Chemical Vapor Deposition

Structure and Unusual Substitution Reaction of Oligoether-Appended β-Diketonato Strontium Complex**

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Metal–organic (MO) CVD is an important industrial process used to deposit metal-containing thin films for the production of microelectronic and optical devices. Much research effort is being focused on developing thin films of $YBa_2Cu_3O_{7-x}$, $BaTiO_3$, $SrTiO_3$, and $Ba_xSr_{1-x}TiO_3$ for possible applications as superconducting, ferroelectric, or high dielectric materials, using MOCVD.[1,2] A challenging problem in this area is the development of volatile metal–organic precursors suitable for MOCVD. Due to the small charge-to-radius ratios of barium and strontium, simple β-diketonate complexes such as $[M(dik)_2]$ ($M = Ba^{II}$ or Sr^{II}, dik = β-diketonate) usually have unoccupied coordination sites causing decomposition and/or oligomerization, major problems in the manufacturing process. To avoid such problems, the adducts of metal β-diketonates with various neutral Lewis bases $[M(dik)_2{\cdot}X]$ (X = neutral Lewis base) have been investigated.[3] However, because of the relatively weak binding energies between the metal ions and the neutral bases, the latter often dissociate from the MO precursors during vaporization and undergo undesirable gas phase reactions. Recently, strontium and barium ion complexes of oligoether-appended β-ketoiminates and β-diketonates have been developed.[4–8] Among these, 1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionate complexes, known as $Ba(methd)_2$ and $Sr(methd)_2$ to CVD engineers, have attracted great attention as promising candidates, not only because they are viscous liquids at room temperature and also volatile, but because they are more stable than the neutral base adducts.[9,10] However, there is a concern that they may exist as polymeric structures because intermolecular coordination by the oligoether lariats may be possible. Furthermore, it is essential to establish the structure–property relationship of the precursors in order to further enhance the properties. Nevertheless, there has been no study concerned with determining the structure of such compounds.

In this work, we studied the structure of an oligoether-appended β-diketonato strontium complex in both solution and solid state. We now report that the complex exists as $[SrL_2]_2$ (**1**) [L = 1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionate] in solution and liquid state, and $[SrLL'(CH_3OH)]_2$ (**2**) [L′ = 1-(2-hydroxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionate] in the solid state. Compound **1** was converted to **2** during crystallization, and the reverse reaction took place when **2** was melted or dissolved in a solvent. A plausible mechanism for this reaction is proposed.

The structure of **1** in $CDCl_3$ was examined by nuclear magnetic resonance (NMR) spectroscopy. Both ^1H and ^{13}C NMR spectra of **1** are indistinguishable from what would be expected from a 1:1 complex between the strontium ion and the ligand, whereas the fast atom bombardment mass spectroscopy (FABMS) result indicates a dimeric structure (vide infra). In addition, the terminal methoxy groups appear as a singlet at δ 3.25, indicating that they are chemically equivalent. Taken together, **1** should have a highly symmetrical structure in which all of the oxygen atoms are bound to the strontium ions (vide infra).

To unambiguously determine the structure, a crystal sample was obtained by standing a solution of **1** (0.61 g, 1.0 mmol) in methanol (5.0 g)/water (one drop, 0.034 g, 1.9 mmol) co-solvent at –5 °C. The crystal structure shows that the compound exists as a dimer. To our surprise, the compound was not **1**, but **2**! Two of the four ligands have been changed from L to L′ upon crystallization, with one molecule of methanol attached to each strontium ion. The structure of **2** is centrosymmetric and each strontium ion is coordinated by eight oxygen atoms, seven from L and L′, and one from methanol (Figs. 1a,b). The strontium ions are bound to the etherial and carbonyl oxygen atoms to produce five- and six-membered ring structures, respectively. Also, one of the carbonyl oxygen of each L is attached to both strontium ions via a μ_2-O bridge. It is worth noting that L produces two 6-membered rings and one five-membered ring with two strontium ions, whereas L′ forms only one six-membered ring via the chelation of the strontium ion by the β-keto enolate moiety. Except for that, L′ has no interaction with the strontium ion. The distance between Sr and etherial oxygen is 2.70 ± 0.01 Å, which is longer than Sr···O=C [2.58 ± 0.02 Å] or Sr···O(Me)H [2.595(3) Å] (Figs. 1b,c). The two Sr atoms are separated by a distance of 4.169(1) Å. Figure 1d shows a monoclinic crystal packing structure of **2** along the *b*-axis. It is clearly evident that there is no intermolecular interaction between the dimer molecules in the unit cell.[11]

