Synthesis and characterization of the first discrete potassium thiolates displaying three different coordination spheres at potassium in one molecule

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Potassium hydride reacts with $HSC_6H_2Pr^i_3$-2,4,6 (HSR) in THF or thf–tmen (tmen = *N,N,N′,N′*-tetramethylethylenediamine) to afford the first discrete, hexameric potassium thiolates $[\{K(SR)\}_2\{K(thf)(SR)\}_2\{K(thf)_2(SR)\}_2]$ 3 and $[\{K(SR)\}_2\{K(thf)(SR)\}_2\{K(tmen)(SR)\}_2]$, 4·thf, exhibiting an unusual box-shaped structure with three different coordination spheres for the three independent potassium atoms.

Sterically demanding thiolate ligands have been attracting increased attention due to their ability to stabilize low coordination numbers in metal thiolate complexes.[1] Examples of structurally characterized lithium thiolato species include the monomeric $Li(thf)_3(SC_6H_2Bu^t_3$-2,4,6),[2] $Li(thf)_3(SC_6H_2Ph_3$-2,4,6)[3] and $Li(pmdta)(SC_6H_2Pr^i_3$-2,4,6) (pmdta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine),[4] the dimeric compounds $[Li_2(thf)_4\{SCH(SiMe_3)_2\}_2]$ and $[Li_2(thf)_{3.5}\{SC(SiMe_3)_3\}_2]$[5] and the trimeric $[Li(thf)(SC_6H_2Bu^t_3\text{-}2,4,6)]_3$.[4] Heavier alkali metal organochalcogenides have recently gained importance due to their enhanced reactivity, allowing the preparation of a large variety of metal organochalcogenides, some of them not available by employment of the corresponding lithium derivatives.[6] The focus of our interest was the preparation and characterization of alkaline-earth metal thiolates and selenolates; sterically demanding potassium organochalcogenides were successfully used for the preparation of discrete species, such as the magnesium and strontium derivatives $[Mg(SC_6H_2Ph_3\text{-}2,4,6)_2]_2$,[7] $Mg(EC_6H_2Bu^t_3\text{-}2,4,6)_2L_2$ (L = Et_2O, thf),[7] and $Sr(EC_6H_2Bu^t_3\text{-}2,4,6)_2(thf)_4$ (E = S, Se).[6]

The crystal structures of several sodium and potassium thiolates have been reported, but almost exclusively, the thiolate containing ligands are bi- or multi-dentate. Up to now, only two heavier alkali metal monodentate thiolato derivatives are well characterized, both containing the ligand $C_6H_2(CF_3)_3$-2,4,6;[8] $[Na\{C_6H_2(CF_3)_3\text{-}2,4,6\}(thf)_2]_\infty$ **1** and $[K\{SC_6H_2(CF_3)_3\text{-}2,4,6\}(thf)]_\infty$ **2** exhibit polymeric struc-tures and display strong secondary interactions between the alkali metal and the fluorine atoms within the *ortho*-CF_3 groups.

The use of multidentate donors such as crown ethers allows the formation of monomeric species, such as the recently characterized thiolates K(18-crown-6)(thf)($SCPh_3$), K(dibenzo-18-crown-6)(thf)($SC_6H_2Pr^i_3$-2,4,6) and K(dibenzo-18-crown-6)($SC_6H_2Bu^t_3$-2,4,6).[9] Remarkable are also the tellurolates $Na(tmen)_2(TeC_6H_2Me_3$-2,4,6) (tmen = *N,N,N′,N′*-tetramethylethylenediamine) and K(18-crown-6)$TeC_6H_2Bu^t_3$-2,4,6.[10]

In this paper the first discrete, hexameric potassium thiolates exhibiting three different coordination spheres at K are presented.

$[\{K(SR)\}_2\{K(thf)(SR)\}_2\{K(thf)_2(SR)\}_2]$ **3** and $[\{K(SR)\}_2\{K(thf)(SR)\}_2\{K(tmen)(SR)\}_2]$, **4**·thf, were synthesized by the reaction of $HSC_6H_2Pr^i_3$-2,4,6(HSR) with 1 equiv. of KH in thf (**3**) or thf–tmen (**4**).† X-Ray crystallographic data‡ show **3** (Fig. 1) and **4**·thf to be hexamers with no close interactions between neighbouring units. The molecules can be described as an array of trimers of dimers; three dimeric units form a box-shaped molecule. The two outer $\{K_2S_2\}$ dimers, comprised of alternating K and S atoms, are related by a centre of symmetry located in the central $\{K_2S_2\}$ unit. Each S atom is attached to one R group, one of the K atoms in the outer dimers is bound to one thf molecule while the other carries either two thf molecules (**3**) or a tmen bi-chelate (**4**). The geometry of the potassium atoms located in the outer $\{K_2S_2\}$ rings is defined by their position as 'corner' atoms of the box-shaped molecule. Each of the outer potassium atoms is bound to three thiolato-S atoms with angles close to 90°. However, a comparison between the two outer K atoms shows no distinct differences in their framework geometry, which does not explain the different coordination numbers observed for the two potassium centres. The potassium atoms located in the central $\{K_2S_2\}$ ring are bound exclusively to four thiolato S atoms, with angles of 90 and 180° respectively. This unusual 'see-saw' geometry resembles the arrangement observed in SF_4. However, a comparison of bonding situation and geometry of **3** and **4** with SF_4 is not valid, since the K–S contacts in **3** and **4** are predominantly ionic, and the bonding in SF_4 covalent.

