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Group 2 Metal Bis(arenecarbochalcogenoato)(Crown Ether) Complexes: Isolation and Structural Analysis

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1. Experimental section

1.1 General considerations

Melting points were determined with a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer. ^{1}H, ^{13}C and ^{77}Se NMR were recorded on a JEOL JNM-α400 instrument at 399.7, and 100.4, and 76.2 MHz, respectively, in DMSO-d_6 or acetone-d_6 containing tetramethylsilane or dimethyl selenide as internal standard. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Potassium arenecarbothioates**[S1]** and sodium**[S2]** and potassium arenecarboselenoates**[S3]** and potassium arenecarbodithioates**[S4]** were prepared according to the procedures described in the literatures. Anhydrous MgI_2, CaI_2, SrI_2, $SrI_2{\cdot}5.5H_2O$ and BaI_2 were purchased from Wako Pure Chemical Ind. Ltd. and used without further purification. Crown ethers [15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) and 18-crown-6 ethers (1,4,7,10,13,16-hexaoxacyclooctadecane)] were purchased from Aldrich and used without further purification. The following solvents were purified under argon and dried as indicated: hexane and tetrahydrofuran (thf), refluxed with sodium metal using benzophenone as indicator and distilled before use: acetone and acetonitrile, distilled over calcium dichloride anhydride, after refluxing for 5 h. All manipulations were carried out under argon.

1.2 Syntheses

Calcium bis(arenecarbothioato)(L) (L = H_2O or THF) **4**

Calcium bis(4-methylbenzenecarbothioato)($(H_2O)_{2.3}$) **4ba**. A suspension of potassium 4-methylbenzenecarbothioate **1b** (0.909 g, 4.70 mmol) in H_2O (15 mL) was added to calcium diiodide (0.690 g, 2.35 mmol) in the same solvent (3 mL) and the mixture was stirred at 24 °C for 1.5 h. The resulting precipitates were filtered off by the use of glass filter. Removal of the solvent under reduced pressure (23 °C/0.4 Pa) gave pale yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 18 °C for 30 min. Filtration of the insoluble parts gave 0.173 g (17%) of the compound **4ba** as pale yellow micro crystals, m.p. 172–178 °C (decomp.) (Found: C, 55.58; H, 4.82; Calc. for $C_{20}H_{20.3}CaO_{4.3}S_2$ (433.68): C, 55.39; H, 4.72%); ν_{max} (KBr)/cm^{-1} 3442, 3360 (br), 2912, 2866, 1612 (COS), 1598, 1523, 1445, 1385, 1310, 1246, 1210, 1157, 1110, 1022, 984, 831 and 728; δ_H(400 MHz; DMSO–d_6; Me_4Si) 2.17 (6 H, s, CH_3), 3.46 (2 H, b, H_2O), 7.02 (4 H, d, J = 8.7 Hz, arom) and 8.14 (4H, d, J = 8.7 Hz, arom); δ_C(100

MHz; DMSO-d_6; Me_4Si) 21.6 (CH_3), 126.8, 128.0, 139.3, 142.6 (arom) and 212.6 (CSO).

Calcium bis(4-methylbenzenecarbothioato)(THF) **4bb**. A suspension of potassium 4-methylbenzenecarbothioate **1b** (0.917 g, 4.84 mmol) in THF (7 mL) was added to calcium diiodide (0.711 g, 2.42 mmol) in the same solvent (3 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off by a glass filter. Removal of the solvent under reduced pressure (26 °C/0.1 Pa) gave yellow solid. Hexane (5 mL) was added to the solid and the mixture was stirred at 20 °C for 1 h. Filtration of the insoluble parts gave 0.431 g (43%) of the compound **4bb** as pale yellow micro crystals, m.p. 187–193 °C (decomp.) (Found: C, 58.04; H, 5.43. Calc. for $C_{20}H_{22}CaO_3S_2$ (414.594): C, 57.94; H, 5.35%); ν_{max} (KBr)/cm^{-1} 3018, 1615 (COS), 1598, 1502, 1446, 1375, 1311, 1249, 1212, 1157, 1110, 1016, 983, 833 and 728; δ_H(400 MHz; DMSO–d_6; Me_4Si) 1.87 (4 H, t, OCH_2), 2.19 (6 H, s, CH_3), 3.81 (4 H, t, CH_2), 7.22 (4 H, d, J = 8.7 Hz, arom) and 8.17 (4 H, d, J = 8.7 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 21.5 (CH_3), 25.4 (THF-CH_2), 67.7 (THF-OCH_2), 127.3, 128.1, 138.7, 141.9 (arom) and 210.1 (CSO).

Strontium bis(4-methylbenzenecarbothioato)(H_2O)$_{1.2}$(THF) **5b**. A suspension of potassium 4-methylbenzenecarbothioate **5b** (0.992 g, 5.24 mmol) in THF (7 mL) was added to $SrI_2\cdot5.5H_2O$ (1.155 g, 2.62 mmol) in the same solvent (3 mL) and the mixture was stirred at 23 °C for 1 h. The resulting precipitates were filtered off. Removal of the solvent under reduced pressure (23 °C/0.1 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.456 g (36%) of the compound **5b** containing both molecules of THF and H_2O as pale yellow micro crystalline solid, m.p. 167–175 °C (decomp.) (Found: C, 49.82; H, 5.27; Calc. for $C_{20}H_{24.2}O_{4.2}S_2Sr$ (483.55): C, 49.68; H, 5.04%); ν_{max} (KBr)/cm^{-1} 3426, 3268 (br), 1602 (COS), 1567, 1468, 1305, 1242, 1210, 1105, 1035, 1010, 978, 875, 817, 778, 707, 664, 613 and 542; δ_H(400 MHz; acetone-d_6; Me_4Si) 1.80 (4 H, t, OCH_2), 2.18 (6 H, s, CH_3), 3.34 (2 H, b, H_2O), 3.82 (4 H, t, CH_2), 7.17 (4 H, d, J = 7.8 Hz, arom) and 8.34 (4 H, d, J = 8.3 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 21.7 (CH_3), 25.5 (THF-CH_2), 68.4 (THF-OCH_2), 68.8 (OCH_2), 126.4, 127.9, 142.0, 141.8 (arom) and 213.4 (CSO).

Barium bis(4-methylbenzenecarbothioato)(THF) **6**. A suspension of potassium 4-methylbenzenecarbothioate **5b** (0.765 g, 4.02 mmol) in THF (7 mL) was added to BaI_2

(0.786 g, 2.01 mmol) in the same solvent (3 mL) and the mixture was stirred at 21 °C for 1 h. The white precipitates (KI) were filtered off. Removal of the solvent under reduced pressure (21 °C/0.2 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.739 g (71%) of the compound **6b** as pale yellow micro crystalline solid, m.p. 177–185 °C (decomp.) (Found: C, 46.74; H, 4.53. Calc. for $C_{20}H_{22}BaO_3S_2$ (511.84): C, 46.93; H, 4.33%); ν_{max} (KBr)/cm^{-1} 2938, 2878, 1605 (COS), 1571, 1456, 1305, 1234, 1210, 1105, 1033, 1009, 977, 864, 817, 778, 715, 676, 643, 612, 509 and 486; δ_H(400 MHz; acetone-d_6; Me_4Si) 1.86 (4 H, t, THF-CH_2), 2.18 (6 H, s, CH_3), 3.76 (4 H, t, THF-OCH_2), 7.07 (4 H, d, J = 7.8 Hz, arom) and 8.19 (4 H, d, J = 8.3 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 21.3 (CH_3), 26.1 (THF-CH_2), 68.3 (THF-OCH_2), 128.5, 129.5, 141.5, 141.6 (arom) and 217.8 (CSO).

Magnesium bis(arenecarbothioato)(15-crown-5)(H_2O) **7**

Magnesium bis(4-methylbenzenecarbothioato)(15-crown-5)(H_2O) **7b**. A suspension of potassium 4-methylbenzenecarbothioate (1.147 g, 6.03 mmol) in THF (8 mL) was added to MgI_2 (0.862 g, 3.10 mmol) in the same solvent (2 mL) and the mixture was stirred at 23 °C for 1 h. The white precipitates (KI) were filtered off by a glass filter. The filtrate was added to 15-crown-5 (0.683 g, 3.10 mmol) in THF solution (6 mL), and the mixture was stirred at 22 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (22 °C/0.2 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 22 °C for 30 min. Filtration of the insoluble parts, followed by recrystallization from a mixed solvent hexane/diethyl ether (2:8) at -20 °C for 15 h, gave 0.715 g (21%) of the compound **7b** as slight yellow micro crystals, m.p. 186–198 °C (decomp.) (Found: C, 55.54; H, 6.72; Calc. for $C_{26}H_{36}MgO_8S_2$ (564.99): C, 55.27; H, 6.42%); ν_{max}(KBr)/cm^{-1} 2940, 2887, 1605 (COS), 1573, 1487, 1467, 1353, 1291, 1250, 1204, 1162, 1092, 1043, 958, 827, 796, 726, 672, 654 and 636; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.19 (6 H, s, CH_3), 3.45 (20 H, s, OCH_2), 3.65 (2 H, b, H_2O), 6.94 (4 H, d, J = 7.8 Hz, arom) and 7.90 (4 H, t, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.9 (CH_3), 69.7 (OCH_2), 127.3, 128.1, 138.3, 142.6 (arom) and 208.0 (CSO).

Magnesium bis(benzenecarbothioato)(15-crown-5)(H_2O) **7a**. Yield: 27% (pale yellow needles): m.p. 162–167 °C (decomp.) (Found: C, 52.30; H, 6.21; Calc. for $C_{26}H_{36}MgO_{10}S_2$ (596.99): C, 52.31; H, 6.08%); ν_{max} (KBr)/cm^{-1} 2945, 2889, 1602 (COS), 1576, 1502, 1465, 1354, 1306, 1252, 1210, 1179, 1153, 1092, 1029, 947, 839, 796, 741, 656 and 631; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.54 (20 H, s, OCH_2), 3.76 (6 H, s, OCH_3), 3.84 (2 H, b, H_2O), 6.77 (4 H, d, J = 8.3 Hz, arom) and 8.30 (4 H, t, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) (OCH_3), 69.7 (OCH_2), 111.7, 129.8, 138.3, 160.3 (arom) and 206.8 (C=O).

Magnesium bis(4-methoxybenzenecarbothioato)(15-crown-5)(H_2O) **7c**. Yield: 34% as pale yellow micro crystals; m.p. 162–167 °C (decomp.) (Found: C, 52.30; H, 6.21; Calc. for $C_{26}H_{36}MgO_{10}S_2$ (596.99): C, 52.31; H, 6.08%); ν_{max} (KBr)/cm^{-1} 2945, 2889, 1602 (COS), 1576, 1502, 1465, 1354, 1306, 1252, 1210, 1179, 1153, 1092, 1029, 947, 839, 796, 741, 656 and 631; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.54 (20 H, s, OCH_2), 3.76 (6 H, s, OCH_3), 3.82 (2 H, b, H_2O), 6.77 (4 H, d, J = 8.3 Hz, arom) and 8.30 (4 H, t, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (OCH_3), 69.7 (OCH_2), 111.7, 129.8, 138.3, 160.3 (arom) and 206.8 (C=O).

Magnesium bis(4-chlorobenzenecarbothioato)(15-crown-5)(H_2O) **7d**. Yield: 42% as pale yellow micro crystals; m.p. 142–148 °C (decomp.) (Found: C, 47.52; H, 5.03; Calc. for $C_{24}H_{30}Cl_2MgO_8S_2$ (605.83): C, 47.58; H, 4.99%); ν_{max} (KBr)/cm^{-1} 2945, 2883, 1587 (COS), 1573, 1502, 1479, 1354, 1202, 1158, 1090, 961, 841 and 728; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.55 (20 H, s, OCH_2), 3.72 (2 H, b, H_2O), 7.27 (4 H, d, J = 8.8 Hz, arom) and 8.09 (4 H, t, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.8 (OCH_2), 126.6, 129.6, 133.7, 144.0 (arom) and 205.5 (C=O).

Calcium bis(arenecarbothioato)(15-crown-5)(H_2O) **8**

Calcium bis(benzenecarbothioato)(15-crown-5)(H_2O) **8a**. Similarly to **8b**, the reaction of potassium benzenecarbothioate **8a** (0.350 g, 3.57 mmol) with CaI_2 (0.310 g, 1.06 mmol) in THF (8 mL), followed by recrystallization from acetone (15 mL) at -20 °C for 5 days gave 0.023 g (4%) of the compound **8a** as slight yellow micro crystals, m.p. 181–187 °C (decomp.) (Found: C, 51.78; H, 6.81; Calc. for $C_{24}H_{32}CaO_8S_2$ (600.17): C, 51.98; H, 6.67%); ν_{max} (KBr)/cm^{-1} 2922, 2881, 1654 (COS), 1618, 1560, 1508, 1491, 1459, 1438, 1355, 1300, 1249, 1207, 1164, 1119, 1089, 1040, 957, 871, 857, 782, 698, 658 and 551; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.15 (20 H, s, OCH_2), 3.75 (2 H, b, H_2O), 7.25 (6 H, d, J = 7.0 Hz, arom) and 8.06 (4 H, d, J = 7.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 68.3 (OCH_2), 126.7, 127.8, 128.9, 144.9 (arom) and 208.6 (CSO).

Calcium bis(4-methylbenzenecarbothioato)(15-crown-5)(H_2O) **8b**. A suspension of potassium 4-methylbenzenecarbothioate (0.303 g, 1.59 mmol) in THF (8 mL) was added to CaI_2 (0.248 g, 0.84 mmol) in the same solvent (2 mL) and the mixture was stirred at 21 °C for 1 h. The resulting white precipitates (KI) were filtered off. The filtrate was added to 15-crown-5 (0.127 g, 0.58 mmol) in THF solution (3 mL) and the mixture was stirred at 20 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.380 g (38%) of **8b** as pale yellow micro crystalline solid. The solid was dissolved in acetone (15 mL). Hexane (5 mL) was slowly added, and the mixture was allowed to stand at -20 °C for 15 h. Filtration of the resulting crystals gave 0.200 g (20%) of the compound **8b** as yellow needles, m.p. 195–200 °C (decomp.) (Found: C, 53.39; H, 7.11. Calc. for $C_{26}H_{36}CaO_8S_2$ (628.85): C, 53.48; H, 7.05%); ν_{max} (KBr)/cm^{-1} 2933, 2921, 2882, 1604 (COS), 1572, 1510, 1488, 1467, 1451, 1353, 1301, 1247, 1219, 1202, 1168, 1124, 1091, 1040, 954, 873, 834, 795, 727, 661, 634, 556, 521 and 493; δ_H (400 MHz; DMSO-d_6; Me_4Si) 2.27 (6 H, s, CH_3), 3.53 (20 H, s, OCH_2), 3.67 (2 H, b, H_2O), 7.03 (4 H, d, J = 8.3 Hz, arom) and 7.97 (4 H, t, J = 8.3 Hz, arom); δ_C (100 MHz; DMSO-d_6; Me_4Si) 20.8 (CH$_3$), 69.1 (OCH$_2$), 127.2, 128.0, 138.0, 142.8 (arom) and 207.3 (CSO).

Calcium bis(4-methoxybenzenecarbothioato)(15-crown-5)(H_2O) **8c**. Yield: 55% as pale yellow micro crystals, m.p. 169–174 °C (decomp.) (Found: C, 50.88; H, 6.76; Calc. for $C_{26}H_{36}CaO_{10}S_2$ (660.85): C, 50.89; H, 6.71%; ν_{max} (KBr)/cm^{-1} 3004, 2930, 2888, 2836, 1602 (COS), 1578, 1499, 1476, 1459, 1355, 1308, 1253, 1216, 1156, 1090, 1029, 949, 848, 671, 654, 544; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.52 (20 H, s, OCH_2), 3.74 (6 H, s, OCH_3), 3.81 (2 H, b, H_2O), 6.77 (4 H, d, J = 8.3 Hz, arom) and 8.07 (4 H, t, J = 8.7 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (OCH$_3$), 69.9 (OCH$_2$), 111.8, 129.8, 137.8, 160.4 (arom) and 208.2 (C=S).

