

Synthesis and characterization of monomeric Ba and Sr complexes with malonate and Lewis base ligands

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Abstract

The reaction of barium or strontium metal in ammonia gas-saturated THF with two equivalents of dimethyl malonate (dmalH) in the presence of tetraethylene glycol dimethyl ether (tetraglyme) or 1,1,4,7,7-pentamethyldiethylenetriamine (pmdt) yields Ba(dmal)₂(tetraglyme) (**1**), Ba(dmal)₂(pmdt) (**2**), Sr(dmal)₂(tetraglyme) (**3**), and Sr(dmal)₂(pmdt) (**4**) as colorless crystals in reasonable yields (45–52%). These complexes have been characterized by spectroscopic methods (IR and ¹H- and ¹³C-NMR) and elemental analysis data. Molecular structures of **1**, **3**, and **4** have been determined by X-ray diffraction studies and have revealed that they are monomeric and the tetraglyme or pmtd ligand wraps around a central metal atom in a meridional plane with the dmal ligands on opposite sides of this plane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Barium; Strontium; Malonate; Precursor

1. Introduction

In recent years there has been considerable interest in Group 2 metal oxide thin films due to their potential for future microelectronics applications such as superconductors (YBa₂Cu₃O₇), high dielectric constant oxides (Ba_xSr_{1-x}TiO₃), and ferroelectric materials (SrBi₂Ta₂O₉) [1]. These thin film materials may be deposited by chemical vapor deposition (CVD) using appropriate precursors and liquid delivery techniques. Recent efforts for the development of precursors have utilized both non-fluorinated and fluorinated Group 2 CVD precursors containing alkoxide, β-diketonate, and related ligands [2]. Monomeric Group 2 metal β-diketonates can be prepared by saturating the metal coordination sphere with polydentate neutral Lewis bases such as polyethers and polyamines, and have found wide application in CVD due to their improved volatilities. However, the coordinated Lewis bases are readily lost

upon sublimation [3]. In order to prevent facile dissociation of the Lewis base units, Rees and Marks have developed new ligand systems in which the polyether units are covalently linked to β-diketone or β-ketoimine backbones [4]. Fluorinated β-diketones such as hexafluoroacetylacetone (hfacH) have also been employed, since the coordinated Lewis bases do not undergo significant dissociation upon sublimation in fluorinated β-diketonates complexes, presumably reflecting the electron-withdrawing nature of the fluorine atoms and the resulting enhanced Lewis acidity of the metal(2+) center. Fluorinated precursors exhibit higher vapor pressures and improved stability, but deposited films are typically contaminated by fluoride impurities [5].

Herein we present synthesis and characterization of monomeric barium and strontium precursors of a β-diester ligand, dimethyl malonate, in which both alkyl groups on the β-diketonate ligand are modified with the alkoxy groups. The electron-withdrawing characteristics of the alkoxy substituents in the malonate ligand is expected to enhance Lewis acidity of the central metal center and thus stabilize the coordinated Lewis base as observed in the fluorinated precursors.

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2. Results and discussion

2.1. Synthesis and characterization of 1–4

Monomeric Group 2 metal β -diketonates are generally prepared by redox reactions between metals and corresponding β -diketones in the presence of Lewis bases [3]. Dimethyl malonate (dmalH), however, remains inert towards barium and strontium metals, which may be ascribed to the lack of enolization of ester compounds [6]. The attempted metathesis reactions between MX_2 ($\text{M} = \text{Ba}, \text{Sr}; \text{X} = \text{Cl}, \text{I}, \text{OOCCH}_3$) and alkali metal (Li, Na) salt of dimethyl malonate have not been successful. Activation of the metals in ammonia gas-saturated ethereal solvents, pioneered by Drake [7], with the malonate and Lewis base ligands in situ leads to a rapid reaction and produces $\text{Ba}(\text{dmal})_2(\text{tetraglyme})$ (**1**), $\text{Ba}(\text{dmal})_2(\text{pmdt})$ (**2**), $\text{Sr}(\text{dmal})_2(\text{tetraglyme})$ (**3**), and $\text{Sr}(\text{dmal})_2(\text{pmdt})$ (**4**) as colorless crystals in reasonable yields (45–52%). Tetraglyme and 1,1,4,7,7-pentamethyldiethylenetriamine (pmdt) have been used as Lewis bases. Formulation of complexes, **1–4**, is supported by elemental analyses. Molecular ion peaks of **1–4** could not be observed in the electron impact (40 and 70 eV) mass spectra. The IR spectra of all the complexes show characteristic bands of $\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{O}$ stretching of the malonate ligand in the 1500–1750 cm^{-1} region.

