

Synthesis and Crystal Structure of [Sr₃{CH₃COCHCOOC(CH₃)₃]₆{CH₃OCH₂CH₂OCH₃]₂]

Soo-Gyun Roh, Byung Jae Bae,[†] Joon Taik Park,^{†,*} and Jong Hwa Jeong*

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

[†]Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejeon 305-701, Korea

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The chemistry of the group 2 metals containing alkoxides¹⁻³ and β -diketonates⁴⁻⁷ is of current interesting area for MOCVD precursors for metal oxide superconductors. Their applications for metal oxide thin films formed from the liquid or gas phase are of prominent importance.⁸ The crystal structure studies for the β -diketonate complexes of group 1 and 2 metals have illustrated that these complexes tend to easily exist as oligomers. An effort to obtain the monomeric complexes for MOCVD precursors is introduction of polydentate ligands to the complexes because those ligands lead to prevent the formation of oligomers which are not proper for the precursors. The complexes containing the polydentate ligands are coordinatively saturated, quite soluble and volatile, which are proper with respect to self-association, hydrate formation and hydrolysis.⁹ The properties of these complexes are mainly affected by factors such as the ligand shielding, polarizability and potential coordination number of the complexes.¹⁰

We have been interested in the synthesis of the strontium complexes using ligands such as β -ketonate, β -ketoiminate, and keto ester in order to obtain monomeric and coordinatively saturated complexes. The structure studies of Sr complexes have not been extensively reported as compared with that of Ba complexes.

The trimeric strontium complexes containing the aryl-oxides¹ and β -diketonates¹¹ ligands have been known as those of triangular arrays but the linear trimeric strontium compound of the β -ketonate ligands has not been reported yet. [Sr₃(OCSOEt)₆(EtOH)₈]¹² was known as the first example of the linear trimeric strontium complex. Accordingly, we wish to report herein synthesis and X-ray structure of a new linear trimeric strontium complex, [Sr₃{CH₃COCHCOOC(CH₃)₃]₆{CH₃OCH₂CH₂OCH₃]₂].

Experimental Section

All manipulations were carried out under an argon atmosphere by using Schlenk techniques. All solvents were freshly distilled prior to use. Sr was purchased from Strem Chemical and used after washing with dry hexane. *tert*-Butylacetoacetate and ethylene glycol dimethyl ether (monoglyme) were obtained from Aldrich Co. and used without purification. IR spectrum was recorded on Bruker EQUINOX-55 FT-IR spectrometer. Elemental analysis was performed on the Chemical Analysis Laboratory of Korea Basic Science Institute at Kyungpook National Uni-

versity.

Preparation of [Sr₃{CH₃COCHCOOC(CH₃)₃]₆{CH₃OCH₂CH₂OCH₃]₂]. To the solution of Sr (0.500 g, 5.70 mmol) in toluene (20 mL) was added monoglyme (0.514 g, 5.70 mmol), and then dropwise added *tert*-butylacetoacetate (1.805 g, 11.40 mmol). The H₂ gas was constantly evolved throughout the addition of the β -keto ester ligand. After the reaction for 24 h at room temperature, the clear solution was dried under vacuum to give the white precipitate. The white precipitate was dissolved in benzene and cooled at 5 to afford colorless crystals (yield 1.87 g, 71% based on strontium metal).

Anal. Calcd. for C₅₆H₉₈O₂₂Sr₃: C, 48.52; H, 7.12. Found: C, 48.55; H, 7.10. IR (KBr, pellet, cm⁻¹): ν 2977 (m), 2928(w), 1643 (vs), 1535 (v), 1418 (m), 1387 (w), 1362 (m), 1248 (vs), 1192 (m), 1154 (vs), 1070 (w), 1052 (w), 975 (s), 856 (w), 788 (w), 745 (w), 568 (w), 464 (w).

Crystal structure determination. A well-shaped crystal in a thin-walled glass capillary was mounted on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements with 25 well-centered reflections ($10 < \theta < 13^\circ$). The intensity data were collected in the θ range of 1.9-25.0° in $\omega/2\theta$ scan mode. Two standard reflections were monitored every one hour during data collection. The data were modified for Lorentz-polarization effects and decay (less than 0.03%). An extinction correction was carried out with 3 ψ scans in the correction range of 0.85-0.99. Crystallographic data and other information are summarized in Table 1

The structure in P2₁/a was solved by direct methods and successive Fourier maps and refined using the SHELXS86 and SHELXL97.^{13,14} An atom of strontium Sr(2) is in special position with an occupancy of 0.5. Hydrogen atoms have been geometrically located. All non-hydrogen atoms were anisotropically refined. Matrix least-squares refinements were carried out by minimizing the function $\sum w(F_o - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = 0.036$; $R_w = 0.040$. Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviations being less than 0.2 and no significant features in the difference map. Relevant bond distances are given in Table 2. ORTEP drawing¹⁵ of the molecule with scheme labels is shown in Figure 1.

