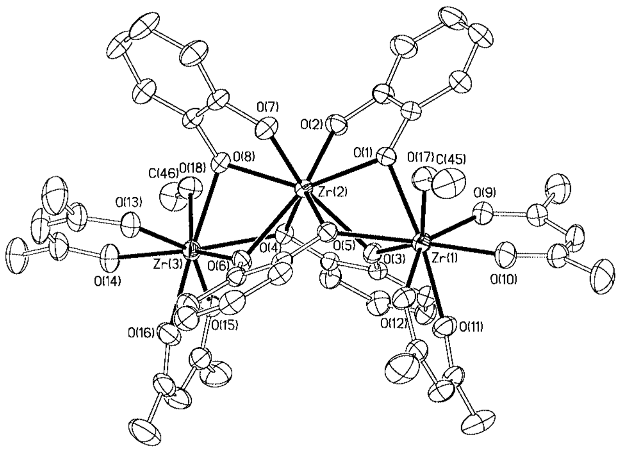

Fig. 1 An ORTEP[9] drawing of complex **1** with thermal ellipsoids shown at the 30% probability level (as in all cases).

The X-ray structural determination suggests that crystals of complex **1** consist of a mixed acetylacetonate and catecholate and two methanol ligands with two non-co-ordinated methanol solvate molecules and another 2.5 equivalents of CH_2Cl_2 solvate molecules packed within the unit cell. The structure of the Zr_3 complex is illustrated in Fig. 1; selected bond lengths and angles are shown in Table 2. The complex is trimeric comprising three zirconium atoms, two methanol molecules, four acac and four catecholate ligands. The Zr · · · Zr distances are non-bonding at 3.3515(5) and 3.3560(5) Å, and are at the long end of the range reported for the Zr_2 mixed alkoxide complexes (3.31–3.50 Å).[8] All three Zr atoms are 8-co-ordinated, having approximate square antiprismatic geometry. The central Zr atom is co-ordinated by all four catecholate ligands, of which two oxygen atoms adopt a terminal bonding mode with short Zr–O distances of 2.099(3) and 2.111(3) Å, while the other six catecholate oxygen atoms are bridging and linked to the Zr atoms at the outer positions. For these outer Zr atoms, their ligand sphere is completed by the further addition of two chelating acac ligands and a neutral methanol molecule. The Zr–O–C(methanol) angles are acute, 130.9(3) and 131.9(3)°. The Zr–O(methanol) bond distances fall into the range 2.255(3)–2.294(3) Å, longer than the Zr–O(acac) bond distances, 2.125(3)–2.173(3) Å. These variations in Zr–O bond distances are a clear indication for the involvement of methanol in the bonding to Zr.

In efforts to extend the scope of the mixed catecholate complexes, we then carried out the reaction of $[Zr(acac)_4]$ with 3,5-di-*tert*-butylcatechol (H_2DBcat), since the bulky *tert*-butyl substituents on H_2DBcat would make the formation of the analogous trimeric complex very difficult, due to the unfavorable steric interaction generated between the DBcat ligands. As a result, the product formed is a Zr_2 complex, $[Zr(acac)_2(DBcat)]_2$ **2**, comprising four acac and two DBcat ligands, eqn. (2). No other stable metal complex was isolated by varying the ratio of H_2DBcat ligand to the starting material $Zr(acac)_4$.

$$2\,[Zr(acac)_4] + 2\,H_2DBcat \longrightarrow [Zr(acac)_2(DBcat)]_2\ \mathbf{2} + 4\,Hacac \qquad (2)$$

Table 1 X-Ray structural data of complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{50.5}H_{63}Cl_5O_{20}Zr_3$	$C_{48}H_{68}O_{12}Zr_2$	$C_{73}H_{122}Cl_6O_{23}Zr_4$
M	1440.92	1019.46	1398.49
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.9458(2)	9.439(2)	13.234(3)
b/Å	14.1348(3)	11.641(3)	14.387(3)
c/Å	17.1990(3)	13.567(4)	25.277(4)
α/°	87.015(1)	113.63(3)	75.95(2)
β/°	87.615(1)	94.22(3)	85.39(2)
γ/°	67.292(1)	101.89(3)	82.52(2)
V/Å^3	3122.4(1)	1316.0(6)	4623(2)
Z	2	1	2
μ(Mo-Kα)/cm^{-1}	7.73	4.50	6.67
Reflections collected	37666	4638	16301
Independent reflections	12767 ($R_{\text{int}} = 0.0373$)	4638 ($R_{\text{int}} = 0.0000$)	10349 ($I \geq 2\sigma(I)$)
R_F; R_{wF^2} [$I > 2\sigma(I)$]	0.045; 0.115	0.032; 0.089	0.049; 0.052