The NMR (^1H and ^{13}C) spectral data of **1–4** are consistent with the molecular structures described herein. The ^1H -NMR spectra of all four complexes in CDCl_3 reveal a characteristic signal (δ 4.00–4.10) for the methyne proton of the malonate moiety, which compares with the methylene resonances at δ 3.60 of the free dimethyl malonate. A downfield shift for the

methyne signals of the β -diketonate ligands upon coordination to the Group 2 metals has been previously noted for various $\text{M}(\beta\text{-diketonate})_2(\text{Lewis base})$ complexes. All four complexes show resonances for one type of malonate, tetraglyme and pmtd ligand environment, implying that molecules **1–4** are stereochemically non-rigid in solution at room temperature. The integral ratio of dimethyl malonate to tetraglyme or pmtd ligand was observed to be 2:1.

The ^{13}C -NMR spectral data have been assigned by comparison with both free ligand and DEPT experiment as shown in Table 1. The resonances of carbonyl and methyne carbons of the dimethyl malonate ligand are shifted to downfield, whereas those for methoxy carbon to upfield, with respect to the free ligand. In contrast with this observation, in β -diketonate complexes, downfield shift of the alkyl group and upfield shift of the carbonyl and methyne groups have been previously observed, which was rationalized on the basis of electron-rich and electron-withdrawing nature of the 1,3-diketonato chelate ring system by Drake and coworkers [3c,3d]. Reversal of chemical shifts observed in the present β -diester complexes compared to the β -diketonate complexes may be attributed to the electron-withdrawing nature of the methoxide group of the malonate ligand. The ^{13}C -NMR chemical shifts of tetraglyme and pmtd ligands in **1–4** are comparable or shifted slightly upfield compared to free ligands (see Table 1), which is consistent with the previous results in $\text{Ba}(\text{tmhd})_2(\text{tetraglyme})$ and $\text{Ba}(\text{hfac})_2(\text{tetraglyme})$ ($\text{tmhdH} = 2,2,6,6\text{-tetramethyl-3,5-heptanedione}$) [3a]. Deposition of thin film with precursors **1–4** is currently under investigation and will be reported elsewhere.

2.2. Crystal structures of 1, 3, and 4

The overall molecular geometries and the atomic labeling schemes of **1**, **3**, and **4** are illustrated in Figs. 1–3. Interatomic distances and angles are listed in Tables 2 and 3, respectively.

The overall structural features of $\text{Ba}(\text{dmal})_2(\text{tetraglyme})$ (**1**) and $\text{Sr}(\text{dmal})_2(\text{tetraglyme})$ (**3**) are similar to those of known $\text{M}(\text{tmhd})_2(\text{tetraglyme})$ ($\text{M} = \text{Ba}, \text{Sr}$) with the tetraglyme wrapping around the metal center in a meridional plane and the two dmal ligands on the opposite sides of this plane. The coordination geometry around central metals of **1** and **3** can be best described as a distorted capped square antiprism with a coordination number of nine. The two tetragonal vertices of the antiprism are defined by the O(1), O(2), O(12), O(13) and the O(5), O(6), O(9), O(10) atoms, with the O(11) atom being capped. The metal–oxygen bonds in both structures fall into two discrete categories; $\text{Ba}-\text{O}_{\text{dmal}} = \text{average } 2.673(10)$ and $\text{Ba}-\text{O}_{\text{glyme}} = \text{average } 2.881(12)$ Å for **1**, $\text{Sr}-\text{O}_{\text{dmal}} = \text{average } 2.523(15)$ Å and $\text{Sr}-\text{O}_{\text{glyme}} = \text{average } 2.754(18)$ Å for **3**. The fact that M–O bonds in