Calcium bis(4-chlorobenzenecarombothioato)(15-crown-5)(H_2O) **8d**. Yield: 48%; pale yellow micro crystals: m.p. 172–176 °C (decomp.) (Found: C, 46.52; H, 5.87; Calc. for $C_{26}H_{38}CaCl_2O_9S_2$ (669.69): C, 46.63; H, 5.72%); ν_{max} (KBr)/cm^{-1} 2967, 2932, 2882, 1654 (COS), 1584, 1571, 1498, 1492, 1477, 1450, 1355, 1248, 1203, 1160, 1085, 1046, 1013, 957, 841, 728 and 648; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.52 (20 H, s, OCH_2), 3.74 (2 H, b, H_2O), 7.27 (4 H, d, J = 8.8 Hz, arom) and 8.08 (4 H, t, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.9 (OCH$_2$), 126.7, 130.0, 134.0, 143.6 (arom) and 206.9 (C=S).

Calcium bis(arenecarbothioato)(18-crown-6) **9**

Calcium bis(benzenecarbothioato)(18-crown-6) **9a**. Similarly to **9b**, the reaction of potassium benzenecarbothioate (0.340 g, 1.93 mmol) with CaI_2 (0.310 g, 1.05 mmol) in THF (10 mL), followed by recrystallization in a mixed solvent of acetonitrile/ethyl ether/hexane (6:3:1) at -20 °C for 24 h gave 0.279 g (46%) of the compound **9a** as pale yellow needles, m.p. 188–196 °C (decomp.) (Found: C, 54.01; H, 6.07; Calc. for $C_{26}H_{34}CaO_8S_2$ (578.75): C, 53.96; H, 5.92%); ν_{max} (KBr)/cm^{-1} 3060, 2919, 1631 (COS), 1581 1491, 1466, 1436, 1352, 1299, 1249, 1205, 1166, 1101, 1027, 1001, 964, 881, 842, 781, 697, 655, 557, 467 and 414; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.51 (24 H, s, OCH_2), 7.27 (6 H, d, J = 7.2 Hz, arom) and 8.10 (4 H, d, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.8 (OCH_2), 126.7, 127.9, 129.1, 144.8 (arom) and 209.1 (*C*OS).

Calcium bis(4-methylbenzenecarbothioato)(18-crown-6) **9b**. A suspension of potassium 4-methylbenzenecarbothioate (0.361 g, 1.90 mmol) in THF (8 mL) was added to CaI_2 (0.323 g, 1.10 mmol) in the same solvent (2 mL) and the mixture was stirred at 24 °C for 1 h. The resulting precipitates (KI) were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.264 g, 1.00 mmol) in THF solution (4 mL), and the mixture was stirred at 24 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave pale yellow micro crystalline solid (0.523 g). The solid was dissolved in acetonitrile (18 mL). Hexane (7 mL) and ether (1 mL) were slowly added, and the mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave 0.327 g (51%) of the compound **9b** as pale yellow needles, m.p. 176–182 °C (decomp.) (Found: C, 53.54; H, 6.92; Calc. for $C_{28}H_{38}CaO_8S_2$ (582.78): C, 53.58; H, 6.88%.); ν_{max} (KBr)/cm^{-1} 2928, 2881, 2753, 1654 (COS), 1608, 1479, 1459 or 1450, 1353, 1287, 1251, 1218, 1205, 1163, 1099, 962, 830, 727, 668, 654, 637, 533, 471 and 458; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.27 (6 H, s, CH_3), 3.49 (24 H, s, OCH_2), 7.03 (4 H, d, J = 8.3 Hz, arom) and 7.99 (4 H, t, J = 8.2 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.8 (CH_3), 69.8 (OCH_2), 127.3, 128.1, 138.6, 142.2 (arom) and 209.2 (*C*OS).

Calcium bis(4-methoxybenzenecarbothioato)(18-crown-6) **9c**. Yield: 28%; pale yellow micro crystals: m.p. 146–151 °C (decomp.) (Found: C, 50.58; H, 6.30; Calc. for $C_{26}H_{38}CaO_{10}S_2$ (614.78): C, 50.79; H, 6.23%); ν_{max} (KBr)/cm^{-1} 2922, 2836, 1603

(COS), 1578, 1500 or 1490, 1459, 1407, 1352, 1307, 1258, 1214, 1156, 1102, 1030, 958, 842, 742, 655, 627, 542 and 509; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.50 (24 H, s, OCH_2), 3.74 (6 H, s, OCH_3), 6.77 (4 H, d, J = 8.8 Hz, arom) and 8.07 (4 H, t, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (OCH_3), 69.8 (OCH_2), 111.8, 129.7, 137.9, 60.4 (arom) and 208.0 (*C*OS).

Calcium bis(4-chlorobenzenecarbothioato)(18-crown-6) **9d**. Yield: 17%; pale yellow micro crystals: m.p. 173–177 °C (decomp.) (Found: C, 46.01; H, 5.57; Calc. for $C_{24}H_{34}CaCl_2O_8S_2$ (625.64): C, 46.07; H, 5.48%); ν_{max} (KBr)/cm^{-1} 2930, 1587 (COS), 1573, 1480, 1463, 1453, 1352, 1287, 1251, 1200, 1158, 1098, 1014, 963, 838, 729, 648, 630, 611 and 489; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.49 (24 H, s, OCH_2), 7.27 (4 H, d, J = 8.8 Hz, arom) and 8.08 (4 H, t, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.8 (OCH_2), 126.6, 129.6, 133.9, 143.6 (arom) and 206.8 (*C*OS).

Strontium bis(arenecarbothioato)(15-crown-5) **10**

Strontium bis(benzenecarbothioato)(15-crown-5) **10a**. Similarly to **10c**, the reaction of potassium benzenecarbothioate (0.380 g, 2.16 mmol) and 15-crown-5 (0.248 g, 1.13 mmol) with $SrI_2 \cdot 5.5H_2O$ (0.494 g, 1.12 mmol) in THF (10 mL) at 23 °C for 1 h, followed by recrystallization from a mixed solvent of acetonitrile/hexane/diethyl ether (5:1.2:1) (37 mL) at -20 °C for 2 days gave 0.052 g (8%) of the compound **10a** as pale yellow needles, m.p. 173–178 °C (decomp.) (Found: C, 47.24; H. 5.48, Calc. for $C_{22}H_{30}O_7S_2Sr$ (558.05): C, 47.34; H, 5.42%); ν_{max} (KBr)/cm^{-1} 2924, 2865, 2832, 1556, (COS), 1506, 1502, 1485, 1464, 1437, 1342, 1302, 1256, 1203, 1162, 1098, 948, 841, 786, 706, 654 and 546; δ_H(400 MHz; acetone-d_6; Me_4Si) 3.25 (20 H, s, OCH_2), 7.14 (4 H, t, J = 8.3 Hz, arom) and 8.09 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 69.9 (OCH_2), 126.8, 128.2, 129.7, 143.8 (arom) and 212.5 (*C*OS).

Strontium bis(4-methylbenzenecarbothioato)(15-crown-5) **10b**. Similarly to **10c**, the reaction of potassium 4-methylbenzenecarbothioate (0.365 g, 1.92 mmol) and $SrI_2 \cdot 5.5H_2O$ (0.471 g, 1.07 mmol) with15-crown-5 (0.298 g, 1.13 mmol) in THF (10 mL) at 20 °C for 1 h, followed by recrystallization from a mixed solvent of acetonitrile/hexane/diethyl ether (2:1:1.5) (18 mL) at -20 °C for 5 days, gave 0.113 g (18%) of the compound **10b** as pale yellow crystals, m.p. 165–170 °C (decomp.) (Found: C, 49.34; H, 5.78; Calc. for $C_{24}H_{34}O_7S_2Sr$ (586.27): C, 49.17; H, 5.85%); ν_{max} (KBr)/cm^{-1} 2923, 2877, 2833, 1566 (COS), 1504, 1487, 1460, 1438, 1352, 1310, 1252, 1206, 1163, 1115, 955, 843, 791, 724, 676, 655 and 551; δ_H(400 MHz; acetone-d_6;

Me_4Si) 2.33 (6 H, s, CH_3), 3.83 (20 H, s, OCH_2), 7.13 (4 H, t, J = 8.3 Hz, arom) and 8.22 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 22.2 (CH_3), 71.2 (OCH_2), 127.9, 129.2, 130.7, 142.1 (arom) and 213.8 (COS).

Strontium bis(4-methoxybenzenecarbothioato)(15-crown-5) **10c**. A suspension of potassium 4-methoxybenzenecarbothioate (0.441 g, 2.07 mmol) in THF (8 mL) was added to $SrI_2{\cdot}5.5H_2O$ (0.436 g, 0.99 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by the use of glass filter. The filtrate was added to 15-crown-5 (0.226 g, 1.03 mmol) in THF solution (6 mL), and the mixture was stirred at 19 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (20 °C/0.4 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave pale yellow micro crystalline solid (0.522 g). The solid was dissolved in acetonitrile (13 mL). Hexane (3 mL) and diethyl ether (4 mL) were slowly added and the mixture was allowed to stand at -20 °C for 6 days. Filtration of the resulting crystals gave 0.057 g (8%) of the compound **10c** as pale yellow crystals, m.p. 168–173 °C (decomp.) (Found: C, 49.24; H, 5.78; Calc. for $C_{24}H_{34}O9S_2Sr$ (618.07): C, 49.17; H, 5.85%); ν_{max} (KBr)/cm^{-1} 2924, 2837, 2832, 1562 (COS), 1505, 1501, 1486, 1464, 1428, 1355, 1308, 1232, 1202, 1153, 1072,1022, 956, 844, 721, 704, 656, 625, 581 and 482; δ_H(400 MHz; acetone-d_6; Me_4Si) 3.63 (20 H, s, CH_2), 3.81 (6 H, s, OCH_3), 7.09 (4 H, t, J = 8.3 Hz, arom) and 8.12 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 55.2 (OCH_3), 69.7 (OCH_2), 116.2, 128.2, 137.78, 160.1 (arom) and 211.4 (COS).

Strontium bis(arenecarbothioato)(18-crown-6) **11**

Strontium bis(benzenecarbothioato)(18-crown-6) **11a**. Similarly to **11b**, the reaction of potassium benzenecarbothioate (0.660 g, 3.74 mmol) in THF (8 mL) and $SrI_2{\cdot}5.5H_2O$ (0.879 g, 2.00 mmol) with 18-crown-6 (0.580 g, 2.19 mmol) in the same solvent (18 mL) at 22 °C for 1 h, followed by recrystallization from a mixed solvent of acetone (6.5 mL) and hexane (0.8 mL) at -20 °C for 1 day gave 0.222 g (18%) of the compound **11a** as pale yellow needles, m.p. 182–187 °C (decomp.) (Found: C, 49.84; H, 5.62; Calc. for $C_{26}H_{34}O_8S_2Sr$ (626.29): C, 49.86; H, 5.47%): ν_{max} (KBr)/cm^{-1} 2923, 2867, 2834, 1560 (COS), 1508, 1500, 1487, 1465, 1438, 1352, 1300, 1252, 1205, 1162, 1099, 958, 843, 781, 696, 656 and 551; δ_H(400 MHz; acetone-d_6; Me_4Si) 3.85 (24 H, s, OCH_2), 7.33 (4 H, t, J = 7.3 Hz, arom), 7.38 (2 H, t, J = 8.8 Hz, arom) and 8.34 (4 H, d, J = 6.8 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 70.8 (O*C*H_2), 127.8, 129.1, 130.7, 144.8 (arom) and 213.8 (*C*OS).

Strontium bis(4-methylbenzenecarbothioato)(18-crown-6) **11b**. A suspension of potassium 4-methylbenzenecarbothioate (0.783 g, 4.11 mmol) in THF (8 mL) was added to $SrI_2 \cdot 5.5H_2O$ (0.947 g, 2.15 mmol) in the same solvent (2 mL) and the mixture was stirred at 26 °C for 1 h. The white precipitates (KI) were filtered off. The filtrate was added to 18-crown-6 (0.685 g, 2.59 mmol) in THF solution (3 mL) and the mixture was stirred at 26 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (22 °C/0.1 Pa) gave yellow wet solid. Hexane (5 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave yellow micro crystalline solid (0.971 g). The solid was dissolved in acetone (14 mL). Hexane (4 mL) was slowly added, and the mixture was allowed to stand at -20 °C for 3 days. Filtration of the resulting crystals gave 0.650 g (50%) of the compound **11b** as pale yellow needles, m.p. 191–196 °C (decomp.) (Found: C, 51.17; H, 6.01; Calc. for $C_{28}H_{38}O_8S_2Sr$ (654.35): C, 51.39; H, 5.85%); ν_{max} (KBr)/cm^{-1} 2922, 1654 (COS), 1608, 1573, 1486, 1351, 1286, 1247, 1202, 1164, 1116, 953, 831, 796, 727, 652, 636, 532 and 472; δ_H(400 MHz; acetone-d_6; Me_4Si) 2.34 (6 H, s, C*H_3*), 3.81 (24 H, s, OC*H_2*), 7.14 (4 H, d, *J* = 8.3 Hz, arom) and 8.24 (4 H, d, *J* = 7.8 Hz, arom); δ_C(100 MHz; acetone-d_6; Me_4Si) 21.3 (*C*H_3), 71.2 (O*C*H_2), 128.2, 129.3, 140.6, 142.4 (arom) and 213.6 (*C*OS).

Strontium bis(4-methoxybenzenecarbothioato)(18-crown-6) **11c.** Yield: 21%; pale yellow micro crystals: m.p. 181–185 °C (decomp.) (Found: C, 48.88; H, 5.63; Calc. for $C_{28}H_{38}O_{10}S_2Sr$ (686.34): C, 49.00; H, 5.58%); ν_{max} (KBr)/cm^{-1} 2990, 2925, 2874, 2835, 1601 (COS), 1578, 1500, 1459, 1348, 1305, 1251, 1210, 1181, 1153, 1099, 1026, 957, 840, 740, 659, 627, 538, 503 and 453; δ_H(400 MHz; acetone-d_6; Me_4Si) 3.83 (6 H, s, OC*H_3*), 3.85 (24 H, s, OC*H_2*), 6.86 (4 H, d, *J* = 8.8 Hz, arom) and 8.32 (4 H, d, *J* = 8.8 Hz, arom). δ_C(100 MHz; acetone-d_6; Me_4Si) 55.6 (O*C*H_3), 70.8 (O*C*H_2), 112.8, 131.0, 138.1, 162.5 (arom) and 212.7 (*C*OS).

Strontium bis(4-chlorobenzenecarbothioato)(18-crown-6) **11d**. Yield: 40%; pale yellow micro crystals: m.p. 184–189 °C (decomp.) (Found: C, 44.62; H, 4.67; Calc. for $C_{26}H_{32}Cl_2O_8S_2Sr$ (695.18): C, 44.92; H, 4.64%); ν_{max} (KBr)/cm^{-1} 2917, 2874, 2832, 1585 (COS), 1575, 1510, 1466, 1352, 1288, 1278, 1252, 1201, 1160, 1101, 1012, 958, 841, 740, 730, 648 and 630; δ_H(400 MHz; acetone-d_6; Me_4Si) 3.85 (24 H, s, OC*H_2*), 7.36 (4 H, d, *J* = 8.3 Hz, arom) and 8.33 (4 H, d, *J* = 8.8 Hz, arom); δ_C(100 MHz;

acetone-d_6; Me_4Si) 70.9 (O*C*H_2), 127.8, 130.7, 136.5, 143.3 (arom) and 212.2 (*C*OS).

Barium bis(arenecarbothioato)(18-crown-6) **12**

Barium bis(benzenecarbothioato)(18-crown-6) **12a**. Similarly to **12b**, the reaction of potassium benzenecarbothioate (0.440 g, 2.50 mmol) and BaI_2 (0.494 g, 1.26 mmol) with 18-crown-6 (0.389 g, 1.47 mmol) in THF (13 mL) at 24 °C for 30 min, followed by recrystallization from a mixed solvent of acetone (80 mL) and hexane (14 mL) -20 °C for 4 days, gave 0.167 g (20%) of the compound **12a** as pale yellow needles, m.p. 174–179 °C (decomp.) (Found: C, 46.03; H, 5.16; Calc. for $C_{28}H_{34}BaO_8S_2$ (676.00): C, 46.19; H, 5.07%); ν_{max} (KBr)/cm^{-1} 2918, 1718 (COS), 1560, 1542, 1515, 1498, 1466, 1348, 1285, 1247, 1203, 1162, 1091, 950, 834, 779, 696 and 656; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.65 (24 H, s, OC*H*$_2$), 7.25 (2 H, d, J = 7.1 Hz, arom), 7.31 (4 H, t, J = 7.1 Hz, arom) and 8.07 (4 H, d, J = 6.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.7 (O*C*H_2), 127.0, 127.8, 129.4, 144.7 (arom) and 208.9 (*C*OS).

