Formation of separated *versus* contact ion triples in heavy alkaline-earth thiolates

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The synthesis and structural characterization of the alkaline-earth thiolates [Sr(18-crown-6)(hmpa)$_2$][SMes*]$_2$ and [Ba(18-crown-6)(hmpa)(SMes*)][SMes*], displaying rare ion association modes with only one or no cation–thiolate linkages are presented.

In contrast to the well explored chemistry of separated organometallic lithium and sodium derivatives, little is known about the ionic association in heteroatomic systems. To date no separated alkoxide or aryloxide ion pairs have been described, and, to the best of our knowledge, only one thiolate, [Li(12-crown-4)$_2$][SMes*] (Mes* = $C_6H_2Bu^t_3$-2,4,6), has been reported.[1] The ion association chemistry of alkaline-earth derivatives is even less explored, which might be explained by the potentially more complex chemistry with three different types of ion association: contact triples with two cation–anion linkages, separated ion triples with no contacts between cation and anions, and semi-separated ion triples displaying one cation–anion contact, while the second anion does not interact with the metal center.

Only few examples of separated heteroatomic alkaline-earth derivatives such as [Mg(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$]$_2$,[2] and [Ca(18-crown-6)(NH$_3$)$_3$][SMes*]$_2$ have been reported.[3] All known strontium and barium chalcogenolates are contract triples, as observed in [Sr(thf)$_4$(=EMes*)$_2$] (E = S, Se),[4] [Sr(NH$_3$)(Py)(μ-SCEt$_3$)$_2$]$_\infty$,[5] [Sr(tmen)$_2${SeSi(SiMe$_3$)$_3$}$_2$],[2] and [Ba(Py)$_5${TeSi(SiMe$_3$)$_3$}$_2$].[2] We present herein the synthesis and structural characterization of the separated [Sr(18-crown-6)(hmpa)$_2$][SMes*]$_2$ **1** (Fig. 1), and the semi-separated [Ba(18-crown-6)(hmpa)(SMes*)][SMes*] **2** (Fig. 2). Compounds **1** and **2** represent examples of the least known association modes for alkaline-earth derivatives.

Several synthetic routes can be utilized for the synthesis of heavy alkaline-earth chalcogenolates, the most efficient of which is the treatment of the ammonia solvated metals with thiol. The insoluble powders, obtained after evaporation of ammonia and addition of thf can be transferred into soluble species by addition of a slight excess of hmpa.†

The Sr center in **1** is eight coordinate, with two strong hmpa donor interactions [2.420(2) Å] in addition to six crown-ether linkages in the range of 2.712(1)–2.736(1) Å. Both, the Sr–hmpa and the crown-ether connections compare well with literature data.[10] The S–C bond length in **1** is observed at 1.771(2) Å, which is slightly shorter than in [Sr(thf)$_4$(SMes*)$_2$],[4] but compares well with Li(12-crown-4)$_2$][SMes*][1] and [Ca(18-crown-6)(NH$_3$)$_3$][SMes*]$_2$.[3]

The comparison of **1** with [Sr(thf)$_4$(SMes*)$_2$] and [Sr(NH$_3$)(Py)(μ-SCEt$_3$)$_2$]$_\infty$ clearly shows that the presence of a multidentate donor (18-crown-6) in combination with a very strong donor (hmpa) greatly affects the ionic association of the resulting complexes. To make the rupture of a Sr–S bond thermodynamically favorable, a significant amount of solvation energy must be provided. Apparently, the donors thf, pyridine or NH$_3$ which are present in the reaction mixtures resulting in the contact triples, do not provide sufficient solvation energy to stabilize a separated Sr cation.

The Ba derivative **2**, which crystallizes with two independent molecules per asymmetric unit, consists of a monocation [Ba(18-crown-6)(hmpa)(SMes*)], and a separated SMes* anion. The Ba centers are eight coordinate with one thiolate [Ba–S 3.012(2) and 3.025(2) Å] and one hmpa contact [Ba–O 2.592(5), 2.594(5) Å], in addition to six crown-ether linkages [2.772(5)–2.807(5) Å]. The Ba atom is slightly displaced from the plane of the six crown-ether oxygen atoms [0.256 and 0.264 Å] towards the hmpa donor, indicating a strong Ba–hmpa interaction. The Ba–S–C angles are observed at 150.8(2) and 153.7(3)°, S–C distances in the contact thiolate are observed at 1.792(7) and 1.805(7); those for the separated anion are identified at 1.777(7) and 1.753(7) Å. The shortest Ba–S distance for the non-coordinating anion is observed at 6.533 Å.