Table 1
Comparison of ^{13}C -NMR data of **1–4** with those of free ligands

Compound	Chemical shifts in CDCl_3
<i>dmalH</i> : $\text{CH}_2(\overset{\text{a}}{\text{C}}\text{OO}\overset{\text{c}}{\text{C}}\text{H}_3)_2$	41.1 (a), 52.5 (c), 166.9 (b)
$\text{Ba}(\text{dmal})_2(\text{tetraglyme})$ (1)	49.3 (c), 61.3 (a), 172.3 (b)
$\text{Ba}(\text{dmal})_2(\text{pmdt})$ (2)	52.5 (c), 64.7 (a), 173.4 (b)
$\text{Sr}(\text{dmal})_2(\text{tetraglyme})$ (3)	49.6 (c), 61.6 (a), 172.8 (b)
$\text{Sr}(\text{dmal})_2(\text{pmdt})$ (4)	49.7 (c), 62.4 (a), 173.3 (b)
<i>tetraglyme</i> : $(\overset{\text{a}}{\text{C}}\text{H}_3\text{O}\overset{\text{b}}{\text{C}}\text{H}_2\overset{\text{c}}{\text{C}}\text{H}_2\text{O}-\overset{\text{d}}{\text{C}}\text{H}_2\overset{\text{e}}{\text{C}}\text{H}_2)_2\text{O}$	59.7 (a), 71.2, 71.3, 72.7 (b–e)
$\text{Ba}(\text{dmal})_2(\text{tetraglyme})$ (1)	59.0 (a), 70.3, 70.5, 71.4 (b–e)
$\text{Sr}(\text{dmal})_2(\text{tetraglyme})$ (3)	59.1 (a), 69.8, 70.3, 70.5, 71.4 (b–e)
<i>pmdt</i> : $\{(\overset{\text{a}}{\text{C}}\text{H}_3)_2\overset{\text{b}}{\text{N}}\overset{\text{c}}{\text{C}}\text{H}_2\overset{\text{d}}{\text{C}}\text{H}_2\}_2-\overset{\text{e}}{\text{N}}\overset{\text{f}}{\text{C}}\text{H}_3$	42.9 (d), 45.9 (a), 58.2, 57.4 (b, c)
$\text{Ba}(\text{dmal})_2(\text{pmdt})$ (2)	42.9 (d), 45.9 (a), 56.2, 57.5 (b, c)
$\text{Sr}(\text{dmal})_2(\text{pmdt})$ (4)	43.5 (d), 45.3 (a), 55.6, 57.1 (b, c)

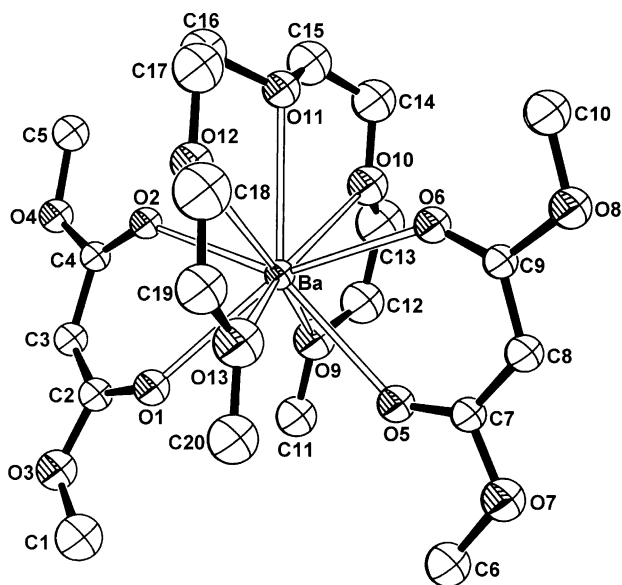


Fig. 1. Molecular structure and atomic labeling scheme for Ba(dmal)₂(tetraglyme) (**1**) with 20% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity.