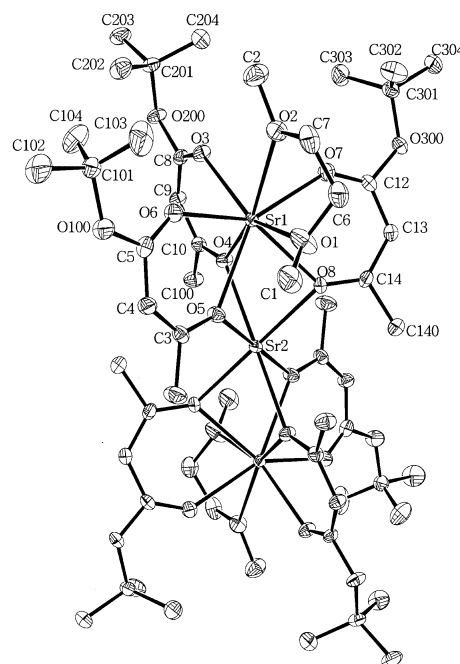
Table 1. Crystal Data for $\text{Sr}_3[\{\text{CH}_3\text{COCHCOOC}(\text{CH}_3)_3\}_6\{\text{CH}_3\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_3\}_2]$

Formula	$\text{C}_{56}\text{H}_{98}\text{O}_{22}\text{Sr}_3$
Fw	1386.24
Crystal system	Monoclinic
a (Å)	16.469(6)
b (Å)	12.182(3)
c (Å)	18.667(5)
β (°)	110.46(3)
V (Å ³)	3527(2)
Z	2
Space group	$P2_1/a$
Crystal shape	Parallelepiped
Crystal color	Colorless
Linear absorption coefficient, μ (cm ⁻¹)	22.54
Density, ρ (gcm ⁻³) _{cal.}	1.31
Radiation	MoK α ($\lambda = 0.71073$ Å)
Scan type	$\omega/2\theta$
θ ranges	1-25°
Temperature of measurement	293(2) K
Indices ranges	$0 \leq h \leq 19, 0 \leq k \leq 14,$ $-22 \leq l \leq 20$
No. of unique data collected	6202 [R(int) = 0.037]
Data / restraints / parameters	3026 / 0 / 369
Final R indices [$I > 3\sigma(I)$]	R = 0.041, $R_w = 0.048$
Goodness of fit on F^2	1.16
Largest diff. and hole	0.51 and -0.81 e/Å ³

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \frac{[\sum w(|F_o| - |F_c|)^2]}{\sum wF_o^2}^{1/2}$$

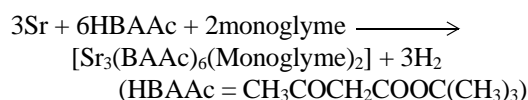
Table 2. Relevant Bond Distances (Å) and Angles (°) for $\text{Sr}_3[\{\text{CH}_3\text{COCHCOOC}(\text{CH}_3)_3\}_6\{\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\}_2]$