Barium bis(4-methylbenzenecarbothioato)(18-crown-6) **12b**. A suspension of potassium 4-methylbenzenecarbothioate (0.389 g, 2.04 mmol) in THF (8 mL) was added to BaI_2 (0.408 g, 1.04 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off. The filtrate was added to 18-crown-6 (0.338 g, 1.27 mmol) in THF solution (3 mL) and the mixture was stirred at 26 °C for 30 min. The resulting precipitates were filtered off by a glass filter, followed by washing with hexane (5 mL) and drying under reduce pressure (20 °C/0.1 Pa) for 1 h, to give pale yellow solid (0.622 g). The solid (0.598 g) was dissolved in acetone (87 mL). Hexane (7 mL) was slowly added, and the mixture was allowed to stand at -20 °C for 17 h. Filtration of the resulting crystals gave 0.267 g (37%) of the compound **12b** as pale yellow needles, m.p. 188–194 °C (decomp.) (Found: C, 47.65; H, 5.55; Calc. for $C_{28}H_{38}BaO_8S_2$ (704.05): C, 47.77; H, 5.44%); ν_{max} (KBr)/cm^{-1} 2920, 2912, 2880, 2855, 1654 (COS), 1560, 1507, 1465, 1348, 1202, 1163, 1092, 959, 831, 727 and 527; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.27 (6 H, s, C*H*$_3$), 3.64 (24 H, s, OC*H*$_2$), 7.05 (4 H, d, J = 7.8 Hz, arom) and 7.97 (4 H, t, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 21.0 (*C*H_3), 69.9 (O*C*H_2), 127.6, 128.0, 138.9, 142.4 (arom) and 208.6 (*C*OS).

Barium bis(2-methoxybenzenecarbothioato(18-crown-6) **12c**. Yield: 3%; colorless micro crystals: m.p. 198–203 °C (decomp.) (Found: C, 45.55; H, 5.24; Calc. for $C_{28}H_{38}BaO_{10}S_2$ (736.10): C, 45.69 H, 5.20%); ν_{max} (KBr)/cm^{-1} 2901, 1654 (COS), 1593, 1560, 1511, 1472, 1449, 1279, 1240, 1206, 1087, 1045, 1021, 960, 829, 770, 679 and 536; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.62 (24 H, s, OCH_2), 3.65 (6 H, s, OCH_3), 6.75 (2 H, t, J = 7.3 Hz, arom), 6.80 (2 H, d, J = 8.3 Hz, arom), 7.06 (4 H, t, J = 7.3 Hz, arom) and 7.24 (2 H, t, J = 6.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 5.56 (OCH_3), 69.9 (OCH_2), 111.8, 119.6, 127.3, 127.9, 140.5, 153.6 (arom) and 210.7 (COS).

Barium bis(4-methoxybenzenecarbothioato)(18-crown-6) **12d**. Yield: 58%; pale yellow micro crystals: m.p. 161–166°C (decomp.) (Found: C, 45.60; H, 5.27; Calc. for $C_{28}H_{38}BaO_{10}S_2$ (736.10): C, 45.69 H, 5.20%); ν_{max} (KBr)/cm^{-1} 2934, 2919, 2887, 2833,1604 (COS), 1582, 1560, 1542, 1505, 1465, 1258, 1210, 1156, 1093, 1031, 961, 943, 856, 834, 811, 742, 657, 626 and 536; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.64 (24 H, s, OCH_2), 3.74 (6 H, s, OCH_3), 6.79 (4 H, d, J = 8.8 Hz, arom) and 8.06 (4 H, d, J = 8.8 Hz, arom). δ_C (100 MHz; DMSO-d_6; Me_4Si) 55.4 (OCH_3), 69.9 (OCH_2), 112.0, 129.6, 137.8, 160.7 (arom) and 208.0 (COS).

Barium bis(4-chlorobenzenecarbothioato)(18-crown-6) **12e**. Yield: 24%; pale yellow micro crystals: m.p. 157–161 °C (decomp.) (Found: C, 41.88; H, 4.41; Calc. for $C_{26}H_{32}BaCl_2O_8S_2$ (744.89); C, 41.92; H, 4.33%); ν_{max} (KBr)/cm^{-1} 2908, 2871, 1587 (COS), 1573, 1505, 1478, 1464, 1389, 1346, 1282, 1247, 1197, 1157, 1091, 1014, 961, 851, 832, 729, 648, 630, 588, 500 and 473; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.63 (24 H, s, OCH_2), 7.30 (4 H, d, J = 8.3 Hz, arom) and 8.07 (4 H, d, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.9 (OCH_2), 127.0, 129.7, 134.3, 143.7 (arom) and 206.8 (COS).

Calcium bis(arenecarboselenoato)(15-crown-5)(H_2O) **13**

Calcium bis(benzenecarboselenoato)(15-crown-5)(H_2O) **13a**. Similarly to **13b**, the reaction of potassium benzenecarboselenoate (0.570 g, 2.60 mmol) and CaI_2 (0.4.01 g, 1.36 mmol) with 15-crown-5 (0.304 g, 1.38 mmol) in THF (16 mL) at 21 °C for 2 h, followed by washing with hexane (10 mL), gave 0.389 g (48%) of the compound **13a** as yellow micro crystals, m.p. 142–148 °C (decomp.) (Found: C, 44.37; H, 5.31; Calc. for $C_{22}H_{32}CaO_8Se_2$ (648.52): C, 44.45; H, 5.28%); ν_{max} (KBr)/cm^{-1} 2925, 1621 (COSe), 1517, 1477, 1456, 1355, 1297, 1249, 1200, 1119, 1087, 950, 906, 872, 628, 775, 695, 634 and 457; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.57 (24 H, s, OCH_2), 3.77 (2 H, b, H_2O), 7.19 (4 H, t, J = 7.1 Hz, arom), 7.35 (6 H, t, J = 7.1 Hz, arom) and 7.98 (4 H, t, J = 7.1

Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (O*C*H_2), 126.5, 127.9, 129.4, 147.3 (arom) and 210.9 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 442.5.

Calcium bis(4-methylbenzenecarboselenoato)(15-crown-5)(H_2O) **13b**. A suspension of potassium 4-methylbenzenecarboselenoate (0.655 g, 2.76 mmol) in THF (8 mL) was added to CaI_2 (0.4.29 g, 1.45 mmol) in the same solvent (2 mL) and the mixture was stirred at 23 °C for 1 h. The white precipitates (KI) were filtered off by the use of glass filter. The filtrate was added to 15-crown-5 (0.315 g, 1.43 mmol) in THF solution (6 mL), and the mixture was stirred at 23 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (22 °C/0.3 Pa) gave yellow wet solid. Hexane (6 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.604 g (63%) of the compound **13b** as yellow micro crystals, m.p. 132–138 °C (decomp.) (Found: C, 44.00; H, 5.64; Calc. for $C_{24}H_{36}CaO_8Se_2$ (710.04): C, 44.07; H, 5.41%); ν_{max} (KBr)/cm^{-1} 2919, 1605 (*C*OSe), 1577, 1463, 1351, 1287, 1249, 1200, 1159, 1098, 971, 909, 842, 824, 791, 719, 629 and 465; δ_H(400 MHz; acetone-d_6; Me_4Si) 2.26 (6 H, s, C*H_3*), 3.55 (24 H, s, OC*H_2*), 3.78 (2 H, b, *H_2*O), 7.03 (4 H, d, J = 7.8 Hz, arom) and 7.96 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 17.8 (*C*H_3), 69.2 (O*C*H_2), 127.2, 128.1, 138.6, 145.0 (arom) and 208.3 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se)-459.2.

Calcium bis(4-methoxybenzenecarboselenoato)(15-crown-5)(H_2O) **13c**. Yield: 52%; yellow micro crystals: m.p. 138–142 °C (decomp.) (Found: C, 42.55; H, 5.51; Calc. for $C_{24}H_{36}CaO_{10}Se_2$ (682.53): C, 42.23; H, 5.32%); ν_{max} (KBr)/cm^{-1} 2932, 2881, 1600 (COSe), 1578, 1501, 1461, 1306, 1254, 1206, 1157, 1087, 1027, 908, 840, 791, 622, 526 and 460; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.68 (24 H, s, OC*H_2*), 3.75 (6 H, s, OC*H_3*), 3.87 (2 H, b, *H_2*O), 6.78 (4 H, d, J = 7.3 Hz, arom) and 8.05 (4 H, d, J = 7.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (O*C*H_3), 68.1 (O*C*H_2), 111.6, 129.9, 140.2, 160.6 (arom) and 209.7 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 438.1.

Calcium bis(4-chlorobenzenecarboselenoato)(15-crown-5)(H_2O) **13d**. Yield: 9%; yellow micro crystals: m.p. 143–148 °C (decomp.) (Found: C, 40.02; H, 4.57; Calc. for $C_{24}H_{32}CaCl_2O_8Se_2$ (717.94): C, 40.18; H, 4.50%); ν_{max} (KBr)/cm^{-1} 2928, 2881, 1617 (COSe), 1574, 1516, 1478, 1400, 1355, 1291, 1249, 1194, 1158, 1086, 949, 907, 839, 803, 730, 629, 571, 468 and 435; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.58 (24 H, s, OC*H_2*), 3.83 (2 H, b, *H_2*O), 7.28 (4 H, d, J = 8.8 Hz, arom) and 8.00 (4 H, d, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.5 (O*C*H_2), 126.3, 130.0, 134.9, 146.2 (arom) and 208.9 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 465.7.

Strontium bis(arenecarboselenoato)(18-crown-6) **14**

Strontium bis(benzenecarboselenoato)(18-crown-6) **14a**. Similarly to **14b**, the reaction of potassium benzenecarboselenoate (0.491 g, 2.24 mmol) and $SrI_2 \cdot 5.5H_2O$ (0.627 g, 1.20 mmol) in THF (8 mL) with 18-crown-6 (0.314 g, 1.19 mmol) at 24 °C for 1 h, followed by recrystallization from a mixed solvent of acetonitrile (5 mL) and hexane (1.8 mL) at -20 °C for 5 days, gave 0.118 g (15%) of the compound **14a** as pale needles, m.p. 142–147 °C (decomp.) (Found: C, 43.03; H, 5.06; Calc. for $C_{26}H_{34}O_8Se_2Sr$ (721.96): C, 43.37; H, 4.76%); ν_{max} (KBr)/cm^{-1} 2921, 2823, 1616 (COSe), 1580, 1515, 1464, 1352, 1252, 1191, 1150, 1098, 969, 913, 841, 771, 692, 683 and 492; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.64 (24 H, s, OCH_2), 7.36 (6 H, t, J = 7.3 Hz, arom) and 8.08 (4 H, d, J = 7.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (O*C*H_2), 126.7, 128.9, 129.4, 146.9 (arom) and 211.2 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 452.1.

Strontium bis(4-methylbenzenecarboselenoato)(18-crown-6) **14b**. A suspension of potassium 4-methylbenzenecarboselenoate (0.650 g, 2.74 mmol) in THF (8 mL) was added to $SrI_2 \cdot 5.5H_2O$ (0.640 g, 1.45 mmol) in the same solvent (2 mL) and the mixture was stirred at 26 °C for 1 h. The white precipitates (KI) were filtered off by the use of glass filter. The filtrate was added to 18-crown-6 (0.370 g, 1.40 mmol) in THF solution (6 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (23 °C/0.2 Pa) gave yellow wet solid. Hexane (6 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave brown micro crystals (0.545 g). The solid (0.200 g) was dissolved in acetonitrile (15 mL). Hexane (8 mL) and diethyl ether (5 mL) were slowly added, and the mixture was allowed to stand at -20 °C for 1 day. Filtration of the resulting crystals gave 0.187 g (17%) of the compound **14b** as pale yellow needles, m.p. 131–138 °C (decomp.) (Found: C, 44.83; H, 5.16; Calc. for $C_{28}H_{38}O_8Se_2Sr$ (750.00): C, 44.95; H, 5.12%); ν_{max} (KBr)/cm^{-1} 2919, 1605 (COSe), 1515, 1463, 1351, 1287, 1249, 1159, 1098, 971, 909, 842, 824, 790, 719, 629 and 466; δ_H(400 MHz; acetone-d_6; Me_4Si) 2.27 (6 H, s, CH_3), 3.62 (24 H, s, OCH_2), 7.05 (4 H, d, J = 7.8 Hz, arom) and 7.97 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.9 (*C*H_3), 69.6 (O*C*H_2), 127.3, 128.1, 139.3, 144.5 (arom) and 210.5 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 446.8.

Strontium bis(4-methoxybenzenecarboselenoato)(18-crown-6) **14c**. Yield: 22%; yellow micro crystals: m.p. 136–141 °C (decomp.) (Found: C, 43.03; H, 4.33; Calc. for $C_{28}H_{38}O_{10}Se_2Sr$ (780.14): C, 43.11; H, 4.1%); ν_{max} (KBr)/cm^{-1} 2919, 2834, 1602 (COSe), 1581, 1503, 1466, 1353, 1288, 1258, 1208, 1159, 1098, 1026, 971, 908, 843, 652, 620, 508, 489 and 475; δ_H(400 MHz; DMSO-*d*$_6$; Me_4Si) 3.65 (24 H, s, OC*H*$_2$), 3.78 (6 H, s, OC*H*$_3$), 6.79 (4 H, d, *J* = 8.8 Hz, arom) and 8.08 (4 H, d, *J* = 8.8 Hz, arom); δ_C(100 MHz; DMSO-*d*$_6$; Me_4Si) 55.0 (O*C*H$_3$), 69.6 (O*C*H$_2$), 111.7, 129.9, 139.6, 160.9 (arom) and 210.0 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-*d*$_6$; Me_2Se) 421.5.

Strontium bis(4-chlorobenzenecarboselenoato)(18-crown-6) **14d**. Yield: 16%; yellow micro crystals: m.p. 156–162 °C (decomp.) (Found: C, 37.63; H, 4.56; Calc. for $C_{24}H_{34}Cl_2O_8Se_2Sr$: C, 37.58; H, 4.47%); ν_{max} (KBr)/cm^{-1} 2922, 1618 (COSe), 1586, 1575, 1500, 1467, 1396, 1352, 1285, 1196, 1157, 1097, 1012, 970, 910, 842, 730, 719, 625, 563 and 470; δ_H(400 MHz; DMSO-*d*$_6$; Me_4Si) 3.66 (24 H, s, OC*H*$_2$), 7.30 (4 H, d, *J* = 8.3 Hz, arom) and 8.11 (4 H, d, *J* = 8.3 Hz, arom); δ_C(100 MHz; DMSO-*d*$_6$; Me_4Si) 69.5 (O*C*H$_2$), 126.6, 129.5, 134.6, 145.6 (arom) and 209.3 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-*d*$_6$; Me_2Se) 463.6.

