

## Synthesis and Structural Characterization of Strontium Complex of Symmetrically Functionalized $\beta$ -Diketimine Ligand

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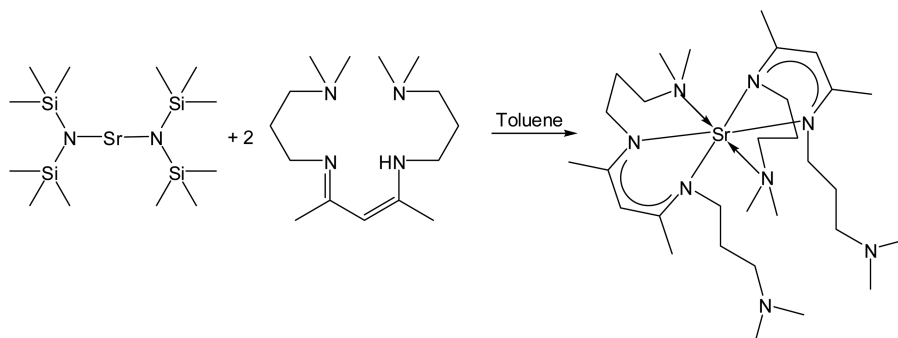
**Key Words :** Strontium complex,  $\beta$ -Diketimine ligand, Tetradentate ligand, Thermal properties, Precursor

The attraction in organometallic chemistry of the heavier alkaline earth elements such as, barium, strontium, and calcium have driven by their potential application in a variety of fields such as organic synthesis,<sup>1</sup> lactide polymerization,<sup>2</sup> and as precursors for the growth of thin films.<sup>3</sup> The synthesis of new compounds of strontium and other alkaline earth metals is often met with challenges such as poor compound stability and solubility. This is mainly because of the tendency of these metals, to form oligomeric compounds with low solubility and poor volatility owing to their large ionic radius combined with a small charge. Typically, three different approaches are used to prevent oligomerization: addition of neutral multidentate Lewis base molecules to the coordination sphere of the metal, use of large and sterically demanding ligands, or use of donor functionalized ligands. Sterically demanding ligands<sup>4</sup> such as  $\beta$ -diketiminates,<sup>5</sup> indenyls,<sup>6</sup> cyclopentadienyls,<sup>7</sup> and guanidates,<sup>4c</sup> which provide greater encapsulation of the metal, result in stable and soluble monomeric compounds. Among these,  $\beta$ -diketimine ligands commonly act as bidentate four-electron donors through the formation of two metal-nitrogen  $\sigma$ -bonds. Aside from the interesting structural features,  $\beta$ -diketimine ligands have been employed as important spectator ligands in catalytic processes, often as cyclopentadienyl or  $\beta$ -diketonato ligand replacements. The versatility of  $\beta$ -diketimine ligands is due to the fact that they can be modified

at both the nitrogen atoms and the carbon atoms of the ligand core to suit different steric and electronic demands of organometallic complexes. In pursuit of novel, structurally interesting alkaline earth metal complexes, we exploited the structural tunability of the  $\beta$ -diketimine ligands to design a new diketimine derivative and its strontium complex. Herein, we present the synthesis and structural characterization of a new strontium complex using newly synthesized symmetrically functionalized  $\beta$ -diketimine ligands.

The strontium complex SrL<sub>2</sub> was synthesized by treating Sr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·2DME with 2 equivalents of  $\beta$ -diketimine (LH) in toluene at room temperature (Scheme 1). The crystals of **1** were grown from a saturated hexane solution at -30 °C. Compound **1** was well characterized by single crystal X-ray diffraction, nuclear magnetic resonance (NMR) spectroscopy (<sup>1</sup>H, <sup>13</sup>C), Fourier-transform infrared (FT-IR) spectroscopy, elemental analysis, and thermogravimetric analysis (TGA).