Table 2 Selected bond distances (Å) and angles (°) of compound **1** (e.s.d.s in parentheses)

Zr(1)···Zr(2)	3.3560(5)	Zr(2)···Zr(3)	3.3515(5)
Catecholate ligands			
Zr(1)–O(1)	2.231(2)	Zr(2)–O(1)	2.218(2)
Zr(2)–O(2)	2.111(3)	Zr(1)–O(3)	2.224(2)
Zr(2)–O(3)	2.211(2)	Zr(2)–O(4)	2.209(2)
Zr(3)–O(4)	2.236(2)	Zr(1)–O(5)	2.219(2)
Zr(2)–O(5)	2.199(2)	Zr(2)–O(6)	2.228(2)
Zr(3)–O(6)	2.207(2)	Zr(2)–O(7)	2.099(3)
Zr(2)–O(8)	2.215(2)	Zr(3)–O(8)	2.235(3)
acac ligands			
Zr(1)–O(9)	2.125(3)	Zr(1)–O(10)	2.173(3)
Zr(1)–O(11)	2.142(3)	Zr(1)–O(12)	2.146(3)
Zr(3)–O(13)	2.130(3)	Zr(3)–O(14)	2.167(3)
Zr(3)–O(15)	2.127(3)	Zr(3)–O(16)	2.141(3)
Methanol ligands			
Zr(1)–O(17)	2.255(3)	Zr(3)–O(18)	2.294(3)
Zr(1)–O(17)–C(45)	131.9(3)	Zr(3)–O(18)–C(46)	130.9(3)

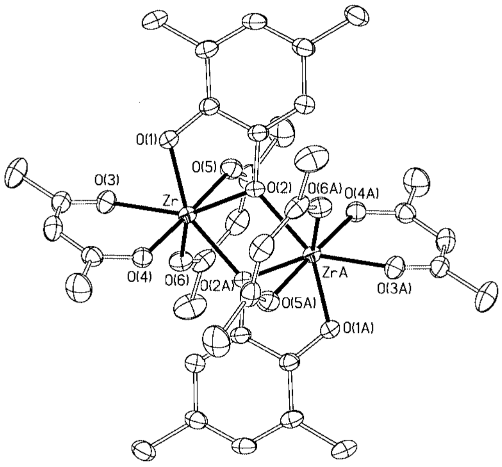

Fig. 2 An ORTEP drawing of complex **2** with the methyl groups of the *tert*-butyl substituents removed for clarity.

The molecular structure of compound **2** is shown in Fig. 2. It possesses two crystallographically related Zr(acac)$_2$(DBcat) units which are linked to each other through two oxygen atoms of the bridging catecholate ligands. Each Zr is further surrounded by five terminal oxygen atoms, four from the acac ligands and one from the remaining oxygen atom of the catecholate. The geometry around the Zr atom can be visualized as an approximate capped trigonal prism, just as in the related 7-co-ordinated acetylacetonate–alkoxide complex [Zr(acac)$_3$(OC$_6$H$_4$NO$_2$-4)].[10] The average Zr–O distance is 2.135 Å, with the shortest distance (Zr–O(1) 2.040(2) Å) involving the terminal-bound oxygen atom of the catecholate ligand; the latter is similar to the aryl Zr–O distance of 2.045(3) Å observed in [Zr(acac)$_3$(OC$_6$H$_4$NO$_2$-4)]. The non-bonding Zr···Zr distance is 3.640(1) Å, significantly longer than the distances observed in **1** and those of all other zirconium alkoxide complexes (3.31–3.50 Å). This increase in the Zr···Zr separation is further substantiated by the acute O(2)–Zr–O(2A) bite angle 66.90(7)° and the large Zr–O(2)–Zr(A) angle 113.10(7)° observed, which confirms the enhanced steric repulsion between the acac and the DBcat ligands.