Barium bis(arenecarboselenoato)(18-crown-6) **15**

Barium bis(benzenecarboselenoato)(18-crown-6) **15a**. Similarly to **15b**, the reaction of potassium benzenecarboselenoate (0.300 g, 1.37 mmol) and BaI_2 (0.290 g, 0.74 mmol) with 18-crown-6 (0.197 g, 0.75 mmol) in THF (12 mL) at 26 °C for 1 h, followed by recrystallization from a mixed solvent of acetone (11 mL) and hexane (1.0 mL) at -20 °C for 4 days, gave 0.148 g (26%) of the compound **15a** as pale yellow needles, m.p. 150–155 °C (decomp.) (Found: C, 40.73; H, 4.46; Calc. for $C_{26}H_{34}BaO_8Se_2$ (769.79): C, 40.57; H, 4.45%); ν_{max} (KBr)/cm^{-1} 2917, 2879, 2826, 1774, 1655 (COSe), 1590, 1528, 1466, 1349, 1285, 1249, 1201, 1159, 1091, 960, 908, 833, 733, 693, 680 and 633; δ_H(400 MHz; DMSO-*d*$_6$; Me_4Si) 3.57 (24 H, s, OC*H*$_2$), 7.23 (6 H, d, *J* = 7.1 Hz, arom), 7.31 (6 H, d, *J* = 7.1 Hz, arom) and 8.02 (4 H, d, *J* = 7.3 Hz, arom); δ_C(100 MHz; DMSO-*d*$_6$; Me_4Si) 69.7 (O*C*H$_2$), 126.9, 128.0, 129.6, 147.4 (arom) and 210.7 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-*d*$_6$; Me_2Se) 443.2.

Barium bis(4-methylbenzenecarboselenoato)(18-crown-6) **15b**. A suspension of potassium 4-methylbenzenecarboselenoate (0.325 g, 1.37 mmol) in THF (8 mL) was added to BaI_2 (0.282 g, 0.72 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates were filtered off by the use of glass filter. The filtrate was added to 18-crown-6 (0.198 g, 0.75 mmol) in THF solution (4 mL) and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (22 °C/0.4 Pa) gave yellow wet solid. Hexane (6 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave yellow micro crystals solid (0.367 g). The solid was dissolved in acetone (10 mL). Hexane (1.0 mL) was slowly added and the mixture was allowed to stand at -20 °C for 5 days. Filtration of the resulting crystals gave 0.033 g (6%) of the compound **15b** as pale yellow needles, m.p. 137–145 °C (decomp.) (Found: C, 42.37; H, 4.95; Calc. for $C_{28}H_{38}BaO_8Se_2$ (798.84): C, 42.15; H, 4.80%); ν_{max} (KBr)/cm^{-1} 2828, 2746, 1718 (COSe), 1605 (COSe), 1523, 1508, 1472, 1429, 1351, 1288, 1249, 1199, 1162, 1092, 1020, 964, 904, 832, 804, 790, 720, 631 and 620; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.33 (6 H, s, CH_3), 3.70 (24 H, s, OCH_2), 7.12 (4 H, d, J = 7.8 Hz, arom) and 8.03 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 21.0 (CH_3), 69.9 (OCH_2), 127.6, 128.0, 138.9, 142.4 (arom) and 208.6 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 447.6.

Barium bis(4-methoxybenzenecarboselenoato)(18-crown-6) **15c**. Yield: 7%; yellow micro crystals: m.p. 145–149 °C (decomp.) (Found: C, 40.54; H, 4.68; Calc. for $C_{30}H_{38}BaO_{10}Se_2$ (831.98): C, 40.53; H, 4.62); ν_{max} (KBr)/cm^{-1} 2917, 2886, 2871, 2832, 1718 COSe), 1654 (COSe), 1603, 1582, 1528, 1522, 1503, 1466, 1350, 1259, 1207, 1160, 1092, 1030, 961, 904, 852, 834, 810, 650, 620, 507, 457; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.68 (24 H, s, OCH_2), 3.75 (6 H, s, OCH_3), 6.78 (4 H, d, J = 7.3 Hz, arom), 8.05 (4 H, d, J = 7.36 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.3 (OCH_3), 69.8 (OCH_2), 112.0, 123.0, 140.3, 161.0 (arom), 209.6 (*C*OSe); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 430.7.

Barium bis(4-chlorobenzenecarboselenoato)(18-crown-6) **15d**. Yield: 11%; brown micro crystals: m.p. 138–143 °C (decomp.), (Found: C, 37.57; H, 3.97; Calc. for $C_{26}H_{32}BaCl_2O_8Se_2$ (838.68): C, 37.23; H, 3.85%); ν_{max} (KBr)/cm^{-1} 2909, 2880, 2825, 1719 (COSe), 1618, 1577, 1522, 1479, 1466, 1395, 1286, 1248, 1194, 1157, 1090, 1014, 961, 906, 831, 729, 624, 560, 468; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.61 (24 H, s, OCH_2), 7.29 (4 H, d, J = 8.8 Hz, arom), 8.05 (4 H, d, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.8 (OCH_2), 126.8, 129.8, 134.6, 146.1 (arom), 208.8 (C=O); δ_{Se}(76.2 MHz; DMSO-d_6; Me_2Se) 468.2.

Calcium bis(arenecarbodithioato)(15-crown-5)(THF)

Calcium bis(benzenecarbodithioato)(15-crown-5)(THF) **16a**. A suspension of potassium benzenecarbodithioate (0.515 g, 2.68 mmol) in THF (8 mL) was added to CaI_2 (0.393 g, 1.34 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off. The filtrate was added to 15-crown-5 (0.293 g, 1.33 mmol) in THF solution (6 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave red wet solid. Hexane (5 mL) and THF (3 mL) were added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.436 g (51%) of the compound **16a** as violet brown micro crystals, m.p. 187–195 °C (decomp.) (Found: C, 52.83; H, 5.79; Calc. for $C_{28}H_{38}CaO_6S_4$ (638.12): C, 52.63; H, 5.99%); ν_{max} (KBr)/cm^{-1} 2924, 2881, 2345, 1645, 1475, 1442, 1356, 1296, 1248 (CSS), 1194, 1163, 1113, 1084, 1045, 991, 953, 901, 872, 827, 769, 688, 654, 590 and 555; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.84 (4 H, t, CH_2), 3.61 (20 H, s, OCH_2), 3.84 (4 H, t, CH_2), 7.14 (4 H, t, J = 7.3 Hz, arom), 7.26 (4 H, t, J = 7.3 Hz, arom) and 8.13 (2 H, d, J = 6.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 25.5 (THF-OCH_2), 68.8 (THF-CH_2), 69.3 (OCH_2), 126.0, 126.2, 128.8, 152.9 (arom) and 250.4 (C=S).

Calcium bis(4-methylbenzenecarbodithioato)(15-crown-5)(THF) **16b**. A suspension of potassium 4-methylbenzenecarbodithioate (0.590 g, 2.86 mmol) in THF (8 mL) was added to CaI_2 (0.420 g, 1.43 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off. The filtrate was added to 15-crown-5 (0.326 g, 1.48 mmol) in THF solution (6 mL) and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) and recrystallization of the resulting wet solid from a mixed solvent of dichloromethane and hexane in refrigerator (-17 °C) gave 0.600 g (63%) of the compound **16b** as deep brown micro crystals, m.p. 197–205 °C (decomp.) (Found: C, 54.23; H, 6.48; Calc. for $C_{30}H_{42}CaO_6S_4$ (666.99): C, 54.02; H, 6.35%); ν_{max} (KBr)/cm^{-1} 2935, 2881, 1638, 1599, 1474, 1458, 1451, 1355, 1299, 1249 (CSS), 1198, 1160, 1114, 1082, 1047, 1013, 981, 952, 904, 872, 824, 786, 714, 639 and 590; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.85 (4 H, t, CH_2), 2.25 (6 H, s, CH_3), 3.54 (20 H, s, OCH_2), 3.83 (4 H, t, CH_2), 6.95 (4 H, d, J = 7.8 Hz, arom) and 8.13 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.7 (CH_3), 25.6 (THF-CH_2), 68.6 (THF-OCH_2), 69.9 (OCH_2), 126.5, 126.6, 137.4, 150.0 (arom) and 249.6 (CSS).

Calcium bis(4-methoxybenzenecarbodithioato)(15-crown-5)(THF) **16c**. A suspension of potassium 4-methoxybenzenecarbodithioate (0.165 g, 0.74 mmol) in THF (8 mL) was added to CaI_2 (0.109 g, 0.37 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off. The filtrate was added to 15-crown-5 (0.097 g, 0.44 mmol) in THF solution (6 mL) and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave crude calcium bis(4-methoxybenzenecarbodithioato)(15-crown-5)(THF) **16c** as brown wet solid. Hexane (5 mL) and acetone (5 mL) were added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.119 g (46%) of the compound **16c** as brown micro crystals, m.p. 176–182 °C (decomp.) (Found: C, 51.83; H, 6.14; Calc. for $C_{30}H_{42}CaO_8S_4$ (698.99): C, 51.55; H, 6.06%); ν_{max} (KBr)/cm^{-1} 2922, 2878, 1654, 1595, 1498, 1458, 1350, 1300, 1254, 1216 (CSS), 1180, 1164, 1098, 1030, 1003, 968, 909, 840, 636, 636 and 598; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.82 (4 H, t, CH_2), 3.56 (20 H, s, OCH_2), 3.75 (6 H, s, OCH_3), 3.84 (4 H, t, CH_2), 6.70 (4 H, d, J = 8.8 Hz, arom) and 8.33 (4 H, d, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 25.6 (THF-CH_2), 55.1 (OCH_3), 68.4 (OCH_2), 68.7 (THF-OCH_2), 111.0, 128.2, 145.0, 160.1 (arom) and 247.9 (*C*SS).

Calcium bis(4-chlorobenzenecarbodithioato)(15-crown-5)(THF) **16d**. A suspension of potassium 4-chlorobenzenecarbodithioate (0.518 g, 2.28 mmol) in THF (8 mL) was added to CaI_2 (0.343 g, 1.17 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by the use of a glass filter. The filtrate was added to 15-crown-5 (0.263 g, 1.19 mmol) in THF solution (6 mL) and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave red wet solid. Hexane (5 mL) and dichloromethane (2 mL) were added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.471 g (57%) of the compound **16d** as red brown micro crystals: m.p. 142–148 °C (decomp.) (Found: C, 47.87; H, 5.09; Calc. for $C_{28}H_{36}CaCl_2O_6S_4$ (706.04): C, 47.51; H, 5.13%); ν_{max} (KBr)/cm^{-1} 2934, 2881, 1654, 1637, 1618, 1560, 1542, 1508, 1475, 1458, 1390, 1354, 1290, 1248 (CSS), 1086, 1011, 951, 907, 872, 836, 517; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.85 (4 H, t, CH_2), 3.55 (20 H, s, OCH_2), 3.82 (4 H, t, CH_2), 7.19 (4 H, d, J = 8.8 Hz, arom), 8.20 (4 H, t, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.8 (OCH_2), 125.9, 127.9, 133.0, 150.1 (arom), 247.6 (*C*SS).

Strontium bis(arenecarbodithioato)(18-crown-6) **17**

Strontium bis(benzenecarbodithioato)(18-crown-6) **17a**. A suspension of potassium benzenecarbodithioate (0.615 g, 3.20 mmol) in THF (8 mL) was added to $SrI_2{\cdot}5.5H_2O$

(0.704 g, 1.60 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.430 g, 1.63 mmol) in THF solution (6 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) and recrystallization of the resulting residue from a mixed solvent of dichloromethane, ether and hexane (2:5:1) in refrigerator (-17 °C) gave 0.684 g (65%) of the compound **17a** as red micro crystals, m.p. 167–172 °C (decomp.) (Found: C, 47.54; H, 5.21; Calc. for $C_{26}H_{36}O_6S_4Sr$ (658.03): C, 47.43; H, 5.20%); ν_{max} (KBr)/cm^{-1} 2920, 2829, 1614, 1589, 1541, 1508, 1469, 1442, 1352, 1298, 1284, 1250, 1205 (CSS), 1171, 1097, 1016, 966, 912, 839, 762, 690, 658, 590 and 542; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.58 (24 H, s, OCH_2), 7.14 (4 H, t, J = 7.3 Hz, arom), 7.22 (4 H, t, J = 7.3 Hz, arom) and 8.13 (2 H, d, J = 6.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (OCH$_2$), 126.1, 126.2, 128.9, 152.9 (arom) and 250.3 (CSS).

Strontium bis(4-methylbenzenecarbodithioato)(18-crown-6) **17b**. Similarly to compound **17a**, a reaction of potassium 4-methylbenzenecarbodithioate (0.441 g, 2.14 mmol) in THF (8 mL) with $SrI_2 \cdot 5.5H_2O$ (0.471 g, 1.07 mmol), followed by treating with 18-crown-6 (0.276 g, 1.04 mmol) in THF solution (7 mL) give 0.397 g (54%) of the compound **17b** as brown micro crystals, m.p. 186–193 °C (decomp.) (Found: C, 48.85; H, 5.55; Calc. for $C_{28}H_{38}O_6S_4Sr$ (686.48): C, 48.99; H, 5.58%); ν_{max} (KBr)/cm^{-1} 2914, 2873, 1601, 1468, 1404, 1352, 1300, 1284, 1250, 1207 (CSS), 1169, 1097, 1018, 970, 914, 841, 822, 787, 640, 592 and 478; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.26 (6 H, s, CH_3), 3.59 (24 H, s, OCH_2), 6.95 (4 H, d, J = 7.8 Hz, arom) and 8.13 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.7 (CH$_3$), 69.6 (OCH$_2$), 126.4, 126.6, 137.5, 149.9 (arom) and 249.6 (CSS).

Strontium bis(4-methoxybenzenearbdithioato)(18-crown-6) **17c**. A suspension of potassium 4-methoxybenzenecarbdithioate (0.372 g, 1.67mmol) in THF (8 mL) was added **7** to $SrI_2 \cdot 5.5H_2O$ (0.387 g, 0.88 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.246 g, 0.93 mmol) in THF solution (4 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa), followed by washing with hexane, gave 0.297 g (47%) of the compound **17c** as brown red micro crystals: m.p. 147–153 °C (decomp.) (Found: C, 49.80; H, 6.02; Calc. for $C_{28}H_{38}O_8S_4Sr$ (718.05): C, 46.81; H, 5.33); ν_{max} (KBr)/cm^{-1} 2917, 2872, 2837, 1597, 1572, 1498, 1472, 1350, 1310, 1258, 1210 (CSS), 1161, 1089, 1050, 1002, 961, 912, 836, 807, 635, 599, 499; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.58 (24 H, s, OCH_2), 3.75 (6 H, s, OCH_3), 6.70 (4 H, d, J = 8.8 Hz, arom), 8.34 (4 H, d, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (OCH_3), 69.6 (OCH_2), 111.0, 128.2, 145.0, 160.2 (arom), 247.6 (*C*SS).

Strontium bis(4-chlorobenzenecarbodithioato)(18-crown-6) **17d**. A suspension of potassium 4-chlorobenzenecarbodithioate (0.497 g, 2.20 mmol) in THF (8 mL) was added to $SrI_2 \cdot 5.5H_2O$ (0.504 g, 1.14 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.301g, 1.14 mmol) in THF solution (7 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) gave brown wet solid. Hexane (10 mL) was added to the wet solid and the mixture was stirred at 25 °C for 10 min. Filtration of the insoluble parts gave 0.364 g (44%) of the compound **17d** as brown micro crystalline solid: m.p. 147–153 °C (decomp.) (Found: C, 42.76; H, 4.47; Calc. for $C_{26}H_{32}Cl_2O_6S_4Sr$ (725.95): C, 42.94; H, 4.4%); ν_{max} (KBr)/cm^{-1} 2917, 2877, 1615, 1584, 1473, 1393, 1351, 1285, 1251, 1203 (CSS), 1163, 1096, 1015, 969, 915, 831, 631, 586, 519; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.60 (24 H, s, OCH_2), 7.19 (4 H, d, J = 8.3 Hz, arom), 8.20 (4 H, t, J = 8.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (OCH_2), 125.9, 127.9, 133.1, 150.9 (arom), 247.6 (*C*SS).

Barium bis(arenecarbodithioato)(18-crown-6) **18**

Barium bis(benzenecarbodithioato)(18-crown-6) **18a**. A suspension of potassium benzenecarbodithioate (0.523 g, 2.72 mmol) in THF (8 mL) was added to BaI_2 (0.99 g, 1.36 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The resulting precipitates were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.362 g, 1.33 mmol) in THF solution (6 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa) and recrystallization from a mixed solvent of acetone, ether and hexane (5 mL) gave 0.685 g (71%) of the compound **18a** as red brown micro crystals, m.p. 197–205 °C (decomp.) (Found: C, 43.88; H, 5.26; Calc. for $C_{26}H_{36}BaO_6S_4$ (710.15): C, 43.97; H, 5.11%); ν_{max} (KBr)/cm^{-1} 2918, 2873, 2853, 2820, 1654, 1560, 1467, 1442, 1428, 1348, 1283, 1246, 1216 (CSS), 1090, 1014, 957, 913, 827, 758, 689, 658, 618, 592 and 473; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.61 (24 H, s, OCH_2), 7.14 (2 H, t, J = 7.3 Hz, arom), 7.23 (4 H, t, J = 7.3 Hz, arom) and 8.14 (4 H, d, J = 7.3 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (O*C*H_2), 126.1, 126.2, 127.9, 152.8 (arom) and 250.2 (*C*SS).