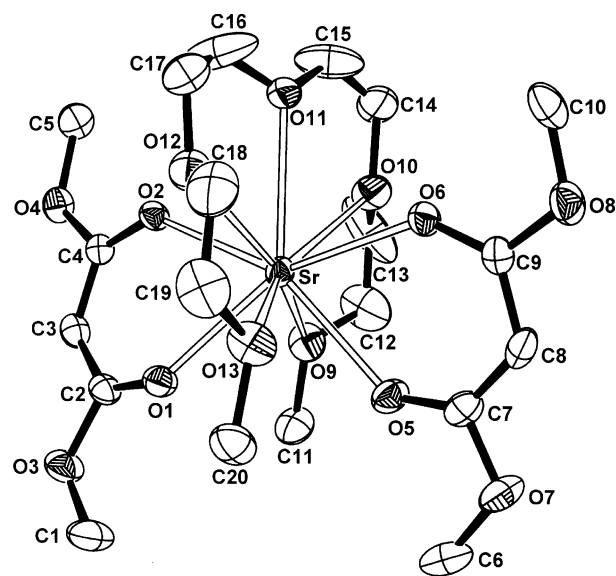


Fig. 2. Molecular structure and atomic labeling scheme for Sr(dmal)₂(tetraglyme) (**3**) with 20% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity.

1 are longer than the corresponding bonds in **3** is consistent with the atomic radius difference of barium and strontium. The tetraglyme ligand adopts a conventional geometry with *gauche* and *anti* relationships around C–C and C–O bonds, respectively. The dihedral angles between the two MO₂ (dmal) planes are 37.8(8)° for **1** and 33.4(8)° for **3**, which compares with 19.3(2)° for Ba(hfac)₂(tetraglyme) and 29.6(2)° for Ba(tmhd)₂(tetraglyme) [3a].

The molecular structure of Sr(dmal)₂(pmdt) (**4**) reveals that the strontium atom is seven-coordinate and

all three nitrogen atoms of the pmtd ligand are coordinated to the metal center in a meridional fashion between the two dmal ligands. The overall structure is similar to that of known Ba(tmhd)₂(pmdt) compound [3e,3f]. The coordination geometry around the strontium atom is a distorted capped trigonal prism defined by O(1), O(5), N(3) and O(2), O(6), N(1) trigonal faces and the capping N(2) atom. The distances from Sr atom to the dmal oxygen atoms range from 2.478(8) to 2.519(7) Å (average 2.502(8) Å). The average Sr–N bond distance is average 2.775(9) Å with the distance to the internal nitrogen N(2) being larger than the others. The dihedral angle between the two dmal ligands is 58.3(2)°, which is much larger than those for **1** and **3**, presumably, due to steric bulkiness of methyl groups on N(1) and N(3) atoms.

3. Experimental

3.1. General comments

All manipulations were carried out by using standard Schlenk techniques and Vacuum Atmospheres HE-439 drybox under a dry, oxygen-free argon atmosphere. All solvents were dried according to standard procedures, distilled under Ar, and stored over 4 Å molecular sieves. Ba and Sr metals were purchased from Strem Chemicals and used after washing with dry C₆H₁₄. The following chemicals were obtained from commercial sources and used as received: dimethyl malonate, tetraethylene glycol dimethyl ether, 1,1,4,7,7-pentamethyldiethylenetriamine (Aldrich); NH₃ (Union Carbide, anhydrous grade). The ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Infrared spectra (KBr)