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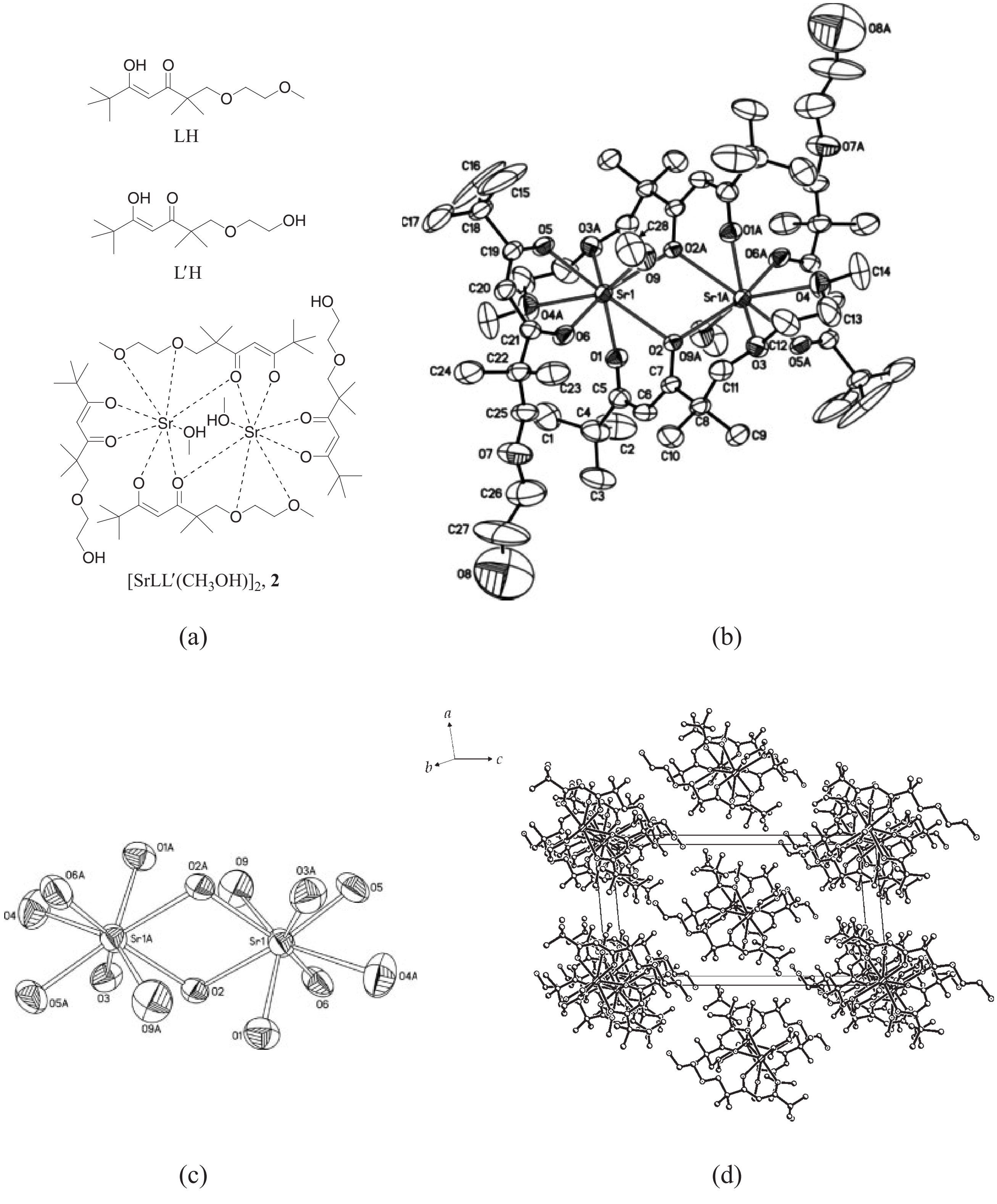


(a) (b)

(c) (d)