Sr(1)-O(1)	2.702(5)	Sr(1)-O(2)	2.733(5)
Sr(1)-O(3)	2.534(4)	Sr(1)-O(4)	2.559(4)
Sr(1)-O(5)	2.582(4)	Sr(1)-O(6)	2.508(4)
Sr(1)-O(7)	2.494(5)	Sr(1)-O(8)	2.608(4)
Sr(2)-O(4)	2.503(4)	Sr(2)-O(5)	2.488(4)
Sr(2)-O(8)	2.499(4)		
O(1)-Sr(1)-O(2)	61.3(2)	O(1)-Sr(1)-O(3)	146.1(2)
O(2)-Sr(1)-O(3)	85.8(1)	O(1)-Sr(1)-O(4)	143.1(2)
O(2)-Sr(1)-O(4)	154.5(1)	O(3)-Sr(1)-O(4)	70.7(1)
O(1)-Sr(1)-O(5)	79.9(2)	O(2)-Sr(1)-O(5)	131.6(2)
O(3)-Sr(1)-O(5)	121.9(1)	O(4)-Sr(1)-O(5)	71.6(1)
O(1)-Sr(1)-O(6)	80.7(2)	O(2)-Sr(1)-O(6)	75.8(2)
O(3)-Sr(1)-O(6)	83.4(2)	O(4)-Sr(1)-O(6)	109.9(2)
O(5)-Sr(1)-O(6)	70.0(1)	O(1)-Sr(1)-O(7)	91.7(2)
O(2)-Sr(1)-O(7)	70.4(2)	O(3)-Sr(1)-O(7)	84.4(2)
O(4)-Sr(1)-O(7)	96.9(2)	O(5)-Sr(1)-O(7)	142.7(1)
O(1)-Sr(1)-O(8)	78.6(2)	O(2)-Sr(1)-O(8)	120.7(1)
O(3)-Sr(1)-O(8)	129.9(1)	O(4)-Sr(1)-O(7)	71.3(1)
O(5)-Sr(1)-O(8)	73.6(1)	O(6)-Sr(1)-O(7)	144.7(2)
O(6)-Sr(1)-O(8)	140.6(1)	O(7)-Sr(1)-O(8)	69.1(1)
O(4)-Sr(2)-O(5)	74.2(1)	O(4)-Sr(2)-O(5)'	105.8(1)
O(4)-Sr(2)-O(8)	74.1(1)	O(4)-Sr(2)-O(8)'	105.9(1)
O(5)-Sr(2)-O(8)	77.2(1)	O(5)-Sr(2)-O(8)'	102.8(1)

**Figure 1.** ORTEX drawing of $\text{Sr}_3[\{\text{CH}_3\text{COCHCOOC}(\text{CH}_3)_3\}_6\{\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\}_2]$ with 20% probability displacement ellipsoids.

Results and Discussion

The linear trimeric strontium complex was derived from the reaction of strontium metal with β -keto-ester ligands and monoglyme in dry THF. This compound is moisture-sensitive and sparingly soluble in hydrocarbon solvents but soluble in polar and protic solvents.



The crystalline strontium complex was produced by recrystallization in benzene. Accordingly, in order to verify the exact structure, we have determined the crystal structure by X-ray method. The crystal structure shown in Figure 1 reveals that the compound is unusual linear trimer which consists of six keto ester and two monoglyme ligands on three strontium atoms. The strontium atoms have two different environments of six-coordinate and eight-coordinate. The six bridging oxygen atoms of the keto ester ligands chelate to the strontium metal inversion center with Sr(2)-O(4) 2.503(4), Sr(2)-O(5) 2.488(4) and Sr(2)-O(8) 2.499(4) Å distances, respectively, with an average Sr(2)-O 2.496(4) Å. The two symmetric Sr(1) atoms have the eight-coordinate with three bridging oxygen atoms, (Sr(1)-O(4) 2.559(4), Sr(1)-O(5) 2.582(4) and Sr(1)-O(8) 2.608(4) Å) and three oxygen atoms (Sr(1)-O(3) 2.534(4), Sr(1)-O(6) 2.508(4) and Sr(1)-O(7) 2.494(5) Å) of the keto-ester ligands, and two oxygen atoms (Sr(1)-O(1) 2.702(5) and Sr(1)-2.733(5) Å) of monoglyme, respectively. Sr(1)-O bonds to bridging oxygen atoms of an average 2.583(4) Å are longer than those to chelating oxygen atoms of an average 2.521(4) Å, while

Sr(2)-O bonds to bridging oxygen atoms of an average 2.496(4) Å are shorter than Sr(1)-O bonds to chelating oxygen atoms of an average 2.521(4) Å and bridging oxygen atoms of an average 2.583(4) Å.

This work may be contrasted with that of the previously studied trimeric β -ketonate strontium complexes.¹¹ However, the strontium complex $[\text{Sr}_3(\text{OCSEt})_6(\text{EtOH})_8]$ ¹² was known as the first example of a linear trimer. This compound has all eight-coordinate geometry for three strontium atoms in contrast to six and eight coordinate geometry of the keto-ester compound. The strontium complex $[\text{Sr}_3(\text{OCSEt})_6(\text{EtOH})_8]$ has the linear trimeric structure due to the saturated eight coordinate environments, the pseudo-triangle trimeric compounds have been formed in matching the saturated and unsaturated coordinated geometry of the strontium atoms incorporating the characterization of ligands. Unique formation of the compound may be attributed to the steric effects of the ligands.

In summary, the reaction of strontium metal with keto ester and monoglyme ligands affords the new linear trimeric complex. The structural studies of the strontium complex with keto ester ligands have newly been contributed to the strontium β -diketonates for new coordination polymers.

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