Barium bis(4-methylbenzenecarbodithioato)(18-crown-6) **18b**. Similarly to **18a**, a reaction of potassium 4-methylbenzenecarbodithioate (0.594 g, 2.88 mmol) with BaI_2 (0.565 g, 1.44 mmol) in THF (10 mL), followed by treating with a THF solution containing 18-crown-6 (0.377 g, 1.43 mmol) gave 0.827 g (78%) yield of the compound **18b** as brown micro crystals, m.p. 175–183 °C (decomp.) (Found: C, 45.54; H, 5.26; Calc. for $C_{28}H_{38}BaO_6S_4$ (736.06): C, 45.68; H, 5.20%); ν_{max} (KBr)/cm^{-1} 2918, 2878, 2824, 2742,1654, 1560, 1541, 1508, 1466, 1349, 1250 (CSS), 1090, 1020, 959, 912, 825, 640 and 590; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.25 (6 H, s, CH_3), 3.61 (24 H, s, OCH_2), 6.95 (4 H, d, J = 7.8 Hz, arom) and 8.13 (4 H, d, J = 7.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 20.7 (*C*H_3), 69.6 (O*C*H_2), 126.5, 126.6, 137.5, 149.9 (arom) and 249.4 (*C*SS).

Barium bis(4-methoxybenzenecarbodithioato)(18-crown-6) **18c**. A suspension of potassium 4-methoxybenzenecarbodithioate (0.457 g, 2.05 mmol) in THF (8 mL) was added to BaI_2 (0.400 g, 1.02 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by the use of a glass filter. The filtrate was added to 18-crown-6 (0.272 g, 1.03 mmol) in THF solution (4 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa), followed by washing with hexane/ether (4:1) gave 0.269 g (34%) of the compound **18c** as red brown micro crystals: m.p. 139–144 °C (decomp.) (Found: C, 43.66; H, 5.06; Calc. for $C_{28}H_{38}BaO_8S_4$ (768.05): C, 43.78; H, 4.99%); ν_{max} (KBr)/cm^{-1} 2917, 2871,2837, 1654, 1597, 1572, 1498, 1472, 1440, 1412, 1350, 1310, 1258, 1210 (CSS), 1161, 1089, 1025, 1002, 961, 912, 836, 807, 635, 599, 499; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.61 (24 H, s, OCH_2), (6 H, s, OCH_3), 6.70 (4 H, d, J = 8.8 Hz, arom), 8.34 (4 H, d, J = 8.8 Hz, arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 55.1 (O*C*H_3), 69.6 (O*C*H_2), 111.0, 128.2, 145.0, 160.2 (arom), 247.6 (*C*SS).

Barium bis(4-chlorobenzenecarbodithioato)(18-crown-6) **18d**. A suspension of potassium 4-chlorobenzenecarbodithioate (0.734 g, 3.28 mmol) in THF (8 mL) was added to BaI_2 (0.682 g, 1.74 mmol) in the same solvent (2 mL) and the mixture was stirred at 25 °C for 1 h. The white precipitates (KI) were filtered off by a glass filter. The filtrate was added to 18-crown-6 (0.467 g, 1.77 mmol) in THF solution (7 mL), and the mixture was stirred at 25 °C for 30 min. Removal of the solvent from the mixture under reduced pressure (25 °C/0.4 Pa), followed by washing with ether, gave 0.568g (42%) of the compound **18d** as red brown micro crystals: m.p. 153–157 °C (decomp.), (Found: C, 40.01; H, 4.48; Calc. for $C_{26}H_{34}BaCl_2O_6S_4$ (777.97): C, 40.09; H, 4.40%); ν_{max} (KBr)/cm^{-1} 2914, 2870, 2820, 1712, 1654, 1585, 1560, 1508, 1467, 1394, 1350, 1283, 1248, 1210 (CSS), 1164, 1089 1015, 958, 914, 830, 631, 586, 518, 479; δ_H(400 MHz; DMSO-d_6; Me_4Si) 3.60 (24 H, s, OCH_2), 7.18 (4 H, d, J = 7.8 Hz, arom), 8.19 (4 H, t, J = 7.8 Hz, 9 arom); δ_C(100 MHz; DMSO-d_6; Me_4Si) 69.6 (OCH_2), 125.9, 127.9, 133.1, 151.0 (arom), 247.5 (*C*SS).

Calcium (alkanecarbothioato)(iodo)(15-crown-5) **19**

Calcium (thioacetato)(iodo)(15-crown-5) **19a**. Similarly to **19c**, the reaction of potassium thioacetato (0.184 g, 1.61 mmol) and CaI_2 (0.488 g, 1.66 mmol) with 15-crown-5 (0.371 g, 1.68 mmol) in THF (13 mL) at 23 °C for 1 h, followed by recrystallization from a mixed solvent of acetone (6 mL) and hexane (0.6 mL) at -20 °C for 30 h, gave 0.192 g (45%) of the compound **19a** as colorless needles, m.p. 202–207 °C (decomp.) (Found: C, 31.27; H, 5.15; Calc. for $C_{12}H_{23}CaIO_6S$ (462.00): C, 31.17; H, 5.01%); ν_{max} (KBr)/cm^{-1} 2940, 2885, 1686 (COS), 1654 (COS), 1637, 1560, 1542, 1534, 1508, 1499, 1475, 1458, 1354, 1297, 1120, 1087, 954, 874, 829, 690 and 588; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.19 (3 H, s, CH_3) and 3.51 (20 H, s, OCH_2); δ_C(100 MHz; DMSO-d_6; Me_4Si) 39.3 (CH_3), 70.1 (OCH_2) and 216.2 (*C*SO).

Calcium (2,2-dimethylpropanethioato)(iodo)(15-crown-5) **19c**. A suspension of potassium 2,2-dimethylpropanethioate (0.310 g, 2.00 mmol) in THF (8 mL) was added to CaI_2 (0.581 g, 1.98 mmol) in the same solvent (2 mL) and the mixture was stirred at 21 °C for 1 h. The resulting precipitates (KI) were filtered off. The filtrate was added to 15-crown-5 (0.441 g, 2.00 mmol) in THF solution (3 mL), and the mixture was stirred at 23 °C for 30 min. The resulting precipitates were filtered off, followed by washing with hexane (5 mL) and drying under reduce pressure (25 °C/0.4 Pa) for 1 h, to give 0.504 g (51%) of the compound **19c** as white micro crystals, m.p. 208–214 °C (decomp.) (Found: C, 38.87; H, 5.68; Calc. for $C_{17}H_{29}CaIO_6S$ (528.06): C, 38.64; H, 5.53%); ν_{max} (KBr)/cm^{-1} 2948, 2884, 1654 (COS), 1618, 1560, 1542, 1522 , 1508, 1475 1458, 1357, 1290, 1248, 1087, 1042, 983, 954, 873, 828, 670 and 550; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.07 (9 H, s, CH_3) and 3.52 (20H, s, OCH_2); δ_C(100 MHz; DMSO-d_6; Me_4Si) 29.9 (CH_3), 47.0 (*C*), 69.9 (OCH_2) and 227.0 (*C*SO).

Barium (alkanecarbothioato)(iodo)(18-crown-6) **20**

Barium (thioacetato)(iodo)(18-crown-6) **20a**. Similarly to **20b**, the reaction of sodium thioacetate (0.246 g, 2.51 mmol) and BaI_2 (0.512 g, 1.31 mmol) with 18-crown-6 (0.358 g, 1.35 mmol) at 23 °C for 1 h in THF (12 mL), followed by recrystallization from a mixed solvent of acetone (33 mL) and hexane (2.5 mL) at -20 °C for 24 h, gave 0.303 g (47%) of the compound **20a** as white needles, m.p. 178–183 °C (decomp.) (Found: C, 27.53; H, 4.70; Calc. for $C_{14}H_{27}BaIO_7S$ (603.96): C, 27.86; H, 4.51%); ν_{max} (KBr)/cm^{-1} 2915, 2889, 2865, 2832, 1626 (COS), 1596, 1535, 1468, 1451, 1434, 1351, 1287, 1252, 1236, 1094, 983, 962, 872, 833, 678, 531 and 484; δ_H(400 MHz; DMSO-d_6; Me_4Si) 2.19 (3 H, s, CH_3) and 3.63 (24 H, s, OCH_2); δ_C(100 MHz; DMSO-d_6; Me_4Si) 39.6 (CH$_3$), 69.8 (OCH$_3$) and 216.0 (COS).

Barium **(***2,2-dimethylpropanethioato***)**(iodo)(18-crown-6) **20b**. A suspension of potassium 2,2-dimethylpropanethioate (0.311 g, 2.22 mmol) in THF (8 mL) was added to BaI_2 (0.448 g, 1.15 mmol) in the same solvent (2 mL) and the mixture was stirred at 26 °C for 1 h. The resulting precipitates were filtered off by the use of glass filter. The filtrate was added to 18-crown-6 (0.315 g, 1.19 mmol) in THF solution (3 mL), and the mixture was stirred at 26 °C for 30 min. The resulting precipitates were filtered off, followed by washing with hexane (5 mL) and drying under reduce pressure (23 °C/0.4 Pa) for 1 h, to give white solid (0.588 g). The solid (0.588 g) was dissolved in acetone (17 mL). Hexane (1 mL) was slowly added, and the mixture was allowed to stand at -20 °C for 48 h. Filtration of the resulting crystals gave 0.143 g (24%) of the compound **20b** as colorless micro needles, m.p. 196–204 °C (decomp.) (Found: C, 29.88; H, 5.19; Calc. for $C_{17}H_{33}BaIO_7S$ (645.74): C, 29.76; H, 5.15%); ν_{max} (KBr)/cm^{-1} 2919, 2862, 2830, 1654 (COS), 1597, 1560, 1530, 1473, 1352, 1287, 1250, 1091, 1037, 964, 874, 838 and 531; δ_H(400 MHz; DMSO-d_6; Me_4Si) 1.18 (9 H, s, CH_3) and 3.83 (24 H, s, OCH_2); δ_C(100 MHz; DMSO-d_6; Me_4Si) 29.2 (CH$_3$), 48.3 (C), 70.3 (OCH$_2$) and 231.9 (COS).

2. X-Ray structure analyses

The measurements were carried out on a Rigaku AFC7R four-circle diffract meter with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). All of the structures were solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. X-ray quality crystals of compounds **8b**, **11b**, **12b** and **14b** were obtained from acetone/hexane, while compounds **9b** and **10c** from acetonitrile/hexane, respectively. The crystals were cut from the grown needles. A suitable crystal was selected under the microscope and mounted on a glass fiber. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and showed no significant intensity variations during the data collection. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections (ψ-scans[S5] for **8b**) were also applied. Crystal data are shown in the references. The structures were solved by direct methods (SHELXT-2014[S6]) and refined by a full-matrix least square method on F^2 for all reflections (SHELXL-2014[S7]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Scattering factors for neutral atoms were from Cromer and Waber[S8] and anomalous dispersion[S9] was used. The final least square cycle included nonhydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. The crystal data, date correction and refinement details are summarized in Table S1. The H atoms, excluding those of water molecule, were placed in idealized positions and refined as riding atoms with isotropic displacement parameters that are 1.2 times of the attached atoms. Those of water molecule were located from difference Fourier maps and their positional parameters were refined with isotropic displacement parameters that are 1.2 times of the oxygen atom.

Table S1 Crystal data and data collection of $Ca(OSCC_6H_4Me\text{-}4)_2(15\text{-crown-}5)(H_2O)$ **8b**, $Ca(OSCC_6H_4Me\text{-}4)(SOCC_6H_4Me\text{-}4)(18\text{-crown-}6)$ **9b**, $Sr(SOCC_6H_4OMe\text{-}4)_2(15\text{-crown-}5)$ **10c**, $Ba(SOCC_6H_4Me\text{-}4)_2(18\text{-crown-}6)$ **12b** and $Sr(SeOCC_6H_4Me\text{-}4)_2(18\text{-crown-}6)\cdot(Me_2CO)$ **14b**

	Compound **8b**	Compound **9b**	Compound **10c**	Compound **12b**	Compound **14b**
empirical formula	$C_{26}H_{36}CaO_8S_2$	$C_{28}H_{38}CaO_8S_2$	$C_{26}H_{34}O_9S_2Sr$	$C_{31}H_{44}BaO_9S_2$	$C_{28}H_{38}O_8Se_2Sr$
formula weight	580.75	606.78	642.27	762.12	748.12
color	pale yellow	yellow	pale yellow	colorless	yellow
crystal system	prismatic	prismatic	prismatic	prismatic	prismatic
unit-cell dimentions	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
(a = Å), (b = Å), (c = Å)	a= 8.867(2) Å	a= 8.082(2) Å	a= 8.606(2) Å	a= 13.490(2) Å	a= 7.686(2) Å
	b= 22.380(2) Å	b= 16.472(2) Å	b= 14.452(2) Å	b= 16.032(1) Å	b= 13.944(2) Å
	c= 14.372(2) Å	c= 22.655(2) Å	c= 22.606(2) Å	c= 8.482(2) Å	c= 14.556(2) Å
α (deg)	90.0000	90.0000	90.0000	94.8300	90.0000
β (deg)	93.6800	99.4400	94.5100	93.1300	99.1700
γ (deg)	90.0000	90.0000	90.0000	107.0590	90.0000
volume of unit cell (Å^3)	2846.1(8)	2975.1(9)	2802.9(8)	1741.4(5)	1540.1(5)
space group	$P2_1$/n (#14)	$P2_1$/c (#14)	$P2_1$/n (#14)	P-1 (#2)	$P2_1$/n (#14)
Z value	4	4	4	2	2
D_{calc} (g/cm^3)	1.355	1.355	1.522	1.453	1.613
crystal size (mm)	0.14 x 0.26 x 0.23	0.14 x 0.17 x 0.26	0.14 x 0.14 x 0.11	0.26 x 0.23 x 0.06	0.17 x 0.17 x 0.20
μ (Mo-K_α) (cm^{-1})	4.13	3.98	21.23	13.08	41.59
temp (°C)	-79.8	-79.8	-79.8	-79.8	-79.8
$\lambda_{\mathrm{MoK}\alpha}$(Å)	0.71069	0.71069	0.71069	0.71069	0.71069
$2\theta_{\mathrm{max}}$ (deg)	55.0 °	55.0	55.0	55.0	55.0
no. of measured reflections	6959	7311	7016	8520	4646
no. of observations ($I > 2\sigma(I)$)	6549	6835	6441	7982	3516
no. of variables	342	354	345	392	179
residuals: R,[a] R_w[b]	0.0618, 0.1542	0.0558, 0.1574	0.0629, 0.15.11	0.0295, 0.0681	0.0465, 0.1060
goodness of fit indicator	1.001	1.018	0.963	1.028	0.997

[a] $R= \Sigma(|F_O|-|F_C|)/\Sigma|F_O|$. [b] $R_w= [\Sigma(|F_O|-|F_C|)^2/\Sigma w|F_O|^2]^{1/2}$, $w= [\sigma^2(F_O)+p^2(F_O)^2/4]^{-1}$.