Fig. 1. Solid state structure of **2**. The ellipsoids are drawn at the 30 % probability level, except the local geometry. The hydrogen atoms are omitted for clarity. a) Chemical structures of LH, L′H, and **2**. b) A single molecular structure with atomic labeling. c) Local geometry about two strontium atoms in a molecule (50 % probability level). d) *b*-axis view of crystal packing. Selected interatomic distances [Å]: Sr1–O1 2.561, Sr1–O2 2.602, Sr1–O2A 2.579, Sr1–O3A 2.692, Sr1–O4A 2.713, Sr1–O5 2.488, Sr1–O6 2.428, Sr1–O9 2.595, Sr1···Sr1A 4.169

Surprisingly, however, the ^1H and ^{13}C NMR spectra of **2** in $CDCl_3$ are identical to those of **1**. Also, the methine carbons of **2** appear at δ 90.06 as a single peak in the ^{13}C NMR spectrum, but separate into two broad peaks at δ 93.58 and δ 88.60 in the solid state cross-polarization/magic-angle spinning (CP/MAS) NMR spectrum (Fig. 2). In addition, the FABMS of **2** in *m*-nitrobenzyl alcohol/glycerol matrix solution reveals that $[Sr_2L_3]^+$ is the dominant fragment without any trace of $[Sr_2L_2L']^+$ or $[Sr_2LL'_2]^+$. This indicates that, in solution, **2** exists as a dimer. All of these results could be explained if, in solution, **2** is transformed to **1**.

To understand how **2** could be converted to **1**, the crystalline powder of **2** was dissolved in methanol-d$_4$ and recrystallized. The NMR spectra shown in Figure 3 reveal that more than 75 % of the methine C–H bond was converted to the C–D bond. This indicates the dynamic nature of the six-membered ring structure containing the strontium ion and the carbonyl oxygen atoms of the β-diketonate moiety, i.e., it dissociates to undergo H–D exchange with MeOH-d$_4$ and then associates. However, there is no change in the terminal methoxy groups, indicating that MeOH-d$_4$ neither reacts with the terminal OH group of L′, nor exchanges with the strontium-bound methanol. In addition, after the melting of **2** at 88 °C, the thermogravimetric and differential scanning calorimetric (TG-DSC) thermograms of **1** and **2** are very similar except for the reduction in mass of **2** in the temperature range 100–150 °C (Fig. 4). This could be due to the transformation of **2** to **1** after melting and evaporation of the water molecules. However, the residue of **2** after the vaporization is more than that of **1**, possibly due to purity degradation caused by the reverse reaction.

All of the results can most reasonably be explained by the unusual substitution reaction shown in Scheme 1. As stated above, the structure of **1** in solution should be symmetrical, with all of the oxygen atoms bound to the strontium ions. The forward reaction proceeds by the attack of the water molecules at the terminal methyl group attached to the Sr^{2+}-bound oxygen to afford **2**. When **2** is melted or dissolved in solution, the reverse reaction takes place by an intramolecular pathway, i.e., the terminal OH group attacks the methyl group of Sr^{2+}-bound methanol to produce **1** and one eq. of water molecule. The rate of this intramolecular substitution reaction should be much faster than that of exchange between strontium-bound methanol and solvent molecules, as indicated by the complete absence of the terminal CD_3 group in the deuterated sample of **1** (vide supra). The driving force for the forward reaction might be the shorter Sr···O(Me)H length than the distance between Sr^{2+} and etherial oxygen (vide supra), and the lattice energy, whereas the reverse reaction may be favored by entropy. Both reactions are apparently catalyzed by the strontium ion acting as the Lewis acid. Finally, the equilibrium is shifted rapidly toward more favored species upon the phase change.

In conclusion, the oligoether-appended β-diketonato strontium complex exists as $[SrL_2]_2$ (**1**) in solution or the liquid state, and $[SrLL'(CH_3OH)]_2$ (**2**) in the solid state. The structural change occurs by the strontium ion catalyzed substitution reaction. Even though **1** is a promising liquid

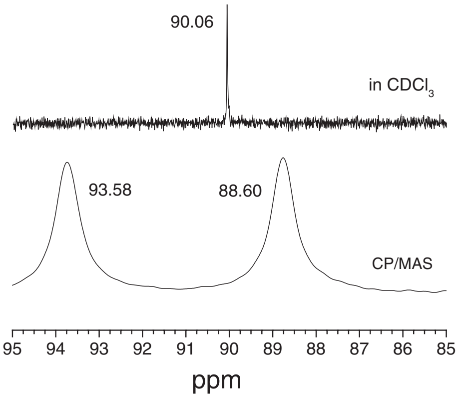


Fig. 2. Solution (upper) and solid-state (lower) NMR spectra of methine carbon in ligands.