Table 3 Selected bond distances (Å) and angles (°) of compound **2** (e.s.d.s in parentheses)

Zr···Zr(A)	3.640(1)	Zr–O(1)	2.040(2)
Zr–O(2)	2.204(2)	Zr–O(2A)	2.159(2)
Zr–O(3)	2.146(2)	Zr–O(4)	2.114(2)
Zr–O(5)	2.127(2)	Zr–O(6)	2.154(2)
O(2)–Zr–O(2A)	66.90(7)	Zr–O(2)–Zr(A)	113.10(7)

The identification of the ^{1}H NMR spectrum becomes an easy task after establishing the crystal structure. The spectrum of **2** recorded in CDCl$_3$ reveals two aromatic proton signals at δ 7.11 and 6.69 and a sharp CH signal of the acac ligand at δ 5.63 with a relative intensity ratio of 2:2:4, followed by three intense signals at δ 1.89, 1.26 and 1.24 with ratio of 24:18:18 in the methyl region. This pattern confirms that two acac ligands of the Zr(acac)$_4$ starting materials have successfully been replaced by one H$_2$DBcat molecule.

Hydrolysis reaction

Repeated recrystallization of compound **1** in a mixture of CH$_2$Cl$_2$ and methanol at room temperature led to the formation of an oily material. This cannot be converted back into the crystalline complex **1**, suggesting the occurrence of some decomposition. In contrast, treatment of **2** with a mixture of CH$_2$Cl$_2$, methanol and a trace amount of water under similar conditions gave a light yellow, needle-like crystalline material (**3**), of which the morphology is obviously different from that of complex **2**. The transformation that leads to formation of complex **3** is best represented by eqn. (3). The ^{1}H NMR spectrum of **3** gives the resonance signals expected for the acac, DBcat and methanol ligands in an approximate ratio

Table 4 Selected bond distances (Å) of compound **3** (e.s.d.s in parentheses)

Zr(1)···Zr(2)	3.371(1)	Zr(1)···Zr(3)	3.580(1)
Zr(1)···Zr(4)	3.561(1)	Zr(2)···Zr(3)	3.545(1)
Zr(2)···Zr(4)	3.545(1)	Zr(3)···Zr(4)	3.449(1)
Oxide			
Zr(1)–O(1)	2.225(4)	Zr(2)–O(1)	2.214(4)
Zr(3)–O(1)	2.097(4)	Zr(4)–O(1)	2.074(4)
Acetylacetonate			
Zr(1)–O(8)	2.195(4)	Zr(1)–O(9)	2.163(4)
Zr(2)–O(10)	2.169(4)	Zr(2)–O(11)	2.191(4)
Zr(3)–O(12)	2.122(4)	Zr(3)–O(13)	2.165(4)
Zr(4)–O(14)	2.156(4)	Zr(4)–O(15)	2.121(5)
Catecholate			
Zr(1)–O(2)	2.185(4)	Zr(1)–O(4)	2.053(4)
Zr(1)–O(5)	2.241(4)	Zr(1)–O(6)	2.282(4)
Zr(2)–O(2)	2.261(4)	Zr(2)–O(3)	2.047(4)
Zr(2)–O(5)	2.190(4)	Zr(3)–O(6)	2.167(4)
Zr(3)–O(7)	2.089(4)		
Methoxide			
Zr(1)–O(16)	2.234(4)	Zr(4)–O(16)	2.113(4)
Zr(2)–O(17)	2.192(4)	Zr(3)–O(17)	2.153(4)
Zr(2)–O(18)	2.303(4)	Zr(4)–O(18)	2.085(4)
Zr(3)–O(19)	2.159(4)	Zr(4)–O(19)	2.143(4)
Zr(4)–O(20)	2.256(5)		