The single-crystal X-ray study revealed that **1** crystallizes in the monoclinic space group C2/c (Details of experimental crystallographic data for **1** are summarized in Table 1). The crystal structure of **1** is shown in Figure 1, where it can be seen that the geometry around the strontium ion is a distorted octahedron. In all the previously reported strontium  $\beta$ -diketimine complexes,<sup>5b,8,9</sup> the valences of the strontium ion were satisfied either by the  $\pi$ -electron cloud of the



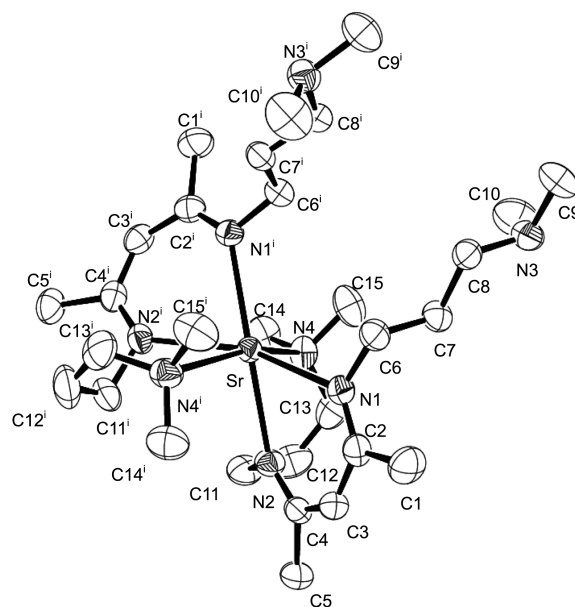
**Scheme 1.** Reaction scheme for the preparation of compound **1**.

**Table 1.** Crystallographic data and data collection parameters for **1**

<b>1</b>	
Formula	Sr(C <sub>15</sub> H <sub>31</sub> N <sub>4</sub> ) <sub>2</sub>
Formula weight	622.50
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	14.998(12)
<i>b</i> (Å)	13.483(11)
<i>c</i> (Å)	17.919(15)
$\alpha$ (°)	90.00
$\beta$ (°)	107.523(18)
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	3455(5)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.197
$\mu$ (mm <sup>-1</sup> )	1.591
<i>F</i> (000)	1344
<i>T</i> (K)	243(2)
<i>hkl</i> range	-21 ≤ <i>h</i> ≤ 21, -19 ≤ <i>k</i> ≤ 18, -25 ≤ <i>l</i> ≤ 21
Scan mode	multi
Meas'd reflns	18288
Reflns used for refinement	5388
Refined parameters	183
<i>R</i> <sup>1</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0478
<i>wR</i> <sup>2</sup> all data	0.1259
GOF on <i>F</i> <sup>2</sup>	1.023
$\rho_{\text{min}}$ (max/min) (e Å <sup>-3</sup> )	0.675, -0.767

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{1/2}.$$

diketiminate ligand (by  $\eta^2$ ,  $\eta^3$ ,  $\eta^5$  bonds), solvent molecules, or halogens. In complex **1**, the bulkiness of the ligands limited the coordination of the strontium to six. The coordination positions of strontium were satisfied by six nitrogen atoms from the two diketiminate (LH) ligands, leaving one amine site free from both ligands. The deviation from the ideal octahedral angle in the crystal structure of **1** might have been due to the steric interaction between the propylamine side chains of the ligands. The nitrogen-strontium-nitrogen bite angles for the  $\beta$ -diketiminate ligand backbone, N(1)–Sr–N(2) and N(1i)–Sr–N(2i), were 71.95(8)°, while the interligand nitrogen-strontium-nitrogen angles were between 123.20(10)° for N(1)–Sr–N(1i) and 100.23(11)° for N(2)–Sr–N(2i), which is a significant deviation from the ideal octahedral angle. The distortion of the geometry was also evidenced from the deviation in the dihedral angle of the N(1)–Sr–N(2) and N(1i)–Sr–N(2i) planes, which was 34.08(9)°. Four among the six Sr–N bonds in **1**, where the nitrogen atoms are from the diketiminate backbone were in the range 2.514(2)–2.573(2) Å, which is slightly longer than normal Sr–N bonds (2.49 Å),<sup>8</sup> while the other two axial Sr–N bonds from the amine side chains showed a longer bond length of 2.744(3) Å for Sr–N(4) and Sr–N(4i), which is shorter than typical Sr–N (amine) (2.8 Å) bonds.<sup>9,10</sup> The distance (N(3)⋯N(3i)) between nonbonded amine side chains was 5.744(7) Å, and the propyl amine side chain was flexible enough for an extended coordination. These two