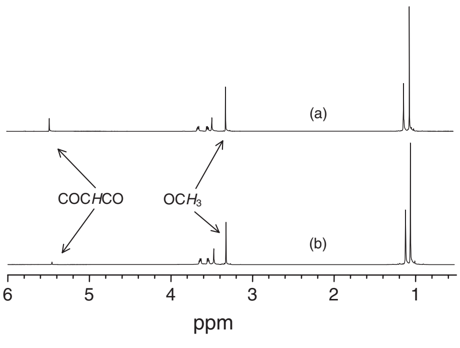


Fig. 3. ^1H NMR spectra ($CDCl_3$) of **2** crystallized in a) methanol and b) methanol-d_4.

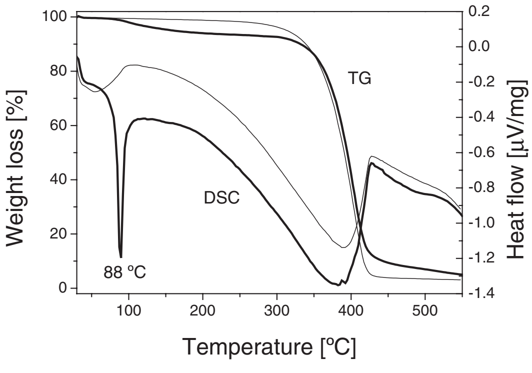
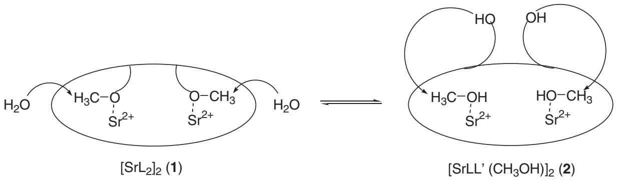


Fig. 4. TGDSC thermograms of **1** (thin lines) and **2** (thick lines) at a heating rate of 10 °C min^{-1} under N_2 flow of 20 mL min^{-1}.



Scheme 1.

precursor of Sr for MOCVD, in terms of the solvent system for storage, delivery, and vaporization of the precursor, methanol is not a desirable solvent for **1**, because of the equilibrium between **1** and **2**.

Experimental

Bis[1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionato] strontium ($\mathrm{SrL_2}$) (**1**) was purchased from Asahi Denka Kogyo K.K. Japan [4]. The compound was crystallized by standing a solution of **1** (0.61 g, 1.01 mmol) in methanol (5.03 g)/water (one drop, 0.034 g, 1.89 mmol) co-solvent for one week at –5 °C.

Solid-state NMR experiments were performed on a Unity Inova 200 NMR spectrometer (Varian) with a 7.5 mm MAS probe head (Chemagnetics) at a resonance frequency of 50.3 MHz and a sample spinning rate of 4 kHz (90° pulse length 4.5 µs, delay time 5 s, CP contact time 2.5 ms).