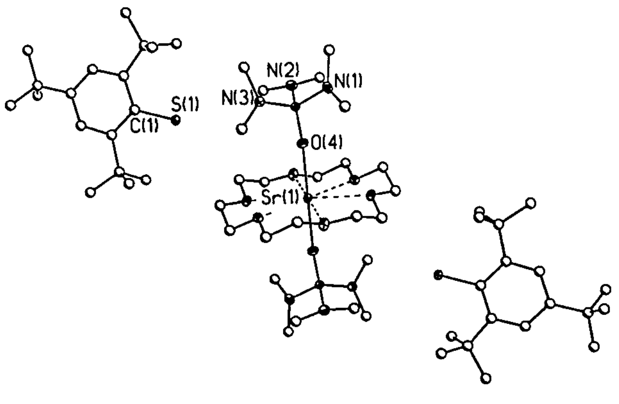

Fig. 1 Computer generated plot of [Sr(18-crown-6)(hmpa)$_2$][SMes*]$_2$ **1**. H atoms have been eliminated for clarity. Sr–O(hmpa) 2.420(2) Å; Sr–O(crown) 2.712(1), 2.718(1), 2.736(1) Å; S–C 1.771(2) Å.

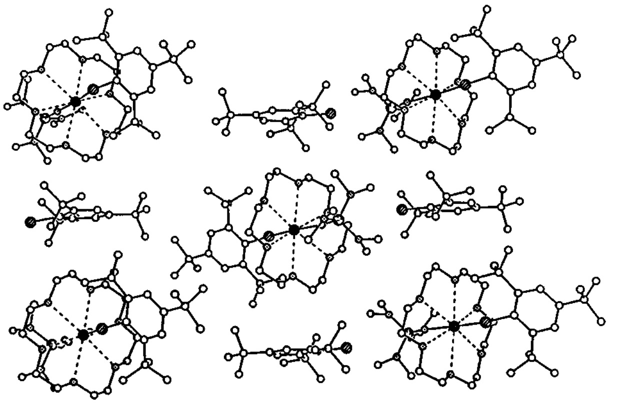

Fig. 2 Computer generated plot showing part of the unit cell in **2**. Ba–S 3.012(2), 3.025(2) Å; Ba–O(hmpa) 2.592(5), 2.594(5) Å; Ba–O(crown) 2.772(5)–2.807(5) Å; S–C (contact) 1.792(7), 1.805(7) Å; S–C (separated) 1.777(7), 1.753(7) Å; Ba–S–C 153.7(3), 150.8(2)°; O(hmpa)–Ba–S 172.8(1), 174.1(1)°.

Several complexes containing Ba–S moieties, where the S atom is part of a S–C–N resonance delocalized system are available for structural comparison to **2**.[6] While the Ba–crown-ether or –hmpa interactions fall in expected ranges,[7] significant differences are observed in the Ba–S distances. The Ba–S lengths in a series of seven-coordinate compounds bearing the 2-mercaptobenzoxazole ligand were observed at a mean value of 3.31(1) Å,[8] while Ba–S interactions in a ten-coordinate trimercaptotriazine derivative are displayed over a range of 3.396(2)–3.692(2) Å.[9] The shorter Ba–S bonds in **2** can be attributed in part to the absence of a second thiolate ligand in the coordination environment of the cation. In addition, the chelating nature of both the mercaptotriazine and the 2-mercaptobenzoxazole ligands might result in the lengthening of the Ba–S bond. The strong Ba–S bond in **2** is further demonstrated by the repeated isolation of **2**, even if very large excesses (up to 12 fold) of hmpa was added to the reaction mixture. The unusually wide Ba–S–C angles of 150.8(2) and 153.7(3)° compare well with those observed in [Ca(18-crown-6)(SMes*)$_2$], where one strong [2.785(2) Å] and one weaker [2.859(2) Å] Ca–S interaction was observed.[7] The environment at the S atom involved in the stronger bond is very similar to that in **2** [Ca–S–C 154.1(2)°].