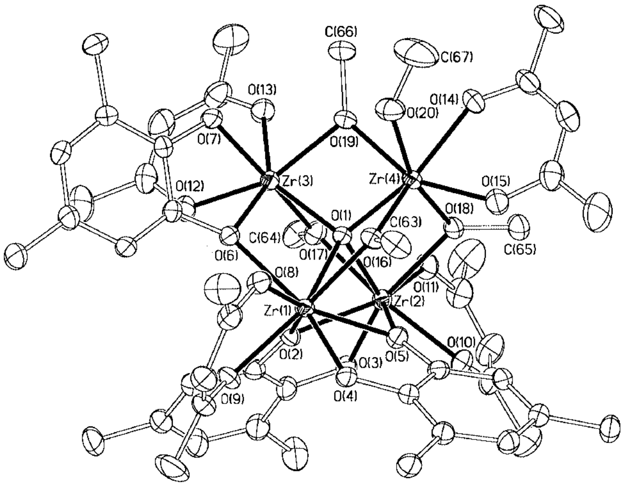

Fig. 3 An ORTEP drawing of complex **3** with the methyl groups of the *tert*-butyl substituents removed for clarity.

$$2\,[Zr(acac)_2(DBcat)]_2 + 5\,MeOH + H_2O \longrightarrow [Zr_4(\mu_4\text{-}O)(acac)_4(DBcat)_3(OMe)_4(MeOH)]\ \mathbf{3} + 4\,Hacac + H_2DBcat \quad (3)$$

of 3:4:5, giving preliminary information about the type of ligands co-ordinated and their relative ratio. Again, as the ^{1}H NMR data are not structurally significant, a single crystal X-ray diffraction study was carried out to establish the exact molecular structure.

Complex **3** is a tetrameric cluster whose structure is shown in Fig. 3 and selected bond distances are listed in Table 4. The basic constructs of the central core consists of four Zr metal atoms co-ordinated to a unique, central μ_4-O oxide ligand. The range of the Zr–O distances 2.074(2)–2.225(4) Å is analogous to that of the Zr–O(oxide) distances (2.11–2.23 Å) in the related oxo complexes $[PbZr_3(\mu_4\text{-}O)(OAc)_2(OPr^i)_{10}]$ and $[Zr_3(\mu_3\text{-}O)(OBu^t)_{10}]$.[11] The resultant $Zr_4(\mu_4\text{-}O)$ core of complex **3** forms a slightly distorted tetrahedral arrangement with non-bonding Zr···Zr distances ranging from 3.580(1) to 3.371(1) Å. The shortest Zr···Zr vector is associated with two bridging oxygen atoms derived from the DBcat ligands. The other five shorter Zr···Zr vectors are each associated with one bridging oxygen atom; four of them are derived from the methoxide and one from the DBcat ligand. The methoxide ligands are obviously produced from methanol in solution, the protons of which are transferred to the acac or the DBcat ligands, which are then eliminated from the complex as neutral molecules.

In addition to the bridging methoxide ligands, there is a neutral ligated methanol which is co-ordinated to the Zr(4) atom. Its identification is based on the long Zr–O distance and the acute Zr–O(20)Me(67) angle observed, and by counting and balancing the charge distribution between ligands and Zr atoms. Moreover, the four remaining acetylacetonate ligands act as typical chelates and are located at the periphery of the $Zr_4(\mu_4\text{-}O)$ core, one on each Zr. Lastly, if we focus only on the local arrangement of all ligated oxygen atoms, complex **3** is analogous to the structurally characterized complex $[Zr_4(\mu_4\text{-}O)(acac)_4(\mu\text{-}OPr^n)_2(OPr^n)_4]$.[12]

Discussion

We have isolated and structurally characterized two new zirconium acetylacetonate–catecholate complexes **1** and **2**. It appears from our study that these reactions are best described as ligand substitutions. At the initial stage two acetylacetonate ligands are replaced by the incoming H_2cat or H_2DBcat molecule, giving a 6-co-ordinated intermediate $[Zr(acac)_2(cat)]$ or $[Zr(acac)_2(DBcat)]$ as depicted by eqns. (4) and (5). For

$$[Zr(acac)_4] + H_2cat \longrightarrow [Zr(acac)_2(cat)] + 2\,Hacac \quad (4)$$

$$[Zr(acac)_4] + H_2DBcat \longrightarrow [Zr(acac)_2(DBcat)] + 2\,Hacac \quad (5)$$

the reaction between $[Zr(acac)_4]$ and H_2DBcat, as the central zirconium atom requires a higher co-ordination number due to the relatively greater ionic radii, the resulting intermediate $[Zr(acac)_2(DBcat)]$ could undergo a dimerization reaction to afford the isolated product **2**, so that each Zr can recover some of the thermal stability by formation of a more stable 7-co-ordinated ligand environment *vs.* the relatively less stable 6-co-ordinated geometry, eqn. (6).