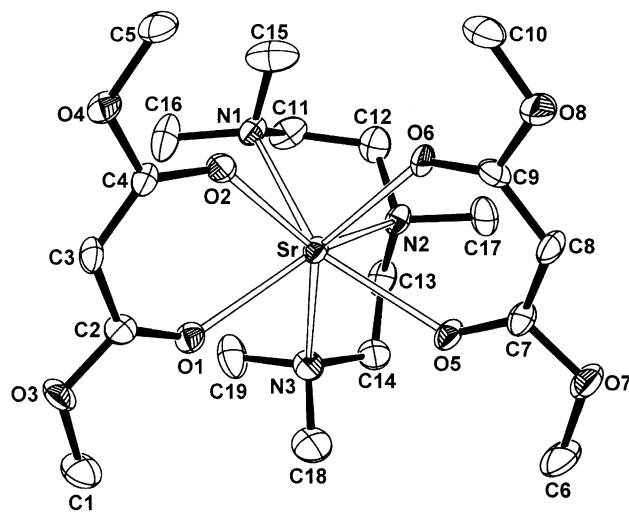


Fig. 3. Molecular structure and atomic labeling scheme for Sr(dmal)₂(pmdt) (**4**) with 20% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) with estimated S.D. values for Ba(dmal)₂(tetraglyme) (**1**), Sr(dmal)₂(tetraglyme) (**3**), and Sr(dmal)₂(pmdt) (**4**)

1		3		4	
Ba–O(1)	2.671(11)	Sr–O(1)	2.490(21)	Sr–O(1)	2.502(8)
Ba–O(2)	2.677(9)	Sr–O(2)	2.529(12)	Sr–O(2)	2.507(7)
Ba–O(5)	2.691(11)	Sr–O(5)	2.527(6)	Sr–O(5)	2.519(7)
Ba–O(6)	2.653(10)	Sr–O(6)	2.547(18)	Sr–O(6)	2.478(8)
Ba–O(9)	2.847(12)	Sr–O(9)	2.763(15)	Sr–N(1)	2.754(9)
Ba–O(10)	2.890(11)	Sr–O(10)	2.739(22)	Sr–N(2)	2.830(9)
Ba–O(11)	2.890(11)	Sr–O(11)	2.750(15)	Sr–N(3)	2.742(10)
Ba–O(12)	2.936(12)	Sr–O(12)	2.778(13)	O(1)–C(2)	1.236(12)
Ba–O(13)	2.843(12)	Sr–O(13)	2.740(21)	O(2)–C(4)	1.229(12)
O(1)–C(2)	1.253(19)	O(1)–C(2)	1.225(9)	O(5)–C(7)	1.237(12)
O(2)–C(4)	1.206(15)	O(2)–C(4)	1.231(8)	O(6)–C(9)	1.208(13)
O(5)–C(7)	1.253(19)	O(5)–C(7)	1.222(10)	C(2)–C(3)	1.395(14)
O(6)–C(9)	1.253(19)	O(6)–C(9)	1.235(9)	C(3)–C(4)	1.382(14)
C(2)–C(3)	1.34(2)	C(2)–C(3)	1.382(11)	C(7)–C(8)	1.378(14)
C(3)–C(4)	1.43(2)	C(3)–C(4)	1.391(10)	C(8)–C(9)	1.413(15)
C(7)–C(8)	1.35(2)	C(7)–C(8)	1.362(17)		
C(8)–C(9)	1.41(2)	C(8)–C(9)	1.412(17)		

Table 3
Selected bond angles (°) with estimated S.D. values for Ba(dmal)₂(tetraglyme) (**1**), Sr(dmal)₂(tetraglyme) (**3**), and Sr(dmal)₂(pmdt) (**4**)

