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Structural characterization of Sr–Ti and Ba–Ti catecholate complexes: single source precursors for $SrTiO_3$ and $BaTiO_3$ binary oxides

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Abstract

Titanium catecholate complex $H_2Ti(cat)_3$ (**1**) is synthesized from the direct reaction of $Ti(O^iPr)_4$ with catechol (H_2cat). Treatment of **1** with NEt_3 gives ionic complex $(HNEt_3)_2[Ti(cat)_3]$ (**2**). Reactions of **1** with $SrCO_3$ or with $BaCO_3$ afford the corresponding catecholate complexes with approximate composition $Sr[Ti(cat)_3]\cdot 3H_2O$ (**3**) and $Ba[Ti(cat)_3]\cdot 3H_2O$ (**4**), of which the formula was proposed according to the previous literature report and microanalytical data. Water soluble crystalline materials $[Sr(H_2O)_5]_2[Ti_2O_2(cat)_4]\cdot 6H_2O$ (**5**) and $[Ba(H_2O)_4(C_3H_6O)]_2[Ti_2O_2(cat)_4]\cdot 2C_3H_6O$ (**6**) are isolated in low yields by repeated recrystallization of **3** and **4** from a mixture of water and acetone at room temperature. The single crystal X-ray diffraction studies reveal that they fail to show the discrete $Ti(cat)_3^{2-}$ unit as suggested previously, but they contain a dimeric $[Ti_2O_2(cat)_4]^{4-}$ fragment with two bridging oxo ligands and two chelating catecholate ligands associated with each Ti atom. The latter is further linked to the hydrated Sr^{2+} or the Ba^{2+} counter cations through axial oxygen atoms of the catecholate ligands and the unique bridging oxo ligand. Crystal data for **5**: $a = 7.8251(1)$, $b = 11.3739(2)$, $c = 11.4980(2)$ Å, $\alpha = 91.942(1)$, $\beta = 100.441(1)$, $\gamma = 103.061(1)°$ with $Z = 1$ in space group $P\bar{1}$. For complex **6**: $a = 9.6450(3)$, $b = 10.2092(3)$, $c = 13.3098(4)$ Å, $\alpha = 18.192(1)$, $\beta = 85.876(1)$, $\gamma = 73.475(1)°$ with $Z = 1$ in space group $P\bar{1}$. Conversion to the respective $SrTiO_3$ and $BaTiO_3$ phases by calcination under oxygen atmosphere is confirmed by TG analysis and X-ray powder analysis.

Conventional routes to perovskite-phase oxides, such as $SrTiO_3$ and $BaTiO_3$, are based on solid-state reaction and often involve the use of readily available starting materials. This solid state reaction generally required mixing of precursor powders by extensive grinding, followed by sintering, repeated milling and calcination [1]. However, this methodology required very high reaction temperature in order to guarantee the effective reaction between the solid-state metal precursors [2,3], but the higher temperature selected may cause some deleterious effects, such as generation of the coarse and inhomogeneous powders of the final materials.

A more advanced approach is to use the mixed-metal titanium oxalate [4–6], citrate [7,8], catecholate [9–11], acylate [12], glycolate [13], or even alkoxide [14–16] precursors to circumvent the problems associated with the incomplete mixing of metal ingredients in solid-state. The purpose for the choice of these precursors is that the organic ligands present in these complexes can improve compatibility between each component, homogeneity at the molecular level, and processibility of the precursors [17,18]. As a result, many high-purity, stoichiometric alkaline earth metal titanate materials in the forms of nano-particles or thin-films have been reproducibly synthesized at a much reduced reaction temperature.

In this article, we wish to report an improved synthesis of titanium catecholate complex $H_2Ti(cat)_3$ (**1**), which is then used as the starting material in preparation of the Sr and Ba catecholate complexes as well as the binary ceramic powders $SrTiO_3$ and $BaTiO_3$. The single crystal X-ray diffraction analysis of the corresponding Sr–Ti and Ba–Ti catecholate complexes revealed the occurrence of a dimeric

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core structure $[Ti_2O_2(cat)_4]^{4-}$, which are in sharp contrast to the previous report of the existence of the discrete titanium tris-catecholate entity $[Ti(cat)_3]^{2-}$ [9–11].

1. Experimental

1.1. General information and materials

$Ti(O^iPr)_4$ and catechol were purchased from Strem and Aldrich Chemical Co., respectively. Solvents were reagent grade and were used as received. All reactions were carried out in air; otherwise, it will be stated specifically. ^1H and ^{13}C NMR spectra were recorded on either a Bruker AM-400 or AMX-300 instrument. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer and all samples were dried under vacuum before making the KBr pellets. The powder X-ray analysis was carried out using Shimadzu XD-5 instrument. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

1.2. Preparation of $H_2Ti(cat)_3$

To a 250 ml reaction flask, catechol (3.3 g, 30 mmol) was first dissolved in a freshly distilled toluene (100 ml) by gentle heating under N_2 atmosphere. The $Ti(O^iPr)_4$ (2.84 g, 10 mmol) was then added dropwise, and the resulting mixture was heated at 80°C for 1 h to give a dark-red suspension. After this red suspension was allowed to cool to room temperature, a dark-red precipitate was collected by filtration and washed with hot toluene (2 × 20 ml), followed by diethyl ether (2 × 20 ml). The precipitate was then dried in vacuo to produce 3.0 g of $H_2Ti(cat)_3$ (8 mmol, 80%).