$$2\,[Zr(acac)_2(DBcat)] \longrightarrow [Zr(acac)_2(DBcat)]_2\ \mathbf{2} \quad (6)$$

For the purpose of comparison, formation of the 7-co-ordinate complex $[Zr(acac)_3(OC_6H_4NO_2\text{-}4)]$ or the bimetallic complex $[\{Zr(acac)_3\}_2(OC_6H_4O\text{-}4)]$ was observed from the reaction of $[Zr(acac)_4]$ with monodentate aryl oxide ligands such as 4-nitrophenol or hydroquinone.[10] In these reactions, replacement of only one acetylacetonate ligand on each Zr was observed in all attempts, irrespective of the amount of the phenol ligand added to the reaction system. This difference in reactivity between phenol *vs.* catechol could be a result of the high tendency to chelate interaction for catechol, which facilitates the elimination of two acetylacetonate ligands.

Moreover, as the acidity of catechol is greater and its size much smaller than that of H_2DBcat, due to the absence of the electron-donating and bulky *t*-butyl substituents, we expect that catechol should be more reactive. As a result, both mono- and di-substituted intermediate species $[Zr(acac)_2(cat)]$ and $[Zr(cat)_2]$ could be obtained during the reaction of $[Zr(acac)_4]$ with catechol, according to eqns. (4) and (7). It is notable

$$[Zr(acac)_2(cat)] + H_2cat \longrightarrow [Zr(cat)_2] + 2\,Hacac \quad (7)$$

that the second, speculated intermediate [Zr(cat)$_2$] is structurally related to the highly unsaturated 4-co-ordinate zirconium halides, amides or alkoxides, which all possess extensive co-ordination unsaturation and are thus highly reactive.[13] Upon addition of methanol during work-up, this intermediate [Zr(cat)$_2$] would react with the less substituted intermediate [Zr(acac)$_2$(cat)] present in the same reaction mixture, affording the isolated trimetallic complex **1**, eqn. (8). The tendency of the intermediate [Zr(cat)$_2$] to form the trimetallic framework is somewhat related to the catenation behavior of a structurally characterized titanium glycolate complex Ti(OCH$_2$CH$_2$O)$_2$,[14] which forms an infinite one-dimensional chain in the solid state, so that each individual titanium metal ion can achieve a fully saturated, 6-co-ordinate ligand environment. Accordingly, the formation of the 8-co-ordinate environment for all three Zr in complex **1** could be the main driving force in providing the thermal stability, explaining the co-ordination of methanol to the Zr.

$$2\,[\mathrm{Zr(acac)_2(cat)}] + [\mathrm{Zr(cat)_2}] + 2\,\mathrm{MeOH} \longrightarrow [\mathrm{Zr_3(acac)_4(cat)_4(MeOH)_2}]\ \mathbf{1} \quad (8)$$

Both complexes **1** and **2** are reactive upon contacting with a mixture of methanol and water for a period of 24 hours. The hydrolysis of **1** failed to afford any well defined crystalline product; however, treatment of **2** with a mixture of wet methanol and CH$_2$Cl$_2$ gave the oxo complex **3**. In this reaction both methanol and water serve as proton sources to cause the elimination of acac and DBcat ligands according to eqn. (3). The delineation of exact mechanism is not possible, but it seems that the central μ_4-O ligand is derived from water, not from the oxygen atom of any other ligands such as methanol, acac or even DBcat.

Conclusion

The products of the reaction between [Zr(acac)$_4$] and catechols are related to the basic properties of the catechol ligands, such as the electronic and steric interaction of the substituents and the tendency for formation of a chelating interaction. Di- and tri-nuclear alkoxide complexes **2** and **1** can be obtained by using 3,5-di-*tert*-butylcatechol and the less bulky catechol, respectively. Upon addition of each catecholate ligand, the number of oxygens co-ordinated to the Zr is reduced by two units, as it promotes the removal of two co-ordinated acetylacetonates according to the charge balance. Furthermore, it seems to us that the co-ordination unsaturation is the key factor for the incorporation of the methanol in **1** during work-up and the involvement of catecholate bridging interaction in both complexes **1** and **2**. The presence of the catecholate ligands also seems to reduce the stability to hydrolysis with respect to the common starting material [Zr(acac)$_4$].