1		3		4	
O(1)–Ba–O(2)	64.5(3)	O(1)–Sr–O(2)	68.9(5)	O(1)–Sr–O(2)	69.2(2)
O(1)–Ba–O(5)	90.0(3)	O(1)–Sr–O(5)	88.3(5)	O(1)–Sr–O(5)	105.6(3)
O(1)–Ba–O(6)	149.3(3)	O(1)–Sr–O(6)	148.1(7)	O(1)–Sr–O(6)	131.5(3)
O(2)–Ba–O(5)	145.9(3)	O(2)–Sr–O(5)	146.1(6)	O(2)–Sr–O(5)	126.6(3)
O(2)–Ba–O(6)	144.9(3)	O(2)–Sr–O(6)	140.6(7)	O(2)–Sr–O(6)	75.6(2)
O(5)–Ba–O(6)	65.8(3)	O(5)–Sr–O(6)	69.3(3)	O(5)–Sr–O(6)	70.4(2)
Ba–O(1)–C(2)	133.9(10)	Sr–O(2)–C(4)	133.1(6)	Sr–O(1)–C(2)	136.3(7)
Ba–O(2)–C(4)	135.2(10)	Sr–O(1)–C(2)	132.8(6)	Sr–O(2)–C(4)	134.9(7)
Ba–O(5)–C(7)	134.5(10)	Sr–O(5)–C(7)	134.7(7)	Sr–O(5)–C(7)	132.8(8)
Ba–O(6)–C(9)	136.2(10)	Sr–O(6)–C(9)	134.9(6)	Sr–O(6)–C(9)	135.1(8)
O(1)–C(2)–C(3)	128.9(14)	O(1)–C(2)–C(3)	129.0(7)	O(1)–C(2)–C(3)	127.3(12)
C(2)–C(3)–C(4)	123.5(14)	C(2)–C(3)–C(4)	122.7(7)	C(2)–C(3)–C(4)	122.7(11)
O(2)–C(4)–C(3)	126.9(14)	O(2)–C(4)–C(3)	127.1(7)	O(2)–C(4)–C(3)	129.0(11)
O(5)–C(7)–C(8)	129.3(16)	O(5)–C(7)–C(8)	129.2(9)	O(5)–C(7)–C(8)	129.5(12)
C(7)–C(8)–C(9)	123.5(15)	C(7)–C(8)–C(9)	124.0(10)	C(7)–C(8)–C(9)	121.9(11)
O(6)–C(9)–C(8)	129.3(14)	O(6)–C(9)–C(8)	127.0(9)	O(6)–C(9)–C(8)	128.5(11)

were obtained with a Bruker EQUINOX-55 FTIR spectrophotometer. The melting points were measured using an electrothermal melting point apparatus under Ar in sealed capillaries and are given uncorrected. Elemental analyses were performed by the staff of the Energy and Environment Research Center at KAIST.

3.2. Syntheses

3.2.1. Ba(dmal)₂(tetraglyme) (**1**)

A THF solution (30 ml) of dimethyl malonate (1.435 g, 10.86 mmol) was added to a suspension of Ba metal (0.748 g, 5.44 mmol) in tetraglyme (1.271 g, 5.72 mmol). Gaseous NH₃ was bubbled into the reaction mixture for 20 min at 0 °C. The solution was stirred for 2 h at 0 °C, and during the reaction treatment with

NH₃ was repeated for ca. 5 min three times in order to ensure that all the Ba had reacted. After filtration, the filtrate was stripped to dryness to give a colorless residue. Recrystallization of the residue in C₆H₅CH₃ at –30 °C gave **1** (1.731 g, 2.77 mmol, 51% based on Ba) as colorless crystals: m.p. 141–143 °C; ¹H-NMR (CDCl₃, 20 °C): δ 3.40 (s, 12H, COOCH₃), 3.49 (s, 6H, OCH₃), 3.73, 3.68, 3.61, 3.52 (m, 4H each, OCH₂CH₂O), 4.04 (s, 2H, CH); ¹³C-NMR (CDCl₃, 20 °C): δ 49.3 (COOCH₃), 59.0 (OCH₃), 61.3 (CH), 70.3, 70.5, 71.4 (OCH₂CH₂O), 172.3 (COO); IR (KBr, cm⁻¹): 2942 m, 1664 s, 1548 s, 1480 s, 1404 w, 1344 w, 1221 m, 1179 w, 1122 s, 1073 vs, 1022 m, 946 w, 878 w, 783 w, 728 w, 696 w, 420 w; Anal. Calc. for C₂₀H₃₆BaO₁₃: C, 38.63; H, 5.84. Found: C, 38.79; H, 6.06%.