1.3. Spectral data for **1**

^1H NMR (400 MHz, acetone-d_6, 298K): δ 6.67 (m, 2H), 6.79 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6, 298K): δ 157.9 (C_6H_4), 116.8 (C_6H_4), 112.5 (C_6H_4). IR (KBr): 3060, 1586, 1479 (vs), 1404, 1248 (vs), 1181, 1103, 1022, 908, 872, 805, 742, 666, 635, 421 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_6Ti$: C, 57.78; H, 3.77. Found: C, 57.74; H, 4.34.

1.4. Reaction of $H_2Ti(cat)_3$ with NEt_3

A mixture of water (40 ml), fine powder of $H_2Ti(cat)_3$ (6.3 g, 26.5 mmol) and excess of NEt_3 (6 ml) was stirred at 80°C for 2 h. After the solution was allowed to cool to room temperature, the solution was filtered and the filtrate was dried under vacuum to give red-orange powdery solids. Recrystallization in a 20:1 mixture of EtOH and water at 5°C afforded 12.1 g of $(HNEt_3)_2[Ti(cat)_3]$ (**2**, 21 mmol, 80%) as red crystalline solids.

1.5. Spectral data for **2**

^1H NMR (300 MHz, D_2O, 298K): δ 1.23 (t, 6H, $^3J_{HH} = 7.4$ Hz), 3.15 (q, 4H, $^3J_{HH} = 7.4$ Hz), 6.42 (m, 2H), 6.62 (m, 2H). Anal. Calcd for $C_{30}H_{44}N_2O_6Ti$: C,62.49; H, 7.69. Found: C, 61.76; H, 7.26.

1.6. Reaction of $H_2Ti(cat)_3$ with $SrCO_3$

To a suspension containing $SrCO_3$ (1.5 g, 11 mmol) in 200 ml of water, the solid sample of $H_2Ti(cat)_3$ (3.8 g, 10 mmol) was added over a period of 1 h. The solution effervesced and the color of solution changed from dark-red to bright-red. After the addition was finished, the solution was heated at 60°C for 1 h to ensure completion of reaction. The unreacted $SrCO_3$ was removed by filtration and water from the filtrate was evaporated on a rotary evaporator. The residue was dried in vacuo to produce 4.5 g of a brown solid (8.5 mmol, 85%) which is assigned with a tentative molecular formula $Sr[Ti(cat)_3]\cdot 3H_2O$ (**3**). This powdery material was further purified by repeated recrystallization in a mixture of acetone and water to afford 0.87 g of $[Sr(H_2O)_5]_2[Ti_2O_2(cat)_4]\cdot 6H_2O$ (**5**, 0.85 mmol, 17%). Single crystals suitable for X-ray diffraction study were obtained from slow diffusion of acetone into an aqueous solution of **3** at room temperature.

1.7. Spectral data for **3**

^1H NMR (300 MHz, D_2O, 298K): δ 6.48 (m, 2H), 6.54 (m, 2H). IR (KBr): 3345 (br), 1630 (br), 1475 (vs), 1385, 1331, 1247 (vs), 1207, 1101, 1020, 865, 804, 756, 631 (br, Ti–O–Ti), 602, 503 (br), 412 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_9TiSr$: C, 42.07; H, 3.53. Found: C, 42.78; H, 3.61.

1.8. Spectral data for **5**

^1H NMR (300 MHz, D_2O, 298K): δ 6.47 (m, 2H), 6.54 (m, 2H). IR (KBr): 3391 (br), 1632 (br), 1484 (vs), 1451, 1334, 1255 (vs), 1100, 1020, 869, 807, 748, 665 (br, Ti–O–Ti), 608 (br), 502 (br), 412 cm^{-1}. Anal. Calcd for $C_{24}H_{36}O_{20}Ti_2Sr_2$: C, 31.48; H, 3.96. Found: C, 31.18; H, 3.50.

1.9. Reaction of $H_2Ti(cat)_3$ with $BaCO_3$

The same procedure for making complex **3** was followed. After removing the unreacted $BaCO_3$, the filtrate was evaporated on a rotary evaporator to produce a red-brown powder (75%) which is assigned with a tentative formula $Ba[Ti(cat)_3]\cdot 3H_2O$ (**4**) accordingly. This powdery material was further purified by repeated recrystallization in a mixture of acetone and water to afford 0.54 g of $[Ba(H_2O)_4(C_3H_6O)]_2[Ti_2O_2(cat)_4]\cdot 2C_3H_6O$ (**6**, 0.45 mmol, 9%). Single crystals suitable for X-ray diffraction study were obtained from slow diffusion of acetone into an aqueous solution of **4** at room temperature.

Table 1
X-ray structural data of complexes **5** and **6**

Compound	**5**	**6**
Formula	$C_{24}H_{48}O_{26}Sr_2Ti_2$	$C_{36}H_{56}O_{22}Ba_2Ti_2$
mol. wt.	1023.66	1211.29
Crystal system	triclinic	triclinic
a (Å)	7.8251(1)	9.6450(3)
b (Å)	11.3739(2)	10.2092(3)
c (Å)	11.4980(2)	13.3098(4)
α (°)	91.942(1)	18.192(1)
β (°)	100.441(1)	85.876(1)
γ (°)	103.061(1)	73.475(1)
Volume (Å^3)	977.37(1)	1229.61(6)
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
μ(Mo–K$_\alpha$) mm^{-1}	3.200	1.967
Temperature	295 K	295 K
Reflections collected	18704	30439
Independent reflections	4484 ($R_{\text{int}} = 0.0449$)	6607 ($R_{\text{int}} = 0.0409$)
R_F; R_{wF^2} [$I > 2\sigma(I)$]	0.038; 0.081	0.029; 0.064