Table S2 Selected bond distances (Å), angles (°) and torsion angles of compounds **8b**, **9b**, **10c**, **12b** and **14b**

Ca(OSCC$_6$H$_4$Me-4)$_2$(15-crown-5)(H$_2$O) **8b**

Bond lengths

Ca(1)–O(1)	2.333(4)	Ca(1)–O(2)	2.350(4)
Ca(1)···S(1)	4.189(4)	Ca(1)···S(2)	4.016(4)
S(1)–C(1)	1.696(6)	S(2)–C(9)	1.693(6)
O(1)–C(1)	1.257(6)	O(2)–C(9)	1.259(6)
Ca(1)–O(8)	2.421(4)	Ca(1)–O(3)	2.591(4)
Ca(1)–O(4)	2.439(4)	Ca(1)–O(5)	2.541(4)
Ca(1)–O(6)	2.494(4)	Ca(1)–O(7)	2.518(4)
S(1)···O(8)	3.194(4)	S(2)···O(8)	3.179(4)
S(1)···H(1)	2.30(4)	S(2)···H(2)	2.39(5)

Angles

S(1)–C(1)–O(1)	124.7(2)	S(2)–C(9)–O(2)	121.5(2)
S(1)–Ca(1)–O(1)	34.5(2)	S(2)–Ca(1)–O(2)	38.7(2)
Ca(1)-O(1)-S(1)	146.2(2)	Ca(1)-O(2)-C(9)	138.4(2)
S(1)-O(8)-S(2) O(5)-	97.0(1)	O(1)-Ca(1)-O(8)	83.5(1)
Ca(1)-O(7)	119.8(1)	O(6)-Ca(1)-O(2)	149.9(1)
S(1)···(1)-O(8)	157.7(1)	S(2)···H(2)-O(8)	171.6(1)

Torsion angle

S(1)–C(1)–O(1)–Ca(1)	20.0(9)	O(3)–Ca(1)–O(4)-O(5)	174.5(1)
S(2)-C(9)–O(2)–Ca(1)	18.5(7)	S(2)–C(9)–C(10)–C(15)	24.6(6)
S(1)–C(1)–C(2)–C(7)	1.7(7)		

Ca(OSCC$_6$H$_4$Me-4)(SOCC$_6$H$_4$Me-4)(18-crown-6) **9b**

Bond lengths

Ca(1)---S(1)	4.639(2)	Ca(1)–S(2)	2.969(2)
Ca(1)–O(1)	2.293(3)	Ca(1)–O(2)	2.410(3)
S(1)–C(1)	1.698(5)	S(2)–C(9)	1.701(4)
O(1)–C(1)	1.256(5)	O(2)–C(9)	1.258(5)
Ca(1)–O(3)	2.635(3)	Ca(1)–O(4)	2.546(3)
Ca(1)–O(5)	2.650(3)	Ca(1)–O(6)	2.649(3)
Ca(1)–O(7)	2.584(3)	Ca(1)–O(8)	2.610(3)

Angles

S(1)–C(1)–O(1)	124.0(4)	S(2)–C(9)–O(2)	121.3(3)
S(1)–Ca(1)–O(1)	20.43(8)	S(2)–Ca(1)–O(2)	56.39(8)
Ca(1)-O(1)-C(1)	170.9(3)	Ca(1)-O(2)-C(9)	105.7(3)
Ca(1)-S(1)-C(1)	41.0(2)	Ca(1)-S(2)-C(9))	74.7(2)
O(1)–Ca(1)-S(2)	151.32(9)	O(1)–Ca(1)-O(2)	150.3(1)

Torsion angles

Ca(1)-S(1)–C(1)–O(1)	5.7(2)	Ca(1)-S(2)–C(9)–O(2)	12.4(3)
S(1)–C(1)–C(2)–C(3)	6.7(6)	S(2)–C(9)–C(10)–C(11)	3.7(6)
O(1)-S(1)-S(2)–O(2)	13.52(4)		

Sr(SOCC$_6$H$_4$OMe-4)$_2$(15-crown-5) **10c**

Bond lengths

Sr(1)–S(1)	3.129(2)	Sr(1)–S(2)	3.019(2)
Sr(1)–O(1)	2.570(5)	Sr(1)–O(3)	2.577(5)
S(1)–C(1)	1.710(7)	S(2)–C(9)	1.718(7)
O(1)–C(1)	1.255(8)	O(3)–C(9)	1.246(8)
Sr(1)–O(5)	2.679(5)	Sr(1)–O(6)	2.796(5)
Sr(1)–O(7)	2.732(5)	Sr(1)–O(8)	2.686(5)
Sr(1)–O(9)	2.660(5)		

Angles

S(1)–C(1)–O(1)	123.2(6)	S(2)–C(9)–O(3)	121.6(2)
S(1)–Sr(1)–O(1)	78.7(1)	S(2)–Sr(1)–O(3)	54.6(1)
Sr(1)-O(1)-C(1)	107.3(1)	Sr(1)-O(3)-C(9)	100.7(4)
S(1)–Sr(1)-S(2)	77.48(6)	O(1)–Sr(1)–O(3)	93.1(1)
O(6)–Sr(1)-O(9)	103.5(2)	S(1)–Sr(1)–O(9)	78.7(1)

Torsion angles

Sr(1)-O(1)–C(1)-S(1)	3.3(7)	Sr(1)–O(3)–C(9)–S(2)	31.6(6)
S(1)–C(1)–C(2)–C(7)	20.8(9)	S(2)–C(9)–C(10)–C(11)	12(1)
O(1)–S(1)–Sr(1)-O(3)	66.3(2)	O(5)–O(6)–Sr(1)–O(7)	123.8(2)
O(8)–O(9)–Sr(1)–O(5)	161.2(2)		

Ba(OSCC$_6$H$_4$Me-4)$_2$(18-crown-6)·Me$_2$CO **12b**

Bond lengths

Ba(1)–S(1)	3.376(1)	Ba(1)–S(2)	3.259(1)
Ba(1)–O(1)	2.780(2)	Ba(1)–O(2)	2.856(2)
S(1)–C(1)	1.708(3)	S(2)–C(9)	1.715(3)
O(1)–C(1)	1.237(4)	O(2)–C(9)	1.242(4)
Ba(1)–O(3)	2.806(2)	Ba(1)–O(4)	2.840(2)
Ba(1)–O(5)	2.835(2)	Ba(1)–O(6)	2.794(2)
Ba(1)–O(7)	2.801(2)	Ba(1)–O(8)	2.807(2)

Angles

S(1)–C(1)–O(1)	123.4(2)	S(2)–C(9)–O(2)	122.5(2)
S(1)–Ba(1)–O(1)	48.83(5)	S(2)–Ba(1)–O(2)	49.84(4)
C(1)–O(1)–Ba(1)	110.3(2)	C(9)–O(2)–Ba(1)	106.0(2)
S(1)–Ba(1)–S(2)	148.38(2)	O(1)–Ba(1)–O(2)	133.83(6)
O(1)–Ba(1)–O(8)	65.65(6)	O(8)–Ba(1)–S(2)	101.27(4)

Torsion angles

Ba(1)–S(1)–C(1)–O(1)	9.1(2)	Ba(1)-S(2)–C(9)–O(2)	11.5(2)
S(1)–C(1)–C(2)–C(3)	178.7(2)	S(2)–C(9)–C(10)–C(15)	4.2(4)
C(1)–S(1)–Ba(1)–O(2)	108.5(1)	O(2)-S(2)–Ba(1)–O(1)	109.3(1)
O(1)–S(1)–O(2)–S(2)	97.74(8)		

Sr(SeOCC$_6$H$_4$Me-4)$_2$(18-crown-6) **14b**

Bond lengths

Sr(1)–Se(1)	3.4923(7)	Sr(1)–O(2)	2.692(3)
Sr(1)–O(1)	2.594(4)	Sr(1)–O(4)	2.818(3)
Se(1)–C(1)	1.864(5)		
O(1)–C(1)	1.247(6)		
Sr(1)–O(3)	2.704(3)		

Angles

Se(1)–C(1)–O(1)	120.9(4)
Se(1)–Sr(1)–O(1)	50.56(8)
C(1)–O(1)–Sr(1)	115.3(3)
O(1)–Sr(1)–O(2)	104.9(1)
O(1)–Sr(1)–O(3)	72.14(1)

Torsion angles

Sr(1)–Se(1)–C(1)–O(1)	17.1(1)
Se(1)-C(1)–C(2)-C(7)	1.3(7)
O(1)-C(11)-C(12)–C(13)	6.1(6)
Se(1)-O(1)-Se(1')-O(1')	180.0(1)

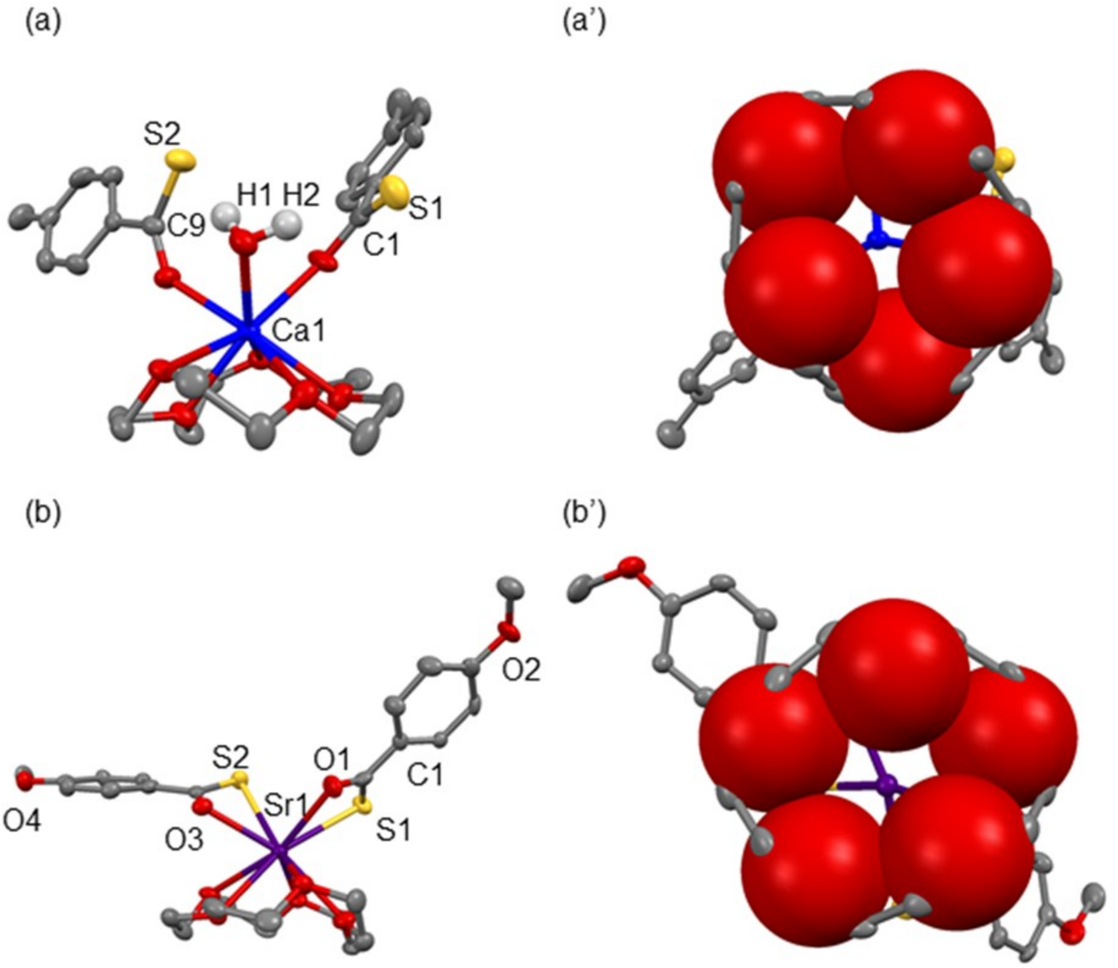

Fig. S1 Side [(a) and (b)] and back side views ((a') and (b') from arrow in (a) and (b), respectively) of Ca($OSCC_6H_4OMe$-4)$_2$ (15-crown-5) **8b** and Sr($OSCC_6H_4OMe$-4)$_2$ (15-crown-5) **10c**, respectively. Deep blue, yellow, red, dark gray, white and violet balls are calcium, sulfur, oxygen, carbon sand strontium atoms, respectively. All hydrogen atoms except for those of H_2O in compound **8b** are omitted for clarity. For (a') and (b'), large red balls show the oxygen atoms of the crown ether in a space filling model.

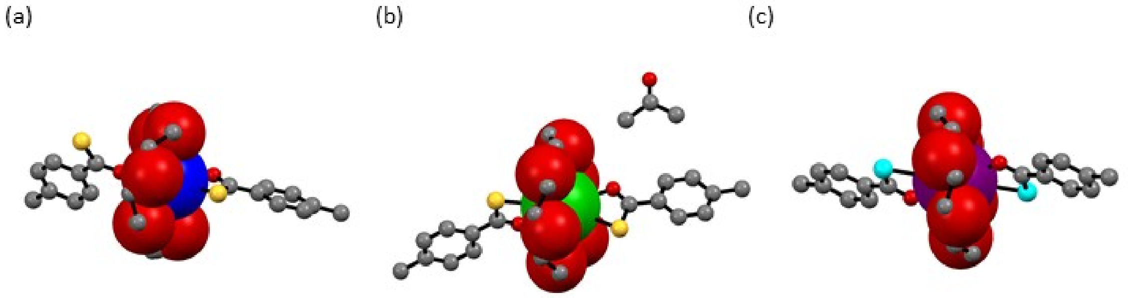

Fig. S2 Structural comparison of (a) Ca(OSCC$_6$H$_4$Me-4)(SOCC$_6$H$_4$Me-4)(18-crown-6) **9b**, (b) Ba(SOCC$_6$H$_4$Me-4)$_2$(18-crown-6)·(Me$_2$CO) **12b,** and (c) Sr(SeOCC$_6$H$_4$Me-4)$_2$(18-crown-6) **14b**. eep blue, violet, green, yellow, light blue, red, and dark gray balls are calcium, strontium, barium, sulfur, selenium, oxygen and carbon atoms, respectively. For (a), large red balls are the oxygen atoms of 18-crown-6 in a space filling model. For (b) and (c), large green and violet balls are barium and strontium atom in a space filling model, respectively.

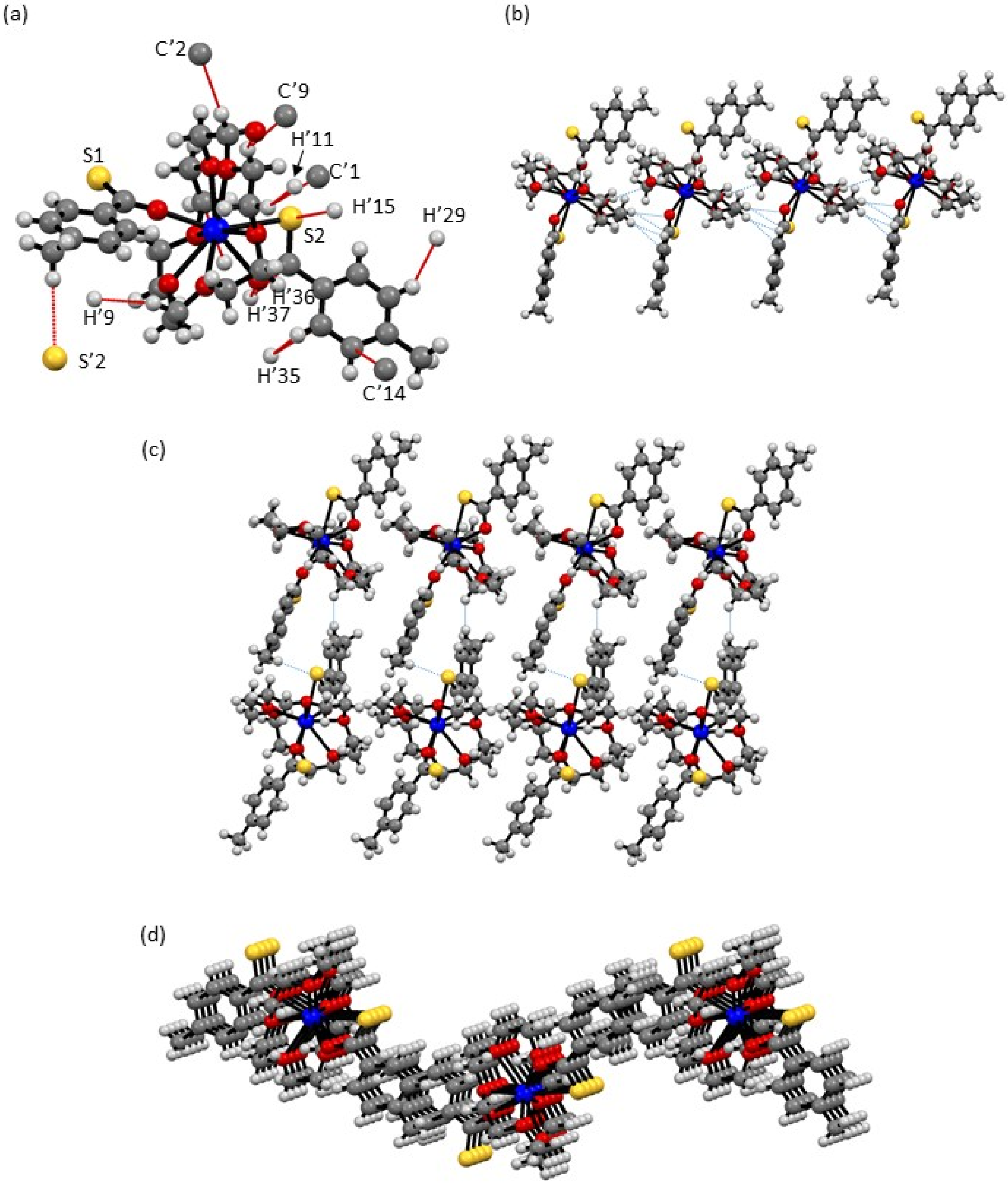

Fig. S3 Intermolecular short contacts (a) and arrangements (b-d) of compound **9b**. Deep blue, yellow, red, dark gray and white balls show calcium, sulfur, oxygen and carbon atoms, respectively. Red for (a) and light blue dotted lines for (b)-(d) show intermolecular short contacts. For (a), dashed atoms are those of neighboring molecules. For (b), one dimensional molecular chain formed by both intermolecular C=O···H$_2$C hydrogen bondings and short contacts between the methylene hydrogen atoms (H$_{CH2}$···H$_{CH2}$). For (c), 2-D sheet formed by both intermolecular C=S···H$_{CH3}$ hydrogen bondings and H$_{CH2}$···H$_{CH2}$ short contacts between the molecular chain. For (d), 3-D networks formed by stacking of the sheet.