3.2.2. *Ba(dmal)₂(pmdt) (2)*

A procedure similar to that used for **1** was followed with Ba metal (1.673 g, 12.18 mmol), dimethyl malonate (3.305 g, 25.02 mmol), and pmdt (2.252 g, 12.99 mmol). Recrystallization of the crude product in C₆H₅CH₃ at –30 °C produced **2** (3.302 g, 5.48 mmol, 45% based on Ba) as colorless crystals: m.p. 115–117 °C; ¹H-NMR (CDCl₃, 20 °C): δ 2.22 (s, 12H, N(CH₃)₂), 2.24 (s, 3H, NCH₃), 2.38, 2.47 (m, 4H each, NCH₂CH₂N), 3.47 (s, br, 12H, OCH₃), 4.00 (s, br, 2H, CH); ¹³C-NMR (CDCl₃, 20 °C): δ 42.9 (NCH₃), 45.9 (N(CH₃)₂), 52.5 (OCH₃), 56.2, 57.5 (NCH₂CH₂N), 64.7 (CH), 173.4 (COO); IR (KBr, cm⁻¹): 2956 m, 2826 w, 2778 w, 1738 s, 1562 s, 1439 s, 1357 s, 1261 m, 1159 m, 1028 s, 934 w, 801 w, 698 m, 595 w, 494 w; Anal. Calc. for C₁₉H₃₇BaN₃O₈: C, 39.84; H, 6.51; N, 7.34. Found: C, 40.01; H, 6.63; N, 7.36%.

3.2.3. *Sr(dmal)₂(tetraglyme) (3)*

A procedure similar to that used for **1** was followed with Sr metal (1.736 g, 19.81 mmol), dimethyl malonate (5.547 g, 41.98 mmol), and tetraglyme (4.593 g, 20.66 mmol). Recrystallization of the crude product in C₆H₅CH₃ at –30 °C afforded **3** (6.022 g, 10.30 mmol, 52% based on Sr) as colorless crystals: m.p. 144–

146 °C; ¹H-NMR (CDCl₃, 20 °C): δ 3.37 (s, 12H, COOCH₃), 3.50 (s, 6H, OCH₃), 3.53, 3.65 (m, 4H each, OCH₂CH₂O), 3.74 (s, br, 8H, OCH₂CH₂O), 4.08 (s, 2H, CH); ¹³C-NMR (CDCl₃, 20 °C): δ 49.6 (COOCH₃), 59.1 (OCH₃), 61.6 (CH), 69.8, 70.3, 70.5, 71.4 (OCH₂CH₂O), 172.8 (COO); IR (KBr, cm⁻¹): 2944 m, 1667 s, 1552 s, 1483 s, 1404 m, 1346 w, 1226 m, 1180 m, 1121 s, 1073 vs, 1025 m, 944 w, 879 m, 784 m, 730 w, 696 m, 423 w; Anal. Calc. for C₂₀H₃₆O₁₃Sr: C, 41.99; H, 6.34. Found: C, 42.39; H, 6.59%.

3.2.4. *Sr(dmal)₂(pmdt) (4)*

A procedure similar to that used for **1** was followed with Sr metal (0.849 g, 9.69 mmol), dimethyl malonate (2.602 g, 19.69 mmol), and pmdt (1.707 g, 9.85 mmol). Recrystallization of crude product in C₆H₅CH₃ at –30 °C yielded **4** (2.421 g, 4.55 mmol, 47% based on Sr) as colorless crystals: m.p. 119–121 °C; ¹H-NMR (CDCl₃, 298 K): δ 2.23 (s, 12H, N(CH₃)₂), 2.33 (s, 3H, NCH₃), 2.38, 2.67 (s, br, 4H each, NCH₂CH₂N), 3.48 (s, 12H, OCH₃), 4.10 (s, 2H, CH); ¹³C-NMR (CDCl₃, 298 K): δ 43.5 (NCH₃), 45.3 (N(CH₃)₂), 49.7 (OCH₃), 55.6, 57.1 (NCH₂CH₂N), 62.4 (CH), 173.3 (COO); IR (KBr, cm⁻¹): 2950 m, 2819 m, 2777 w, 1741 s, 1666 s, 1583 s, 1459 s, 1365 m, 1259 w, 1154 w, 1128 m, 1087