Several factors affect the ion association in alkali and alkaline-earth chalcogenolates. The balance between steric congestion about the cation and tendency towards maximization of cation–anion interactions is nicely demonstrated in the ion triples [Sr(18-crown-6)(hmpa)$_2$][SMes*]$_2$ **1** and [Ba(18-crown-6)(hmpa)(SMes*)][SMes*] **2**. The smaller Sr cation (CN 8: 1.40 Å)[10] is unable to accommodate one SMes* ligand while maintaining strong crown ether coordination. In the presence of the strong donor hmpa, the Sr–S bond is ruptured (shortest resulting Sr–S 6.301 and 7.252 Å), and hmpa donor molecules occupy the coordination sites perpendicular to the crown ether plane. Ligation by hmpa provides the needed cation coordination while being sterically less demanding than the thiolate anions. This result might be compared to [Ca(18-crown-6)(SMes*)$_2$],[3] isolated in the absence of hmpa. This reaction was carried out in thf, which is apparently unable to provide the necessary solvation energy for the stabilization of a separated cation. The addition of hmpa to the corresponding Ba reaction, results in **2**: the larger Ba cation (CN 8: 1.56 Å)[10] enables the close approach of one thiolate ligand and one hmpa donor.

The synthesis and characterization of the first Sr separated ion triple, **1**, and the novel, unusual intermediate between a contact and a separated ion triple **2**, contributes significantly to the understanding of the association chemistry of the alkaline-earth elements. The detailed analysis of structural parameters gives important insight into the nature and strength of alkaline-earth metal–ligand and –donor interactions, while providing information about the preferred alkaline-earth metal environment. Our work in this area of chemistry is continuing and will be subject of forthcoming publications.

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Notes and References

† *Synthetic procedures*: all reactions were performed under anaerobic and anhydrous conditions. HSMes* was prepared by published procedures.[11] **CAUTION**: hmpa [hexamethylphosphoramide, P(O)(NMe$_2$)$_3$] is a suspected carcinogen and should be handled in a well ventilated fumehood using gloves. *General procedure* for **1** and **2**: a 100 ml Schlenk flask was charged with 1.0 mmol of metal, 0.26 g (1.0 mmol) of 18-crown-6 and 0.56 g (2.0 mmol) of HSMes*. Approximately 25 ml of predried $NH_{3(l)}$ was condensed into the flask. The deep-blue solution was stirred at -78 °C for 1 h and then warmed up to room temp. 25 ml of thf was added. A heavy yellow–white suspension persisted even after brief heating. As hmpa was added dropwise (0.70 ml, 4.0 mmol), the reaction gradually cleared then became cloudy-white once again. The solution was heated briefly to reflux and immediately filtered through a Celite padded frit. **1**: colorless blocks formed on cooling to room temperature in 16% yield (0.20 g). Mp: shrinking at approximately 215 °C and an irreversible melt at 245–250 °C. ^{1}H NMR ([^{2}H$_8$]thf), δ 7.06 (s, 4H), 3.83 (s, 24H), 2.62 (d, 36H), 1.74 (s, 36H), 1.24 (s, 18H); ^{13}C{^{1}H}NMR ([^{2}H$_8$]thf), δ 150.16, 150.10, 120.77, 71.01, 39.15, 37.34, 32.44, 32.03; IR (Nujol), 2920s, 1592w, 1461s, 1377s, 1354m, 1285s, 1190m, 1155s, 1095s, 1024m, 981s, 966s, 876w, 839w, 757s, 616w, 483m cm^{-1}. **2**: colorless crystals formed almost instantly out of a yellow filtrate in 19% yield (0.21 g). Melting to an oily residue at 175–180 °C, decomposition above 200 °C. ^{1}H NMR ([^{2}H$_5$]py) δ 7.59 (s, 4H), 3.82 (s, 24H), 2.58 (d, 18H), 2.19 (s, 36H), 1.46 (s, 18H); ^{13}C{^{1}H}NMR ([^{2}H$_5$]py), δ 139.37, 121.37, 70.98, 39.52, 37.31, 34.80, 32.61, 32.03; IR (Nujol), 2854s, 1593w, 1462s, 1377s, 1349w, 1283w, 1246w, 1195w, 1166w, 1087m, 1042w, 979w, 957m, 875w, 833w, 723m, 480w cm^{-1}.