Table 2
Selected bond distances (Å) and angles (deg) of **5** (esd. in parentheses)

Ti–O(1)	1.981(2)	O(1)– C(1)	1.357(4)
Ti–O(2)	2.021(2)	O(2)– C(6)	1.350(3)
Ti–O(3)	1.998(2)	O(3)– C(7)	1.360(3)
Ti–O(4)	2.022(2)	O(4)– C(12)	1.352(4)
Ti–O(5)	1.881(2)	Ti–O(5)	1.896(2)
Sr–O(1)	2.687(2)	Sr–O(3)	2.635(2)
Sr–O(5)	2.563(2)	Sr–O(6)	2.773(2)
Sr–O(6)	2.802(2)	Sr–O(7)	2.666(3)
Sr–O(8)	2.601(2)	Sr–O(9)	2.638(2)
Sr–O(10)	2.669(3)		
∠Ti–O(5)– Ti	97.72(8)	∠Sr–O(6)– Sr	114.04(7)
∠O(5)– Ti–O(5)	82.28(8)	∠O(6)– Sr–O(6)	65.96(7)

1.10. Spectral data for 4

^{1}H NMR (300 MHz, D_2O, 298 K): δ 6.48 (2H), 6.54 (m, 2H). IR (KBr): 3394 (br), 1626 (br), 1475 (vs), 1451, 1328, 1246 (vs), 1101, 1018, 866, 802, 740, 632 (s, br), 605 (br), 504 (br), 414 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_9BaTi$: C, 38.36; H, 3.22. Found: C,38.22; H, 3.27.

1.11. Spectral data for 6

^{1}H NMR (300 MHz, D_2O, 298K): δ 6.48 (m, 2H), 6.54 (m, 2H). IR (KBr): 3371 (br), 1635 (br), 1482 (vs), 1448, 1335, 1255 (vs), 1100, 1021, 870, 806, 750, 661 (br, Ti–O–Ti), 630, 605 (s, br), 492 (br), 438 cm^{-1}. Anal. Calcd for $C_{30}H_{44}O_{20}Ba_2Ti_2$: C, 32.87; H, 4.02. Found: C,31.86; H, 3.55.

1.12. X-ray crystallography

Single crystal X-ray diffraction data was measured on a Bruker-axs SMART CCD diffractometer using radiation $\lambda(\text{Mo–K}_\alpha) = 0.7107$ Å. Data collection was executed using SMART program. Crystal decay was monitored by repeating data collection for the initial 50 frames and at the end of experiment. Refinement of the unit cell constants was achieved by using SAINT program. The structure was determined by the Direct Method and using SHELXTL/PC program. Anisotropic displacement parameters were used for all non-hydrogen atoms, while the hydrogen atoms were given a fixed isotropic displacement parameters.

Crystallographic refinement parameters of **5** and **6** are summarized in Table 1; selected bond distances and angles are presented in Tables 2 and 3, respectively.

2. Results

2.1. Synthesis

In these studies, the easily accessible titanium isopropoxide complex $Ti(O^iPr)_4$ was selected as the sole starting material for all catecholate complexes. Thus, treatment of

Table 3
Selected bond distances (Å) and angles (deg) of **6** (esd. in parentheses)

Ti–O(1)	1.997(2)	O(1)– C(1)	1.348(3)
Ti–O(2)	2.040(2)	O(2)– C(6)	1.353(3)
Ti–O(3)	1.989(2)	O(3)– C(7)	1.349(3)
Ti–O(4)	2.045(2)	O(4)– C(10)	1.349(3)
Ti–O(5)	1.866(2)	Ti–O(5)	1.871(2)
Ba–O(1)	2.812(2)	Ba–O(3)	2.777(2)
Ba–O(5)	2.736(2)	Ba–O(6)	2.878(2)
Ba–O(6)	2.975(3)	Ba–O(7)	2.834(2)
Ba–O(8)	2.757(2)	Ba–O(9)	2.823(3)
Ba–O(10)	2.802(2)	O(10)– C(13)	1.198(4)
∠Ti–O(5)– Ti	97.48(7)	∠Ba–O(6)– Ba	113.15(6)
∠O(5)– Ti–O(5)	82.52(7)	∠O(6)– Ba–O(6)	66.85(6)

$Ti(O^iPr)_4$ with 3 equiv. of catechol (H_2cat) in toluene gives formation of titanium catecholate complex (**1**) $H_2Ti(cat)_3$. This reaction is simple and straightforward. Isolation of the product $H_2Ti(cat)_3$ requires only filtration, rinsed with warm toluene and then with anhydrous diethyl ether, followed by removal of residual solvent under vacuum. As indicated in Eq. (1), the whole transformation can be considered as an alkoxide exchange reaction [19,20], giving off relatively nontoxic isopropanol as the coproduct. As a result, this method is much better than the previously reported approach which involves a ligand exchange reaction using $TiCl_4$ as source in nonaqueous medium or in 1 M HCl solution due to the release of obnoxious, corrosive HCl gas under these conditions [Eq. (2)] [9–11].