Table 4
Crystal data and structure refinement for **1**, **3**, and **4**

	1	3	4
Empirical formula	C ₂₀ H ₃₆ O ₁₃ Ba	C ₂₀ H ₃₆ O ₁₃ Sr	C ₁₉ H ₃₇ N ₃ O ₈ Sr
Formula weight	621.83	572.11	523.14
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions			
<i>a</i> (Å)	12.904(3)	19.025(3)	10.211(2)
<i>b</i> (Å)	12.376(2)	12.202(3)	17.615(3)
<i>c</i> (Å)	18.210(2)	12.971(2)	14.860(9)
β (°)	105.87(1)	116.01(1)	106.86(3)
<i>V</i> (Å ³)	2797.3(8)	2706.2(9)	2558(2)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (mg m ⁻³)	1.477	1.404	1.358
Absorption coefficient (mm ⁻¹)	1.476	2.051	2.152
<i>F</i> (000)	1264	1192	1096
Crystal size (mm)	0.45 × 0.42 × 0.33	0.56 × 0.56 × 0.40	0.63 × 0.36 × 0.20
θ range for data collection (°)	2.01–23.00	2.05–23.00	2.08–22.00
Index ranges	–11 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 13	–18 ≤ <i>h</i> ≤ 20, –13 ≤ <i>k</i> ≤ 13, –14 ≤ <i>l</i> ≤ 0	–10 ≤ <i>h</i> ≤ 10, –0 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 15
Reflections collected	4039	3852	2510
Independent reflections	3898 [<i>R</i> _{int} = 0.0680]	1883 [<i>R</i> _{int} = 0.0461]	2388 [<i>R</i> _{int} = 0.0596]
Data/parameters	3898/308	1883/307	2388/280
Final <i>R</i> indices, [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> = 0.0678, <i>R</i> _w = 0.1788	<i>R</i> = 0.0368, <i>R</i> _w = 0.0728	<i>R</i> = 0.0631, <i>R</i> _w = 0.1111
Goodness-of-fit on <i>F</i> ² ^b	1.044	1.058	1.022
Largest difference peak and hole (e Å ⁻³)	1.407 and –1.064	0.354 and –0.182	0.409 and –0.446

^a $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $R_w = [(\sum \omega(|F_o| - |F_c|)^2) / \sum \omega |F_o|^2]^{1/2}$.

^b Goodness-of-fit = $[\sum \omega(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

s, 1029 m, 936 w, 887 w, 785 m, 701 m, 578 w; Anal. Calc. for $C_{19}H_{37}N_3O_8Sr$: C, 43.62; H, 7.13; N, 8.03. Found: C, 43.89; H, 7.45; N, 8.08%.

3.3. X-ray crystallographic study of **1**, **3**, and **4**

Single crystals suitable for X-ray diffraction studies were obtained by slow recrystallization in toluene at $-30\text{ }^\circ\text{C}$. Crystals were mounted in thin-walled glass capillaries under an Ar atmosphere, and the capillaries were temporarily sealed with Si grease and then flame-sealed. The determination of unit cell parameters, orientation matrix, and the collection of intensity data were made on an Enraf–Nonius CAD-4 diffractometer utilizing graphite-monochromated $Mo\text{-}K_\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$) at ambient temperature. Lorentz and polarization corrections were applied to the intensity data while no absorption correction was applied. Intensities of three standard reflections monitored every 4 h showed no significant decay over the course of data collection. Relevant crystallographic details are summarized in Table 4.

All calculations were performed using the SHELXS86 and SHELXL97 computer programs [8]. Scattering factors for all atoms were included in the software package. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. In the final cycle of refinement, the mean shift/estimated S.D.s were less than 0.001.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168808, 168809, and 168810 for compounds **1**, **3**, and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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