An examination of possible metal–hydrogen contacts revealed no strong agostic interactions, the closest contacts between potassium and hydrogen atoms are 3.00 Å [H(23B)] (**3**) and 2.86 Å [H(43A)] (**4**). The K–S bond distances in **3** and **4** are in good accord with those observed in **2**.[8] The average K(1)–S bond lengths are 3.28 (**3**) and 3.26 Å (**4**); the corresponding K(2)–S contacts are 3.10 (**3**) and 3.19 Å (**4**), with the shorter values observed at the four-coordinate potassium centre. The K(3)–S distances in the central $\{K_2S_2\}$ dimer are 3.16 (**3**) and 3.18 Å (**4**). K···K contacts in both molecules range from 4.2 to 4.7 Å, which is slightly below the sum of radii for metallic potassium (2.35 Å),[11] but can be explained by the lower coordination number of the potassium atoms in **3** and **4**,

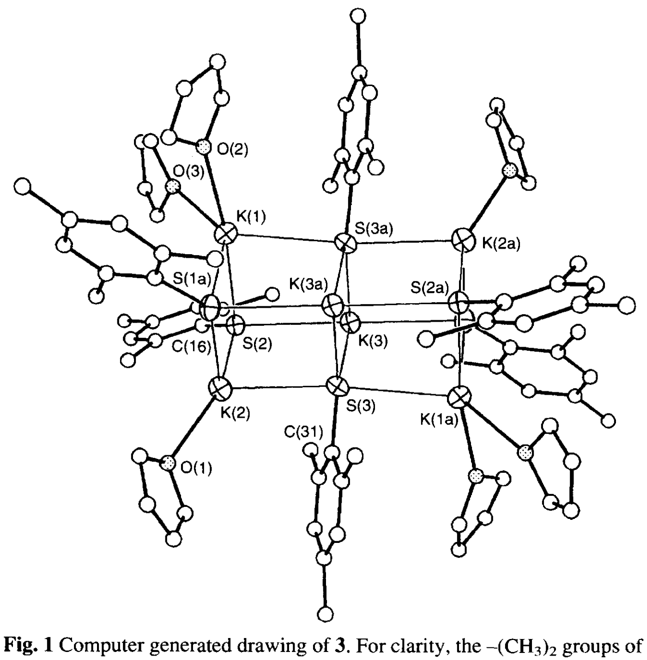

Fig. 1 Computer generated drawing of **3**. For clarity, the $-(CH_3)_2$ groups of the SR ligands and all hydrogen atoms have been omitted.

relative to metallic potassium; therefore the K···K interactions are not significant. The S–C distances are unremarkable with average values of 1.79 (**3**) and 1.77 Å (**4**).

^{1}H NMR studies of **3** show equivalent signals for all thf and R groups, indicating a rapid exchange of thf groups and a structural change of **3** in solution. A possible solution structure could be a hexagonal-prismatic arrangement, available from the solid-state structure by bond elongation between potassium and sulfur in the central $\{K_2S_2\}$ dimer and migration of one thf molecule to the central potassium atoms. Variable-temperature ^{1}H NMR studies show dynamic behaviour for the R groups, consisting of a splitting of the *ortho* isopropyl signals at −50 °C in a 2 : 1 pattern. However, no separation of the thf signals is observed, indicating a very low energy barrier for the exchange of thf groups.

Compounds **3** and **4** are the first examples of discrete potassium thiolates stabilized only by steric bulk of the thiolates and coordinating ligands. No secondary Lewis acid–base interactions are needed to preclude polymerization. Both compounds display unusual box-shaped or 'triple-decker' stack structures with three distinctly different environments for the three independent potassium centres. This geometrical arrangement has not been observed for akali metal organochalcogenides, but related structural patterns have been observed for the mixed-metal amides $Li_{4-x}Na_{2+x}(N{=}CPhBu^t)_6$,[12] $Li_4Na_2\{N{=}C(NMe_2)_2\}_6$[13] and the sodium enolate $Li_2Na_4\{OC({=}CH_2)Bu^t\}_6{\cdot}(NHPr^i)_2$.[14]

Our investigations are continuing and further details of these systems will be subject of forthcoming publications.