$$Ti(O^iPr)_4 + 3H_2cat \rightarrow H_2Ti(cat)_3 + 4Pr^iOH \qquad (1)$$

$$TiCl_4 + 3H_2cat \rightarrow H_2Ti(cat)_3 + 4HCl \qquad (2)$$

$$H_2Ti(cat)_3 + 2NEt_3 \rightarrow (HNEt_3)_2[Ti(cat)_3] \qquad (3)$$

The red catecholate complex **1**, which is insoluble in water, can be easily dissolved in polar organic solvents such as methanol, THF and acetone, forming stable orange–red solution in air. Initial characterization of **1** has been achieved using ^1H NMR study and microanalysis, the latter is presented in Table 4. The exact solid-state structure has not been obtained as no suitable single crystal can be grown in all attempts. However, a further characterization of **1** was achieved using a neutralization reaction with excess triethylamine according to Eq. (3). This reaction gives isolation of the expected quaternary ammonium salt $(HNEt_3)_2[Ti(cat)_3]$ (**2**), whose structure has been unambiguously determined by X-ray diffraction study [11]. Thus, although we cannot propose the exact molecular structure of **1** due to lack of single crystal X-ray diffraction data, it seems appropriate to say that the titanium atom of **1** is arranged in an octahedral array of six oxygen atoms derived from three chelating catecholate ligands.

After completion of the identification for complex **1**, we then proceed to synthesize the corresponding Sr–Ti and Ba–Ti heterometallic complexes. Thus, treatment of **1** with $SrCO_3$ in aqueous solution afforded a red–orange solution. After removal of unreacted $SrCO_3$ by filtration, evaporation of the filtrate to dryness gave formation of a red–orange powdery material **3**. This material is tentatively identified as $Sr[Ti(cat)_3]\cdot 3H_2O$ based on its microanalysis data as well as the molecular formula proposed in literature [9–11]. Accordingly, the heterometallic Ba–Ti complex $Ba[Ti(cat)_3]\cdot 3H_2O$ (**4**) was prepared using an essentially identical experimental approach.

Interestingly, crystalline materials of complexes **5** and **6** were obtained in low yields by slow diffusion of acetone into a concentrate aqueous solution of **3** and **4** at room temperature, respectively. The IR spectra of crystalline samples of **5** and **6** were first recorded, showing a spectral pattern almost identical to that of the powdery samples **3** and **4**, respectively. This information confirms that all of them were composed by the essentially identical IR active functional groups. However, the microanalytical data of **5** and **6** show a substantially reduction in their carbon contents with respect to that of the powdery samples **3** and **4**, suggesting that these crystalline samples may possess a very different molecular composition (Table 4). Moreover, after we scrutinize the IR spectra more carefully, we noted that the relative intensity of the signals at 665 and 661 cm^{-1} of the respective samples of **5** and **6** has increased substantially with respect to that of the powdery samples [11]. The detection of this distinctive Ti–O stretching signal clearly indicates presence of the bridging Ti(μ–O)Ti fragments, which should not be existed in the proposed structural formula $M[Ti(cat)_3]\cdot 3H_2O$ of the powdery samples **3** and **4**, M = Sr or Ba. Thus, single crystal X–ray diffraction studies were carried out to delineate their exact molecular structures.

2.2. Description of the structures

An X-ray structural study of **5** shows that its crystal structure is best represented as a hydrated ionic complex with formula $[Sr(H_2O)_5]_2[Ti_2O_2(cat)_4]\cdot 6H_2O$. A view emphasizing the central $Ti_2(\mu\text{–}O)_2$ dimer unit is shown in Fig. 1, while the bond distances and angles are presented in Table 2. The

Table 4
Microanalytical data for complexes **1** ~ **6**

Sample	Proposed formula	Calculated (wt%)	Found (wt%)
1	$H_2Ti(cat)_3$	C, 57.78; H, 3.77	C, 57.74; H, 4.34
2	$(HNEt_3)_2[Ti(cat)_3]$	C, 62.49; H, 7.69	C, 61.76; H, 7.26
3[a]	$Sr[Ti(cat)_3] \cdot 3H_2O$	C, 42.07; H, 3.53	C, 42.78; H, 3.61
4[a]	$Ba[Ti(cat)_3] \cdot 3H_2O$	C, 38.36; H, 3.22	C, 38.22; H, 3.27
5[b]	$[Sr(H_2O)_5]_2[Ti_2O_2(cat)_4]$	C, 31.48; H, 3.96	C, 31.18; H, 3.50
6[b]	$[Ba(H_2O)_4(C_2H_6O)]_2[Ti_2O_2(cat)_4]$	C, 32.16; H, 4.09	C, 31.86; H, 3.55

[a] The previously proposed formula; see Ref. [10].

[b] The formula where loss of non-coordinated solvates has occurred during sample drying.

$[Ti_2O_2(cat)_4]^{4-}$ anion possesses two bridging oxo ligands and four bidentate chelating catecholate ligands. The $Ti_2(\mu{-}O)_2$ unit thus formed, which are related by a crystallographical center of inversion, consists of a rhomboidal arrangement with internal angle 82.28(8)° at the titanium metal and 97.72(8)° at the oxo ligand. The Ti···Ti distance is 2.844(1) Å as compared with 2.719(1) Å found in the neutral acetylacetonato complex $[TiO(acac)_2]_2$ [22], and 2.819(1) Å reported for ionic catecholato complex $K_4[TiO(cat)_2]_2 \cdot 2H_2O$ [21]. The Ti–O_{oxo} vectors are nearly symmetrical with bond distances, Ti–O(5) = 1.881(2) Å or 1.896(2) Å, showing the occurrence of partial Ti=O multiple bonding interaction. For comparison, the Ti–O bonds associated with the catecholate ligands are in the range 1.981(2) ~ 2.022(2) Å, of which the Ti–O_{cat} distances trans to the bridging oxo ligands O(5) (2.021(2) ~ 2.022(2) Å) are longer than the cis distances (1.981(2) Å ~ 1.998(2) Å). This bond elongation is in accord with the expected structural trans influence of the oxo ligand, which is an excellent π-donor ligand [23–25].