‡ The crystals were mounted as described earlier.[12a] Crystal data for **1** and **2**·0.5C$_7$H$_8$ were collected at 150 K with Mo-Kα radiation (λ = 0.710 73 Å), Bruker SMART CCD diffractometer, graphite monochromator, Oxford Instruments Cryojet low temperature device. Both structures were solved and refined using the SHELXTL program package.[12b] An absorption correction was applied using the program system SADABS.[12c] **1**: M = 632.64, crystal dimensions 0.20 × 0.15 × 0.15 mm, μ = 0.882 mm^{-1}, scan range $3° < 2\theta < 57°$, monoclinic, space group $P2_1/n$, a = 10.5771(3), b = 17.5403(5), c = 19.8293(7) Å, β = 91.152(1)°, V = 3678.1(2) Å^3, Z = 2, D_c = 1.142 g cm^{-3}, 22232 measured, 8569 independent reflections (R_{int} = 0.0329), 358 refined parameters. R_1 [$I > 2\sigma(I)$] = 0.0441, R_1 (all data) = 0.0667. **2**·0.5C$_7$H$_8$: M = 2363.73, crystal dimensions 0.30 × 0.30 × 0.30 mm, μ = 0.744 mm^{-1}, scan range $2 < 2\theta < 50°$, monoclinic, space group $P2_1/n$, two independent molecules per asymmetric unit, one disordered solvent toluene molecule, a = 21.2127(3), b = 14.2323(2), c = 43.2258(1) Å, β = 90.613(1)°, V = 13049.4(3) Å^3, Z = 4, D_c = 1.203 g cm^{-3}, 63 151 measured, 22 564 independent reflections (R_{int} = 0.0681), 1222 refined parameters, R_1[$I > 2\sigma(I)$] = 0.0855, R_1 (all data) = 0.1436. Some of the hmpa donors and Bu^t groups in **2** are disordered and have been refined utilizing split positions and a set of restraints. CCDC 182/1005.

1 K. Ruhlandt-Senge, U. Englich, M. O. Senge and S. Chadwick, *Inorg. Chem.*, 1996, **35**, 5820.

2 D. E. Gindelberger and J. Arnold, *Inorg. Chem.*, 1994, **33**, 6293.

3 S. T. Chadwick, U. Englich, B. Noll and K. Ruhlandt-Senge, *Inorg. Chem.*, in press.

4 K. Ruhlandt-Senge, K. Davis, S. Dalal, U. Englich and M. O. Senge, *Inorg. Chem.*, 1995, **34**, 2587.

5 A. P. Purdy, A. D. Berry and C. F. George, *Inorg. Chem.*, 1997, **36**, 3370.

6 D. Barr, A. T. Brooker, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith and D. Wright, *J. Chem. Soc., Chem. Commun.*, 1989, 893; J. H. Burns and R. M. Kessler, *Inorg. Chem.*, 1987, **26**, 1370.

7 A. L. Rheingold, C. B. White and B. S. Haggerty, *Acta Crystallogr., Sect. C*, 1993, **49**, 808; J. A. T. Norman and G. P. Pez, *J. Chem. Soc., Chem. Commun.*, 1991, 971.

8 P. Mikulcik, P. R. Raithby, R. Snaith and D. S. Wright, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 428; F. A. Banbury, M. G. Davidson, A. Martin, P. R. Raithby, R. Snaith, R. K. L. Verhorevoot and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 1152.

9 K. Henke and D. A. Atwood, *Inorg. Chem.*, 1998, **37**, 224.

10 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

11 J. M. A. Baas, H. van Bekkum, M. A. Hofnagel and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 1110; W. Rundel, *Chem. Ber.*, 1968, **101**, 2956.

12 (*a*) H. Hope, *Prog. Inorg. Chem.*, 1994, **41**, 1; (*b*) G. M. Sheldrick, SHELXTL-PLUS, Program Package for Structure Solution and Refinement, Siemens, Madison, Wisconsin, 1996; (*c*) G. M. Sheldrick, SADABS, Program for Absorption Correction Using Area Detector Data, University of Göttingen, Germany, 1996.

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