**Figure 1.** Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) Sr–N(1) 2.573(2), Sr–N(2) 2.514(2), Sr–N(4) 2.744(3), N(1)–Sr–N(2) 71.95(8), N(1)–Sr–N(1i) 123.20(10), N(2)–Sr–N(2i) 100.23(11), N(2i)–Sr–N(1) 156.89(7), N(2)–Sr–N(4) 73.16(9), N(1)–Sr–N(4) 102.35(9), N(2)–Sr–N(4i) 95.74(8), N(2)–Sr–N(4) 73.16(9), N(1)–Sr–N(4i) 85.80(9), N(4)–Sr–N(4i) 162.99(9).

free coordination sites can be used for the synthesis of bimetallic complexes containing strontium ion.

The absence of an –NH peak in the <sup>1</sup>H NMR of **1** compared to the free diketiminate ligand was a clear indication of metal-ligand bond formation. The methyl groups of  $\beta$ -diketiminate ligand backbone appeared as a singlet at  $\delta$  2.00 in **1**, which were downfield compared to the free ligands ( $\delta$  1.74). The twelve methyl group protons attached to the side chain amine also moved downfield to a value of  $\delta$  2.14 for complex **1** compared to  $\delta$  2.12 in the free ligand. The hydrogen atoms on the  $\beta$ -CH fragments of the  $\beta$ -diketiminate ligands in **1** resonated at  $\delta$  4.52, which were upfield compared to the free ligand ( $\beta$ -CH) (LH)  $\delta$  4.59. In the <sup>13</sup>C {<sup>1</sup>H} NMR spectra, the  $\beta$ -CH fragment in **1** resonated at  $\delta$  93.9 and was upfield compared to the free ligand ( $\beta$ -CH) (LH)  $\delta$  94.8.

The FT-IR spectra of complex **1** showed a strong peak at 1560 cm<sup>-1</sup>, which is consistent with the partial C=N double bond character shown by the previously reported  $\beta$ -diketiminate complexes.<sup>11</sup> Thermogravimetric analysis of the complex **1** was carried out from room temperature to 900 °C (Figure 2) under a constant flow of nitrogen gas. Complex **1** decomposed in one step, losing about 76% of its mass in the 140–320 °C region, and this might have been due to the evaporation of the compound and possible decomposition of the product, finally leaving about 20% nonvolatile residue at 500 °C. The reason for the significant amount of residues was the decomposition of the complex during the TG analysis into nonvolatile compounds.

In summary, a new strontium  $\beta$ -diketiminate complex was synthesized and characterized. The crystal structure of the

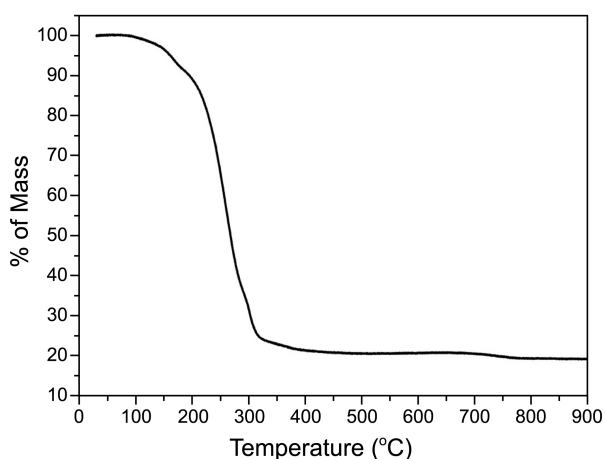


Figure 2. Thermogravimetric curve of **1**.

complex showed two free amine groups from the ligand side chains which might be useful in the synthesis of bimetallic complex containing strontium ion. The thermo-gravimetric analysis of complex **1** displayed single step decomposition, leaving 20% of nonvolatile residue. The studies to explore this compound as a possible strontium precursor for the growth of thin films of SrTiO<sub>3</sub> (STO), and Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> (BSTO) using MOCVD techniques are in progress.