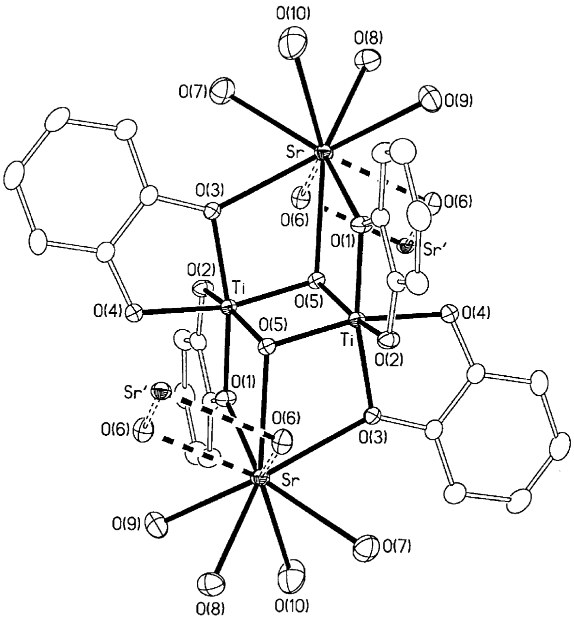

Fig. 1. ORTEP drawing of complex **5** looking down the $[Ti_2O_2(cat)_4]^{4-}$ fragment with thermal ellipsoids shown at the 30% probability level. The O(6) atoms of ligated waters, related to each other by a center of inversion, form two Sr···O···Sr bridging interactions to the atom Sr′ of neighboring molecules.

In addition, the $[Ti_2O_2(cat)_4]^{4-}$ anionic unit is flanked by two $Sr(H_2O)_5^{2+}$ cations located at the trans disposition of the planar $Ti_2(\mu{-}O)_2$ unit through the axial catecholate oxygen atoms and one bridging oxo ligand. Although the molecular stoichiometry indicates that each of these Sr^{2+} cations possesses only five coordinated water molecules, the strontium atom is actually surrounded by nine oxygen donor atoms. The first one is the oxo ligand O(5) of the $Ti_2(\mu{-}O)_2$ fragment, giving the shortest Sr–O separation 2.563(2) Å. The second and third oxygen donor atoms are derived from the catecholate ligands, for which two slightly longer coordination distances, Sr–O(1) = 2.687(2) Å and Sr–O(3) = 2.635(2) Å, are observed. These Sr–O distances are, in turn, comparable with those of four other oxygen atoms O(7), O(8), O(9) and O(10) of terminally coordinated water molecules, showing Sr–O distances in the range 2.638(2) ~ 2.669(2) Å.

Moreover, the oxygen atoms O(6) of the fifth water molecule, which are related by a crystallographical operation of inversion, occupy the last two positions of the coordination polyhedron with two nearly identical bond distances 2.773(2) and 2.802(2) Å. This bonding interaction is indicated by the respective Sr–O(6) dash-lines depicted in Fig. 2, of which the overall coordination environment of the Sr^{2+} cation center is best considered as a tricapped trigonal prism. It is notable that these water molecules are engaging as bridging ligands between this $Sr(H_2O)_5^{2+}$ cationic center and the adjacent $Sr'(H_2O)_5^{2+}$ cation of neighboring complex, as the observed Sr′– O(6) distances are identical to the Sr–O(6) distances due to the crystallographical inversion operation discussed earlier. This bridging interaction is somewhat analogous to that observed in the recently characterized β-diketonate complex $[Sr_2(thd)_4(diglyme)_2(\mu{-}H_2O)]$ [26], in which a unique water molecule sitting symmetrically between two $[Sr(thd)_2(diglyme)]$ units was observed with a slightly longer Sr–O_{water} separation 2.967(7) Å.

Moreover, crystal structure of the Ba–Ti catecholate

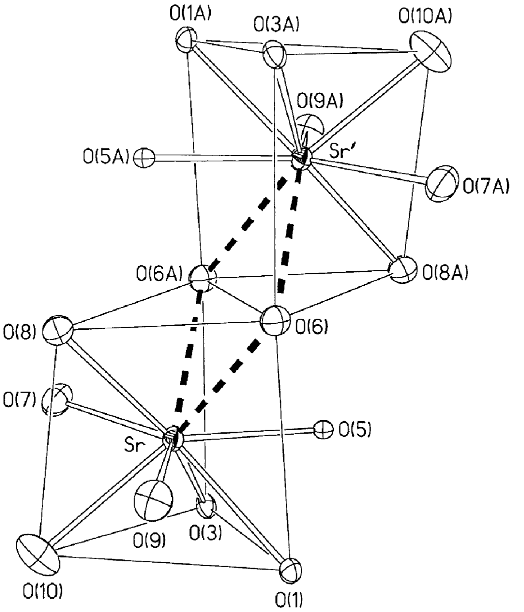

Fig. 2. ORTEP drawing of complex **5** emphasizing on the coordination environment of $[Sr(H_2O)_5]_2^{4+}$ fragment.