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Footnotes

† All reactions were performed under anaerobic and anhydrous conditions. HSR was prepared by published procedure;[15] tmen was refluxed over CaH_2 and distilled. KH, commercially available as a 35 mass% suspension in mineral oil, was washed twice with hexane (30 ml) to remove the mineral oil and then dried *in vacuo*.

3: To a suspension of 0.147 g KH (3.67 mmol) in a mixture of 20 ml hexane and 5 ml thf was added a solution of 0.87 g HSR (3.68 mmol) dissolved in 20 ml hexane slowly *via* cannula. The reaction started immediately, recognizable by the formation of hydrogen gas. The mixture was stirred for 2 h, the resulting slightly cloudy, colourless solution was then filtered over a Celite padded filter frit and stored at −30 °C for 24 h to yield 0.91 g (72%) of clear colourless needles suitable for X-ray diffraction studies. Mp > 350 °C. IR (Nujol) ν(cm^{-1}): 1300.0s, 1238.4m, 1221.2w, 1160.5w, 1129.7, 1102.0w, 1054.8s, 932.5w, 897.7w, 871.8m, 754.7w, 722.3w, 635.9w, 521.9w. ^{1}H NMR (300 MHz, C_6D_6, isotropic shifts at 25 °C): δ, 7.13 (s, 12 H, *m*-H), 4.16 (spt., 12 H, *o*-CH), 3.42 (m, 24 H, thf), 2.91 (spt., 6H, *p*-CH), 1.45 (d, 72 H, *o*-Pr^i), 1.35 (d, 36 H, *p*-Pr^i).

4: A solution of 0.47 g HSR (2 mmol) in 20 ml of thf was added dropwise to a suspension of 0.080 g of KH (2 mmol) in 10 ml of thf. The colourless, slightly cloudy reaction mixture was stirred for 1 h after which 5 ml of tmen were added *via* syringe. This mixture was stirred for 18 h after which it was filtered through a Celite padded filter frit. The volume of the solution was reduced to 10 ml. After storage at −30 °C for several days, 0.38 g (55% yield) of colourless crystals were obtained. Mp > 350 °C. IR (Nujol) ν(cm^{-1}): 1545.7w, 1300.4m, 1238w, 1160.0m, 1130m, 1101.8m, 1056.0s, 917.0m, 872.0m, 754.1m, 722.3s, 635.9w, 521.6m, 481.9w. ^{1}H NMR (300 MHz, C_6D_6, isotropic shifts at 25 °C): δ, 7.35 (s, 12 H, *m*-H), 4.07 (spt, 12 H, *o*-CH), 3.55 (m, 8 H, thf), 2.93 (spt, 6 H, *o*-CH), 2.34 (s, 8 H, tmen), 2.12 (s, 24 H, tmen), 1.57–1.43 (m, 80 H, *o*-Pr^i, thf), 1.41 (d, 36 H, *p*-Pr^i).

‡ *Crystal data*: at 213 K with Mo-Kα radiation (λ = 0.71073 Å), Rigaku AFC5S diffractometer, graphite monochromator, MSC LT device. **3**: M = 2079.7, crystal dimensions: 0.5 × 0.3 × 0.1 mm, μ = 0.354 mm^{-1}, scan range 0 < 2θ < 45°, monoclinic, space group $P2_1/n$, a = 15.071(3), b = 25.301(5), c = 17.866(4) Å, β = 113.01(3)°, U = 6270(3) Å^3, Z = 2, D_c = 1.102 g cm^{-3}, 5283 measured, 4758 independent reflections, 2332 [$I > 2\sigma(I)$] data, 385 refined parameters. Due to a weak data set the phenyl rings were refined as rigid groups. The C_3H_7 groups vibrate considerably as indicated by the large displacement parameters of the carbon atoms; the thf groups were included in the refinement using identical displacement parameters for the carbon atoms; R = 0.103, wR_2 = 0.110. **4**: M = 2095.8, crystal dimensions: 0.2 × 0.15 × 0.6 mm, μ = 0.336 mm^{-1}, scan range 0 < 2θ < 50°, monoclinic, space group $P2_1/c$, a = 18.324(4), b = 14.323(3), c = 26.300(5) Å, β = 106.39(3)°, U = 6622(3) Å^3, Z = 2, D_c = 1.051 g cm^{-3}, 12836 measured, 11617 independent reflections, 4511 [$I > 3\sigma(I)$] data, 588 refined parameters. The structure contains a thf molecule, in which the carbon atoms linked to oxygen are disordered, they were refined using 50% split positions. The C_3H_7 groups vibrate considerably as indicated by the large displacement parameters of the carbon atoms. The additional thf solvent molecule, present in each asymmetric unit is disordered, and was refined using 50% split positions for two different molecule orientations. The positions for the oxygen atoms could not be located, therefore all atoms were refined as carbons. R = 0.105, wR_2 = 0.123. Due to weakly diffracting crystals in compounds **3** and **4**, the number of observed data was limited, resulting in relatively high R-values, however, standard deviations for structural parameters are not above standard ranges. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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