Acknowledgements

We thank China Petroleum Corporation of Taiwan, R. O. C. for financial support (Grant No. NSC 88-CPC-M-007-001).

References

1 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969; C. N. R. Rao and B. Raveau, *Transition Metal Oxides*, VCH Publishers, New York, 1995; N. Y. Turova, E. P. Turevskaya, M. I. Yanovskaya, A. I. Yanovsky, V. G. Kessler and D. E. Tcheboukov, *Polyhedron*, 1998, **17**, 899.

2 A. C. Jones, T. J. Leedham, P. J. Wright, D. J. Williams, M. J. Crosbie, H. O. Davies, K. A. Fleeting and P. O'Brien, *J. Eur. Ceram. Soc.*, 1999, **19**, 1431.

3 G. Garcia, A. Figueras, J. Casado, J. Llibre, M. Mokchah, G. Petot-Ervas and J. Calderer, *Thin Solid Films*, 1998, **317**, 241.

4 C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990; J. M. Marshall, N. Kirov, A. Vavrek and J. M. Maud (Editors), *Future Directions in Thin Film Science and Technology*, World Scientific, Singapore, 1997; A. Grafov, E. Mazurenko, G. A. Battiston and P. Zanella, *J. Phys. IV*, 1995, **5**, C5; B. Malic, I. Arcon, M. Kosec and A. Kodre, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 343; A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, D. J. Williams, K. A. Fleeting, H. O. Davies, D. J. Otway and P. O'Brien, *Chem. Vap. Deposition*, 1998, **4**, 197.

5 J. Si, S. B. Desu and C.-Y. Tsai, *J. Mater. Res.*, 1994, **9**, 1721; J. A. Belot, R. J. McNeely, A. Wang, C. J. Reedy, T. J. Marks, G. P. A. Yap and A. L. Rheingold, *J. Mater. Res.*, 1999, **14**, 12.

6 M. Adachi, K. Okuyama, S. Moon, N. Tohge and Y. Kousaka, *J. Mater. Sci.*, 1989, **24**, 2275; Z. Xue, B. A. Vaartstra, K. G. Caulton, M. H. Chisholm and D. L. Jones, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 213; K. A. Fleeting, P. O'Brien, A. C. Jones, D. J. Otway, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 2853; K. A. Fleeting, P. O'Brien, D. J. Otway, A. J. P. White, D. J. Williams and A. C. Jones, *Inorg. Chem.*, 1999, **38**, 1432.

7 L. A. DeLearie and C. G. Pierpont, *Inorg. Chem.*, 1988, **27**, 3842; D. J. Darensbourg, K. K. Klausmeyer and J. H. Reibenspies, *Inorg. Chem.*, 1996, **35**, 1529.

8 D. M. Choquette, W. E. Buschmann, M. M. Olmstead and R. P. Planalp, *Inorg. Chem.*, 1993, **32**, 1062; T. J. Boyle, R. W. Schwartz, R. J. Doedens and J. W. Ziller, *Inorg. Chem.*, 1995, **34**, 1110; W. J. Evans, M. A. Ansari and J. W. Ziller, *Inorg. Chem.*, 1999, **38**, 1160.

9 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

10 W. J. Evans, M. A. Ansari and J. W. Ziller, *Polyhedron*, 1998, **17**, 299.

11 R. Schmid, H. Ahamdane and A. Mosset, *Inorg. Chim. Acta*, 1991, **190**, 237; L. G. Hubert-Pfalzgraf, S. Daniele, R. Papiernik, M.-C. Massiani, B. Septe, J. Vaissermann and J.-C. Daran, *J. Mater. Chem.*, 1997, **7**, 753; Z. A. Starikova, E. P. Turevskaya, N. I. Kozlova, N. Y. Turova, D. V. Berdyev and A. I. Yanovsky, *Polyhedron*, 1999, **18**, 941.

12 P. Toledano and M. I. Clement Sanchez, *C. R. Acad. Sci., Ser. 2*, 1990, **311**, 1161.

13 R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269.

14 D. Wang, R. Yu, N. Kumada and N. Kinomura, *Chem. Mater.*, 1999, **11**, 2008.

15 SMART and SAINT, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1995.

16 G. M. Sheldrick, SHELXTL version 5.03, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1994.