complex **6** is also established by single-crystal X-ray diffraction study. As indicated in Fig. 3, the core geometry of central $[Ti_2O_2(cat)_4]^{4-}$ unit and the relative location of the Ba^{2+} counter cations are all very similar to that observed for the previously discussed Sr–Ti complex **5**. Beside these similarities, two significant differences in structure are observed. First, the barium cation now carries one acetone molecule to replace a water ligand within the coordination sphere. The corresponding $Ba-O_{acetone}$ distance (2.802(2) Å) shows little variation from the rest of $Ba-O_{water}$ distances (2.757(2) ~ 2.834(2) Å), or from the Ba–O distances of a variety of barium complexes that reported in literature [27,28]. This information suggests that the donor capability of acetone is comparable to those of water and other oxygen donor molecules of the barium complexes. Furthermore, the double Ba···O···Ba′ bridging interactions now consist of the oxygen donor atoms which are located at one vertex of the trigonal prism and at central position of the nearby rectangular face. This change is easily identified by the structural drawing of the dimeric $Ba(H_2O)_4(C_3H_6O)]_2^{4+}$ unit shown in the Fig. 4, which gives a special emphasis on the polyhedral arrangement of all oxygen donor atoms with respect to the barium cation centers. At this moment, no suitable explanation can be proposed to account for this changing of the bridging interaction between the Ba^{2+} cations.

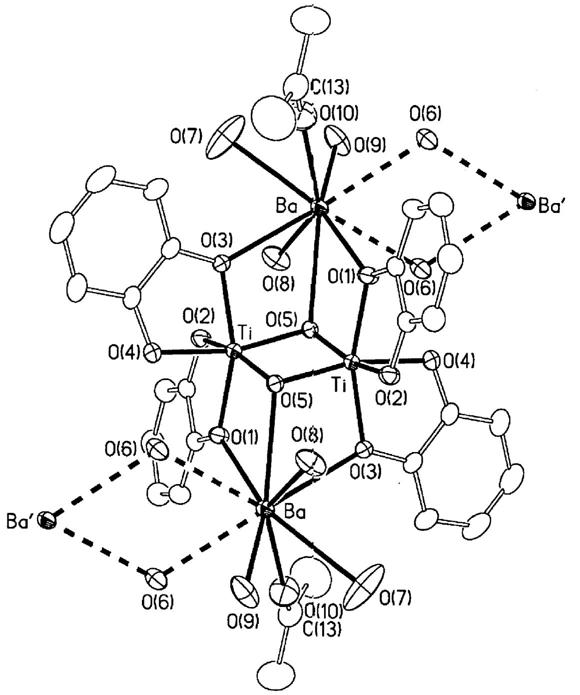

Fig. 3. ORTEP drawing of complex **6** looking down the $[Ti_2O_2(cat)_4]^{4-}$ fragment with thermal ellipsoids shown at the 30% probability level. The O(6) atoms of ligated waters, related to each other by a center of inversion, form two Ba···O···Ba′ bridging interactions to the atom Ba′ of neighboring molecules.

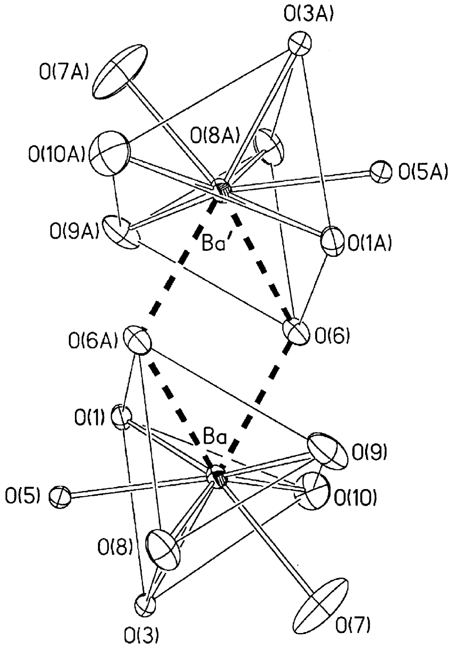

Fig. 4. ORTEP drawing of complex **6** emphasizing on the coordination environment of $[Ba(H_2O)_4(C_3H_6O)]_2^{4+}$ fragment.

2.3. Conversion to binary titanate oxides

TG analysis of complexes **5** and **6** has been carried out

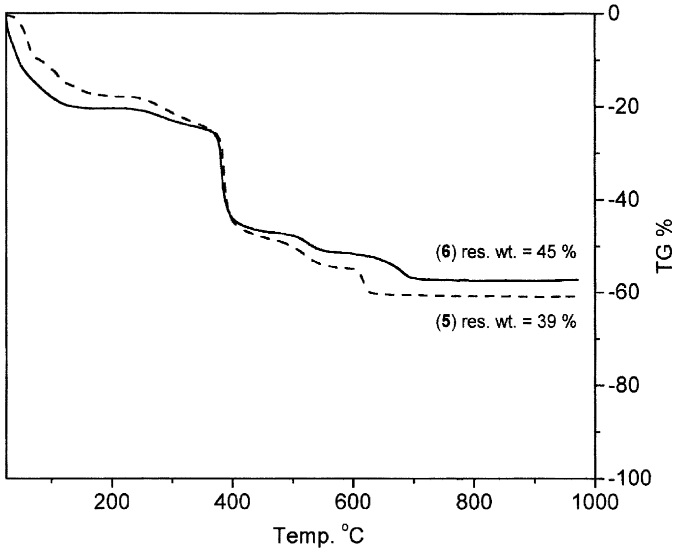

Fig. 5. TGA diagram of complexes **5** and **6**; the experiments were conducted in O_2 and with a temperature ramp of 10°C/min.

under O_2 atmosphere. For both sample, multiple-stage weight losses arising from the elimination of associated water and volatile products from the combustion processes were observed at the temperature below 600°C, and no further change of weight was observed passing this temperature (Fig. 5). The residual weights obtained at 1000°C, **5**: 39% and **6**: 45%, were fully consistent with the theoretical residual weight of 40% (**5**) and 42.6% (**6**), which are calculated according to the completely conversion to the $SrTiO_3$ and $BaTiO_3$ phases, respectively.