Analytical data of **2**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.04 [s, 9H, $\mathrm{C(C}H_3\mathrm{)_3}$], 1.11 [s, 9 H, $\mathrm{C(C}H_3\mathrm{)_2}$], 3.31 [s, 3H, $\mathrm{OC}H_3$], 3.47 [s, 2H, $\mathrm{(CH_3)_2CC}H_2\mathrm{O}$], 3.52 [m, 2H, $\mathrm{OC}H_2\mathrm{CH_2O}$], 3.65 [m, 2H, $\mathrm{OCH_2C}H_2\mathrm{O}$], 5.48 [s, 1H, $\mathrm{COC}H\mathrm{CO}$]. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 24.55 ($\mathrm{C(}C\mathrm{H_3)_2}$), 28.57 ($\mathrm{C(}C\mathrm{H_3)_3}$), 41.04 ($C\mathrm{(CH_3)_3}$), 45.19 ($C\mathrm{(CH_3)_2}$), 59.12 ($\mathrm{O}C\mathrm{H_3}$), 70.93 ($\mathrm{O}C\mathrm{H_2CH_2O}$), 71.52 ($\mathrm{OCH_2}C\mathrm{H_2O}$), 79.97 ($\mathrm{(CH_3)_2C}C\mathrm{H_2O}$), 90.06 ($\mathrm{CO}C\mathrm{HCO}$), 194.55 ($C\mathrm{O}$), 199.77 ($C\mathrm{O}$). ^{13}C CP/MAS NMR (200 MHz): 24.06, 25.15, 26.50, and 27.75 ($\mathrm{C(}C\mathrm{H_3)_2}$), 29.75 and 30.15 ($\mathrm{C(}C\mathrm{H_3)_3}$), 41.86 and 43.06 ($C\mathrm{(CH_3)_3}$), 46.02 and 47.08 ($C\mathrm{(CH_3)_2}$), 58.33 ($C\mathrm{H_3OH}$), 59.51 ($\mathrm{O}C\mathrm{H_3}$), 70.02, 71.73, and 73.08 ($\mathrm{O}C\mathrm{H_2CH_2O}$), 79.27 (br, $\mathrm{(CH_3)_2C}C\mathrm{H_2O}$), 88.60 and 93.58 ($\mathrm{CO}C\mathrm{HCO}$), 196.50, 197.30, and 202.55 ($C\mathrm{O}$). Anal. Calcd. for $\mathrm{C_{56}H_{104}O_{18}Sr_2}$: C, 54.21; H, 8.45. Found: C, 54.70; H, 8.90. Calcd Sr content (%, ICP-AES): 14.12. Found: 15.44 [12]. Mass spectrometry (FAB+, *m*-nitrobenzyl alcohol/glycerol matrix) *m*/*z*: 1203 {$\mathrm{[Sr_2L_4{-}H]^+}$, 1}, 1147 {$\mathrm{[Sr_2L_4{-}{}^{\mathit{t}}Bu]^+}$, 3}, 1073 {$\mathrm{[Sr_2L_4{-}C(CH_3)_2CH_2OCH_2CH_2OCH_3]^+}$, 4}, 947 {$\mathrm{[Sr_2L_3]^+}$, 100}, 601 {$\mathrm{[SrL_2{-}H]^+}$, 7}, 345 {$\mathrm{[SrL]^+}$, 24}. (ESI+, methanol/acetonitrile solvent) *m*/*z*: 947 {$\mathrm{[Sr_2L_3]^+}$, 100}, 345 {$\mathrm{[SrL]^+}$, 12}.

Crystal data of **2**, $\mathrm{Sr_2(C_{14}H_{25}O_4)_2(C_{13}H_{23}O_4)_2(CH_3OH)_2}$: $M_\mathrm{r} = 1240.63$, block, dimensions 0.40 mm × 0.30 mm × 0.20 mm, monoclinic, $P2_1/n$, $a = 11.5388(12)$ Å, $b = 14.1786(13)$ Å, $c = 21.534(2)$ Å, $\beta = 95.176(2)°$, $V = 3508.7(6)$ Å^3, $Z = 2$, $\rho_\mathrm{calcd} = 1.172$ g cm^{-3}, $F(000) = 1320$, $2\theta_\mathrm{max} = 56.70°$. The data were collected on a Siemens SMART CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at 298 K and were corrected for Lorentz and polarization effects. The first fifty frames were re-collected at the end of the process to monitor crystal decay; no significant decay was observed. The absorption corrections applied (SADABS, $\mu = 1.579$ mm^{-1}, $T_\mathrm{max}/T_\mathrm{min} = 0.928/0.726$) [13]. The structure was solved by direct methods and refined by the full-matrix least squares technique against F^2 for all data using SHELXTL software [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their parent atoms. Final residuals were $R1 = 0.0568$ and $wR2 = 0.1227$ for 8463 reflections with $I > 2\sigma(I)$, and $R1 = 0.1652$, $wR2 = 0.1557$ for all 22 949 data (343 parameters). Residual electron densities were 0.554 e Å^{-3} and –0.281 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-163858. Copies of the data can be obtained free for charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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