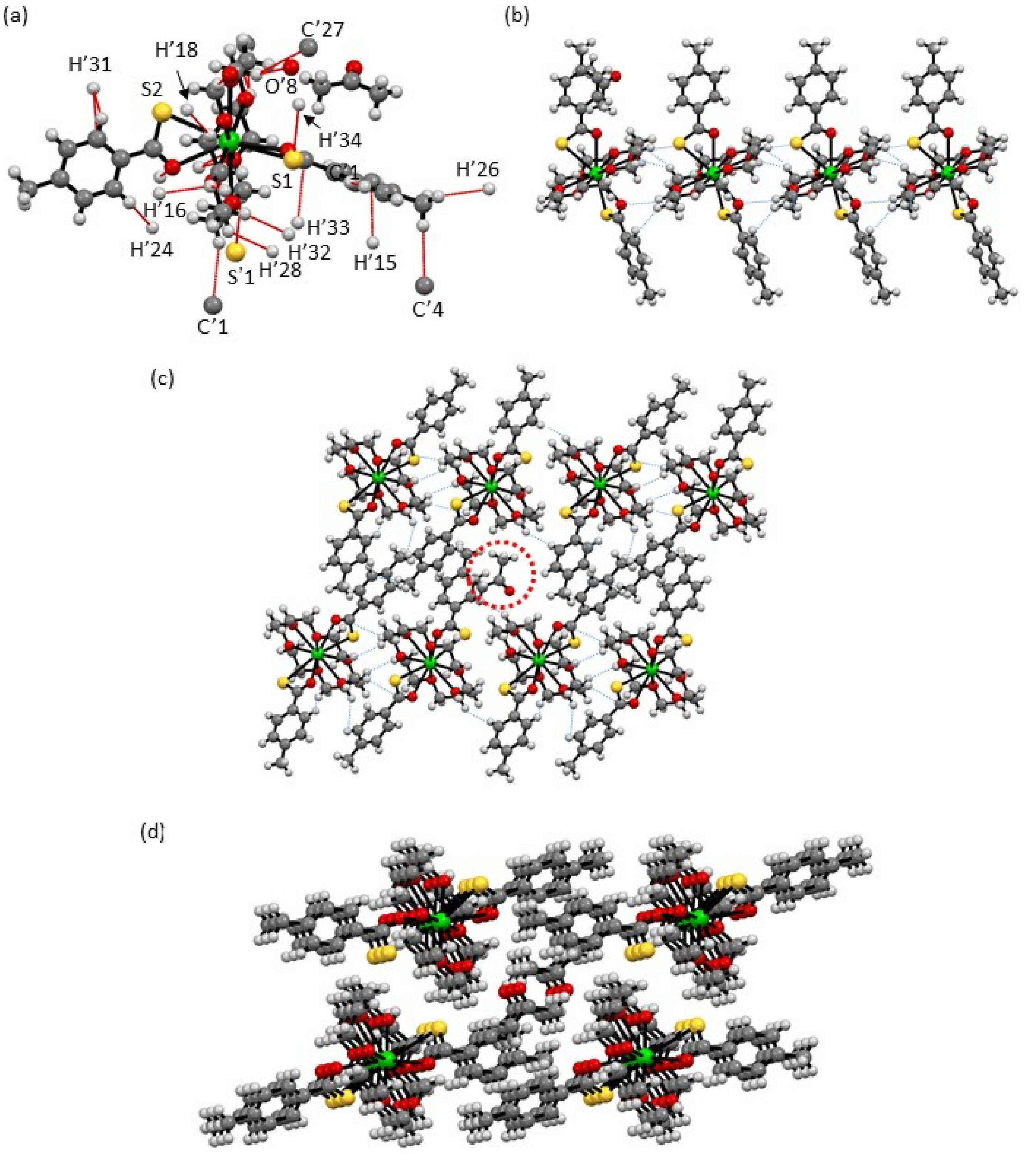

Fig. S4 Intermolecular short contacts (a) and molecular arrangements (b-c) of compound **12b**. Green, yellow, red, dark gray and white balls show barium, sulfur, oxygen, carbon and hydrogen atoms, respectively. For (a), dashed atoms are those of neighboring molecules. For (b), one dimensional molecular chain formed by short contacts of these molecular chains. For (c), 2-D sheet formed by intermolecular CH···O hydrogen bond between these molecular chains. For (d), 3-D networks formed by stacking of these sheets. Red for (a) and light blue dotted lines for (b) show intermolecular short contacts. For (b) and (c), the solvent molecules Me_2CO trapped in the central channel are shown in a red dotted circle, respectively.

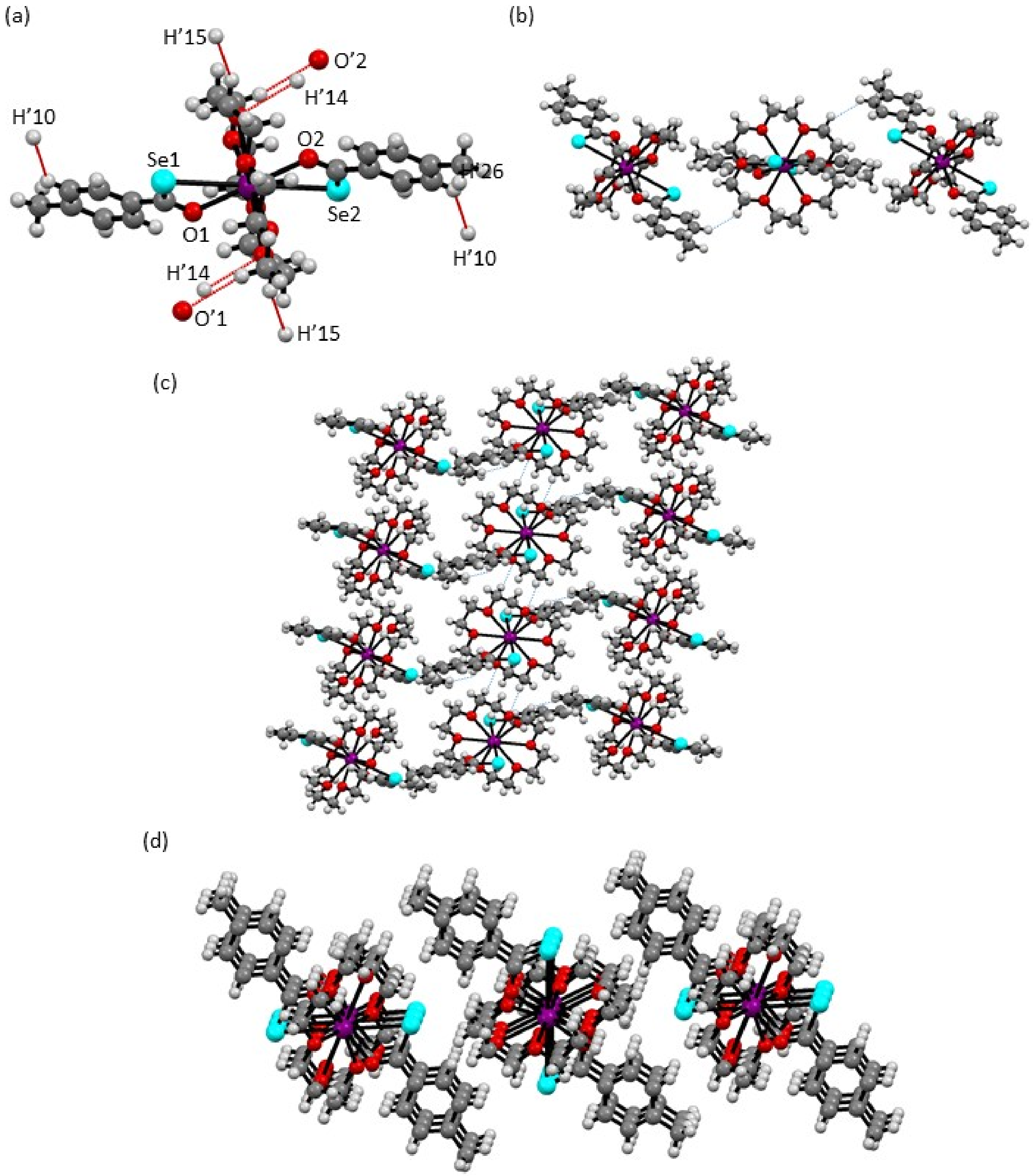

Fig. S5 Intermolecular short contacts (a) and molecular arrangements (b-d) of compound **14b**. Violet, pink, red, dark gray and white balls show strontium, selenium, oxygen, carbon and hydrogen atoms, respectively. Red for (a) or light blue dotted lines for (b)-(c) show intermolecular short contacts. For (a), dashed-atoms are those of neighboring molecules. For (b), one dimensional chain formed by the intermolecular $H_{CH2}\cdots H_{arom}$ contacts. For (c), 2-D sheet formed by short contacts of these molecular chains. For (d), 3-D networks formed by stacking of these sheets.

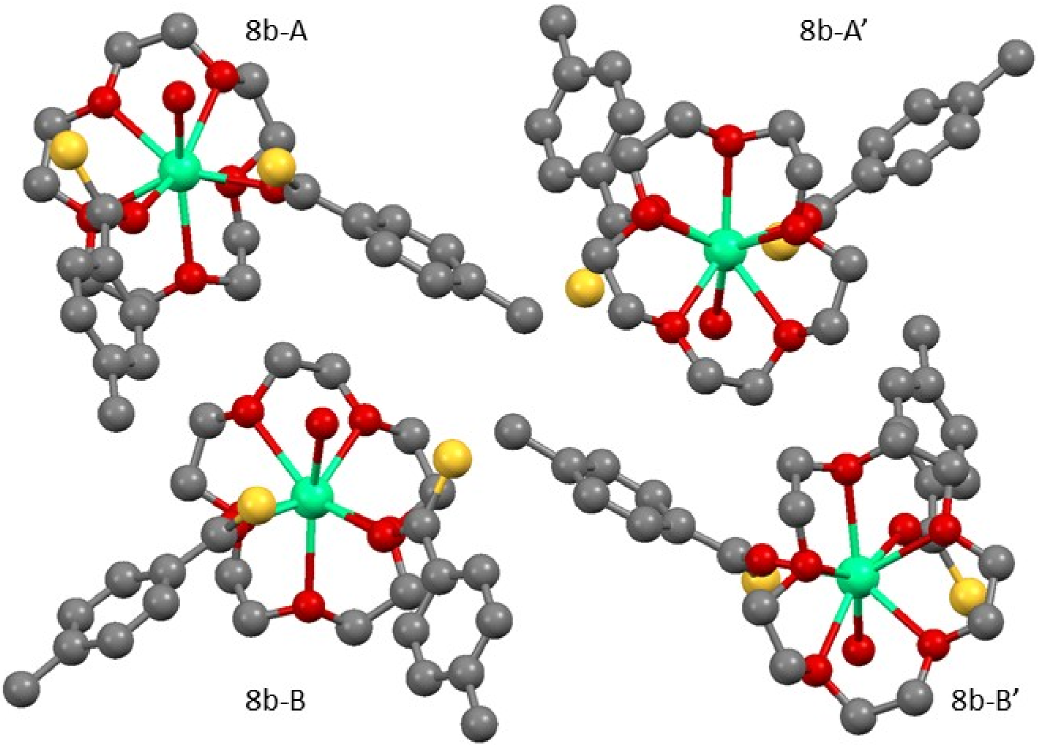

Fig. S6 Packing of Ca(OSCC$_6$H$_4$Me-4)$_2$(15-crown-5)·(H$_2$O) **8b** view down the a-axis. Green, yellow, gray and red balls are calcium, sulfur, carbon and oxygen atoms, respectively. All hydrogen atoms are omitted for clarity. Structures **8b-A**, **8b-A'**, **8b-B** and **8b-B'** are enantiomorphic, each other.

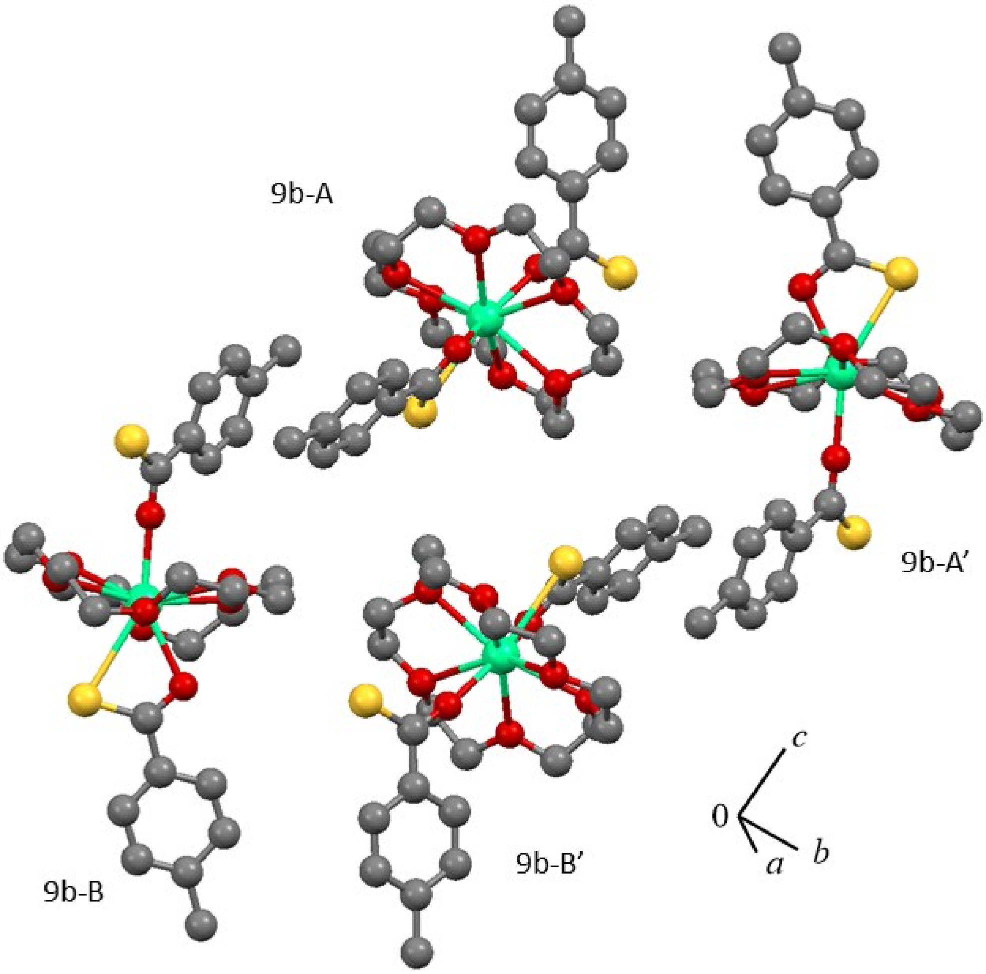

Fig. S7 Packing of Ca(OSCC$_6$H$_4$Me-4)(SOSCC$_6$H$_4$Me-4)(18-crown-6) **9b** view down the a-axis. Green, yellow, gray and red balls are calcium, sulfur, carbon and oxygen atoms, respectively. All hydrogen atoms are omitted for clarity. Structures **9b-A**, **9b-A'**, **9b-B** and **9b-B'** are enantiomorphic, each other.