The development of a crystalline $SrTiO_3$ or $BaTiO_3$ ceramic phase was investigated by decomposing samples of **5** or **6** under oxygen at five temperature settings 500, 600, 700, 800 and 900°C for 2 h, and the resulting ceramic samples were examined by X-ray powder analysis. The XRD patterns of the solid materials formed by calcination are shown in Fig. 6. Samples of complex **5** calcined at 500°C exhibited peaks due to cubic $SrTiO_3$, but the peak is slightly broader. However, all peaks turned much sharper upon increasing the temperature, which are in agreement with the formation of larger aggregates. Samples of complex **6** calcined at 500°C also exhibited broader peaks due to cubic $BaTiO_3$, consisting with formation of fine particulates [29]. Upon increasing the temperature to 800°C, the peaks turned much sharper, but the relative intensities of the diffraction peaks showed no significant variation with those at 500°C. Therefore, the formation of fully crystalline $BaTiO_3$ ceramics appeared to occur at a lower temperature of 700 ~ 800°C compared with the traditional solid-state reactions that carried out at 1050 ~ 1150°C using TiO_2 and $BaCO_3$ as starting materials [30,31]. Furthermore, the diffraction peaks of other metal oxide phases, such as TiO_2 and BaO were not observed, except for a peak due to $BaCO_3$ at the lower temperature between 500 ~ 600°C. This $BaCO_3$ phase disappeared upon raising the calcination temperature to 700°C, showing the involvement of stoichiometric amount of barium and titanium atoms in the starting samples.

3. Discussion

Prior workers have prepared Sr–Ti and Ba–Ti catecholate complexes from the acid-base reaction of both **1** and **2** with alkaline earth metal carbonate or with hydroxide complexes, and they suggest that the resulting heterometallic complexes **3** and **4** consist of hydrated alkaline earth cations and titanium catecholate anions $[Ti(cat)_3]^{2-}$ [9–11]. However, the X-ray structural analysis of complexes **5** and **6**, which are the crystalline samples obtained from complexes **3** and **4**, show the occurrence of dimeric $[Ti_2O_2(cat)_4]^{4-}$ unit. Apparently, the incorrect structure assignments for **3** and **4** are attributed to a believe that the $[Ti(cat)_3]^{2-}$ anions of the titanium precursor are stable against hydrolysis during all purification and isolation processes This chemical behavior is implicated by the successful characterization of the tris(glycolate) complex $[Ti(O_2C_4H_4)_3]^{2-}$ [32], and the closely related ionic complex **2** as the sole product from treatment of **1** with triethylamine, the latter is found to possess a discrete $[Ti(cat)_3]^{2-}$ anion and two equivalent of $HNEt_3^+$ counter cations [21].

However, the reaction of $(NH_4)_2[Ti(cat)_3]$ with more basic KOH has led to formation of the metal complex $K_4[Ti_2O_2(cat)_4]$ containing a dimeric $[Ti_2O_2(cat)_4]^{4-}$ unit [Eq. (4)], which was characterized by X-ray structural study [21]. The formation of $[Ti_2O_2(cat)_4]^{4-}$ has been attributed to a rapid hydrolysis of $[Ti(cat)_3]^{2-}$ anion by ligand exchange between the catecholate and the hydroxyl anion

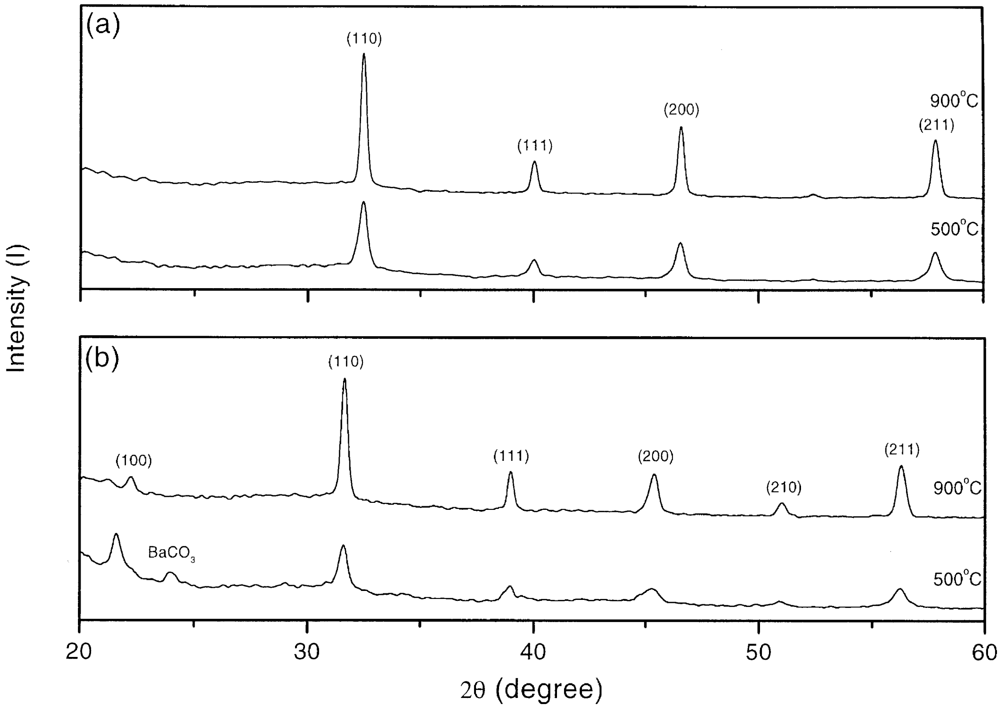

Fig. 6. The XRD patterns for (a) $SrTiO_3$ and (b) $BaTiO_3$ samples obtained from calcination of complexes **5** and **6**, respectively.