### Experimental Section

Sr[N(SiMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2DME was prepared by the literature method.<sup>12</sup> All reactions were carried out in inert dry condition using standard Schlenk techniques or in argon filled glove box. Hexane and toluene were purified by Innovative Technology PS-MD-4 solvent purification system. All other chemicals were purchased from Aldrich and used as received. NMR spectra were recorded on Bruker 300 MHz spectrometer with C<sub>6</sub>D<sub>6</sub> as solvent and standard. IR spectra were obtained from Nicolet Nexus FT-IR spectrophotometer. Elemental analyses were carried out on Thermo Scientific OEA Flash 2000 Analyzer. Thermogravimetric analyses were carried out on SETARAM 92-18 TG-DTA instrument.

**Synthesis of N<sup>1</sup>-((Z)-4-(3-(Dimethylamino)propylamino)pent-3-en-2-ylidene)-N<sup>3</sup>,N<sup>3</sup>-dimethyl propane-1,3-diamine (LH).** A mixture of *N,N*-diisopropyl-2,4-pentanediketimine (78 g, 0.43 mol) and *N,N*-dimethyl-1,3-propanediamine (44 g, 0.43 mol) was heated at 130 °C for 14 h. The isopropyl amine formed during this reaction was removed by vacuum, and the resultant was further purified by vacuum distillation affording LH. (bp: 150 °C/0.02 mmHg, 23 g, 0.085 mol, 20%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 1.74 (s, 6H), 1.76 (quintet, 4H), 2.12 (s, 12H), 2.33 (t, 4H, *J* = 7.0 Hz), 3.22 (t, 4H, *J* = 6.74 Hz), 4.59 (s, 1H), 11.46 (s, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz) δ 19.4, 30.2, 44.7, 45.7, 57.8, 94.8, 160.2. FT-IR (KBr, cm<sup>-1</sup>): 2940 (m), 2860 (m), 2820 (m), 2771 (m), 1630 (vs), 1560 (s), 1500 (w), 1460 (m), 1440 (m), 1378 (w), 1338 (w), 1080 (w), 1042 (w), 834 (w), 723 (m). EI-MS, *m/z* (%): 268 (58) [M<sup>+</sup>].

**Synthesis of SrL<sub>2</sub> (1).** LH (0.537 g, 2 mmol) in 5 mL of

toluene was added drop wise to a stirring solution of Sr[N(SiMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2DME (0.59 g, 1 mmol) in toluene (10 mL). After stirring for 15 h at room temperature, the reaction mixture was evaporated to dryness to obtain a yellow solid. The residue was then re-dissolved in hexane and filtered through 0.2 μm filter. The hexane was then evaporated to obtain the product as yellow crystalline solid. X-ray quality crystals were grown from a concentrated hexane solution upon cooling. Yield: 0.56 g (90%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 1.61 (quintet, 4H, *J* = 6.7 Hz), 2.00 (s, 6H), 2.14 (s, 12H), 2.30 (t, 4H, *J* = 6.4 Hz), 3.45 (t, 4H, *J* = 6.9 Hz), 4.52 (s, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz) δ 21.5, 30.3, 45.5, 47.5, 58.2, 93.9, 163.9. FT-IR (KBr, cm<sup>-1</sup>): 2940 (m), 2860 (m), 2820 (m), 2771 (m), 1630 (s), 1560 (s), 1490 (s), 1459 (s), 1420 (s), 1340 (s), 1269 (w), 1155 (w), 1062 (w), 1042 (w), 1009 (w), 830 (w), 726 (w), 710 (m). EI-MS, *m/z* (%): 268 (58) [L<sup>+</sup>]. Anal. Calcd for C<sub>30</sub>H<sub>62</sub>N<sub>6</sub>Sr (622.5): C, 57.88; H, 10.04; N, 18.00. Found: C, 57.63; H, 10.39; N, 18.59.

**X-ray Crystallography.** Single crystals of **1** were grown from a saturated hexane at -30 °C. A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. Reflection data were collected on a Bruker Apex II-CCD area detector diffractometer, with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The hemisphere of reflection data were collected as ω scan frames with 0.3°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by SMART program.<sup>13</sup> Data reduction was performed using SAINT software.<sup>14</sup> The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.<sup>15</sup> The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on *F*<sup>2</sup> by using the SHELXTL/PC package.<sup>16</sup> Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

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**Supporting Information.** Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-853154 for compound **1**. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic DataCentre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +441223336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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