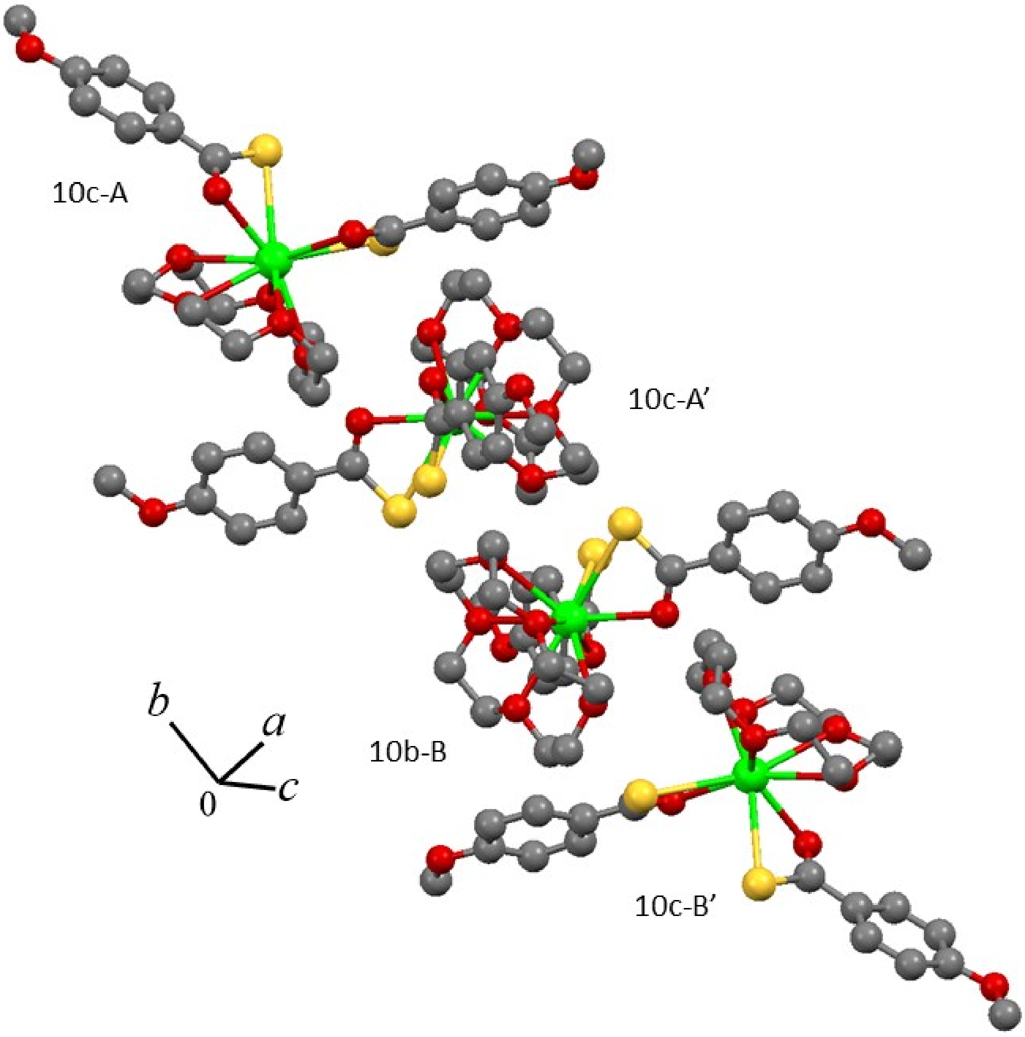

Fig. S8 Packing and (b) intermolecular short contacts of Sr(SOCC$_6$H$_4$OMe-4)$_2$(15-crown-5) **10c** view down the a-axis. Green, yellowt, gray and red balls are strontium, sulfur, carbon and oxygen atoms, respectively. All hydrogen atoms are omitted for clarity. Structures **10c-A**, **10c-A'**, **10c-B** and **10c-B'** are enantiomorphic, each other.

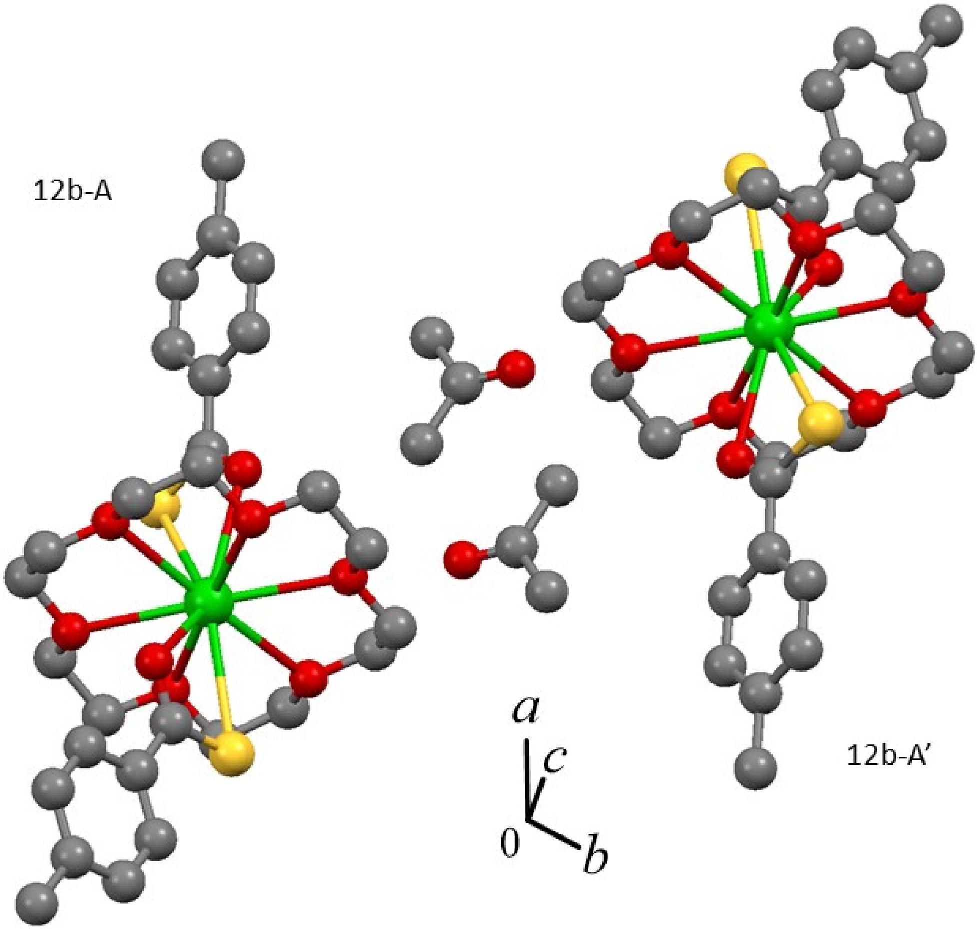

Fig. S9 Packing of Ba(SOCC$_6$H$_4$Me-4)$_2$(18-crown-6)·(Me$_2$CO) **12b** view down the c-axis. Green, yellow, gray and red balls are barium, sulfur, carbon and oxygen atoms, respectively. All hydrogen atoms are omitted for clarity. Structures **12b-A** and **12b-A'** are enantiomorphic, each other.

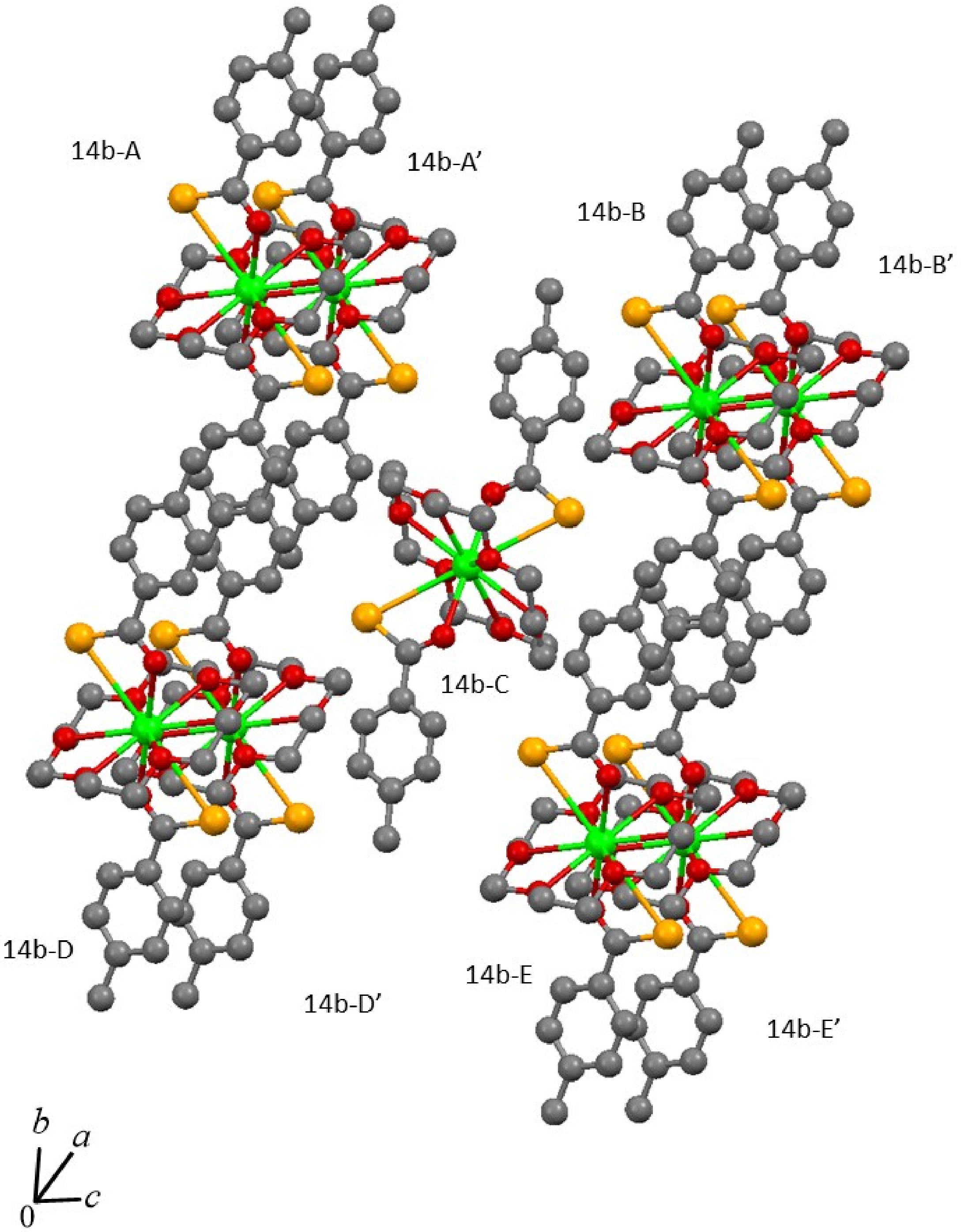

Fig. S10 Packing of Sr(SeOCC$_6$H$_4$Me-4)$_2$(18-crown-6) **14b** view down the a-axis. Green, dark yellow, gray and red balls are strontium, selenium, carbon and oxygen atoms, respectively. All hydrogen atoms are omitted for clarity. Structures **14b-A**, **14b-A'**; **14b-B**, **14b-B'**; **14b-C**; **14b-D**, **14b-D'**; and **14b-E**, **14b-E'** are enantiomorphic, each other.

Spectroscopic measurement

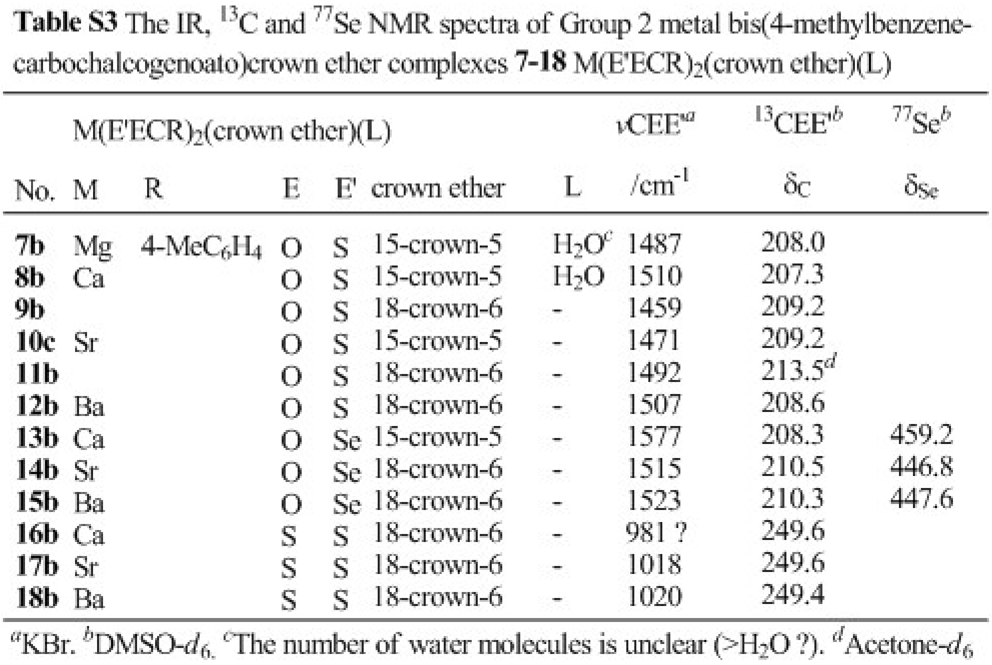

Table S3 The IR, ^{13}C and ^{77}Se NMR spectra of Group 2 metal bis(4-methylbenzenecarbochalcogenoato)crown ether complexes **7-18** $M(E'ECR)_2$(crown ether)(L)

	$M(E'ECR)_2$(crown ether)(L)						$\nu CEE'^a$	$^{13}CEE'^b$	$^{77}Se^b$
No.	M	R	E	E'	crown ether	L	/cm^{-1}	δ_C	δ_{Se}
7b	Mg	4-MeC_6H_4	O	S	15-crown-5	H_2O^c	1487	208.0	
8b	Ca		O	S	15-crown-5	H_2O	1510	207.3	
9b			O	S	18-crown-6	-	1459	209.2	
10c	Sr		O	S	15-crown-5	-	1471	209.2	
11b			O	S	18-crown-6	-	1492	213.5^d	
12b	Ba		O	S	18-crown-6	-	1507	208.6	
13b	Ca		O	Se	15-crown-5	-	1577	208.3	459.2
14b	Sr		O	Se	18-crown-6	-	1515	210.5	446.8
15b	Ba		O	Se	18-crown-6	-	1523	210.3	447.6
16b	Ca		S	S	18-crown-6	-	981 ?	249.6	
17b	Sr		S	S	18-crown-6	-	1018	249.6	
18b	Ba		S	S	18-crown-6	-	1020	249.4	

^{a}KBr. ^{b}DMSO-d_6. ^{c}The number of water molecules is unclear (>H_2O ?). ^{d}Acetone-d_6

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