present in aqueous solution, see Eq. (5).

$$2(NH_4)_2Ti(cat)_3 + 6KOH \rightarrow K_4[Ti_2O_2(cat)_4] + 4NH_4OH + 2HcatK \quad (4)$$

$$2[Ti(cat)_3]^{2-} + 2OH^- \leftrightarrow [Ti_2O_2(cat)_4]^{4-} + 2Hcat^- \quad (5)$$

Moreover, it has been reported that the equilibrium described in Eq. (5) can be further driven to the right by increasing the pH value because of the large concentration of hydroxyl anion present in solution [21]. Thus, we may rule out the possibility that the as-prepared powdery samples **3** and **4** contain only the discrete catecholate $[Ti(cat)_3]^{2-}$ unit as reported previously [9,11], based on the fact that the basicity of $SrCO_3$ and $BaCO_3$ is relatively stronger. Moreover, we may also ruled out the second hypothesis that the $[Ti_2O_2(cat)_4]^{4-}$ anion is produced during crystallization of the powdery samples **3** and **4** upon addition of a mixture of water and acetone. This is because that the recrystallization is always carried out under a much lower temperature (25°C) with respect to that used for their original synthesis (70°C), thus the possibility for the conversion from $[Ti(cat)_3]^{2-}$ to $[Ti_2O_2(cat)_4]^{4-}$ anions seems quite unlikely.

Alternatively, we may suggest that the samples of **3** and **4** are composed of either an inseparable mixture of $[Ti(cat)_3]^{2-}$ and $[Ti_2O_2(cat)_4]^{4-}$ anions, or a pure sample containing only the $[Ti_2O_2(cat)_4]^{4-}$ anion. In both cases, purification of **3** and **4** by recrystallization would give raise to the isolation of crystalline complexes **5** and **6** with the $[Ti_2O_2(cat)_4]^{4-}$ anion, while the monomeric $[Ti(cat)_3]^{2-}$ anion would remain in the solution or forming the non-crystalline or powdery precipitates if it were present. Moreover, the possibility of involvement of only $[Ti_2O_2(cat)_4]^{4-}$ anion in the as-prepared samples is disfavored as their micro-analysis data have consistently showed higher carbon contents vs the data of the crystalline samples of **5** and **6**.

Based on all these experimental facts, we may conclude that the as-prepared powdery sample of **3** and **4**, which were isolated by freeze drying under vacuum, consist of compound materials involving both the $[Ti(cat)_3]^{2-}$ and the $[Ti_2O_2(cat)_4]^{4-}$ anions. In accordance with our delineation, the checkers of Inorganic Syntheses have also mentioned the detection of a weak IR stretching band in the region 650 cm^{-1} during repeated examining the preparation procedures of the titanate complex **4**. This signal is subsequent assigned to the Ti–O functional group of the dimeric $[Ti_2O_2(cat)_4]^{4-}$ anion as a contaminant present at low level [33].

4. Concluding remarks

The catecholate complex **1** with a proposed composition of $H_2Ti(cat)_3$ was prepared and has been utilized in the preparation of the corresponding ammonium, strontium and barium complexes **2**, **3** and **4**. The ammonium complex **2** consists of a discrete $[Ti(cat)_3]^{2-}$ unit, in which the Ti^{4+} cationic center is coordinated by three chelating catecholate ligands. For the strontium and barium complexes **3** and **4**, they are not involving a pure complex anion of $[Ti(cat)_3]^{2-}$ as reported early, but contain an inseparable mixture of the $[Ti(cat)_3]^{2-}$ anion and the $[Ti_2O_2(cat)_4]^{4-}$ anion, the latter is caused by partial hydrolysis of the $[Ti(cat)_3]^{2-}$ anion during initial preparation. Purification of **3** and **4** by recrystallization gives raise to the isolation of crystalline samples of **5** and **6**, of which the $[Ti_2O_2(cat)_4]^{4-}$ anions precipitates out with the counter cations Sr^{2+} or Ba^{2+}, and separated from the monomeric $Ti(cat)_3^{2-}$ anions that remain soluble in the solvent or crystallized out as non-crystalline powdery materials. According to the single crystal X-ray analyses, the structures of **5** and **6** involve alternating building blocks of $M_2(H_2O)_n^{4+}$ cation, $M = Sr^{2+}$ or Ba^{2+}, and $[Ti_2O_2(cat)_4]^{4-}$ anion, linked by oxygen atoms of the bridging oxo fragments, the catecholate ligands and the water solvate molecules.

Finally, although the exact structural formula of the titanate fragments seems to be different, the relative ratio between Sr and Ti and between Ba and Ti elements remain identical for all samples. Thus, calcination of the crystalline samples of complexes **5** and **6** in air at above 700°C would also give formation of the expected, binary oxide materials $SrTiO_3$ and $BaTiO_3$.

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Supplementary Materials. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge BC2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition No. 163074 for complex **5** and No. 163075 for complex **6**.

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