

Comparison of the X-Ray Crystal Structures of the Sodium and Potassium 2,4,6-Tris(trifluoromethyl)phenoxides (RO⁻) and 2,4,6-Tris(trifluoromethyl)benzenethiolates (RS⁻); [Na(OR)(thf)₂]₂, [K(OR)(thf)₂(μ-thf)]₂, [Na(SR)(thf)₂·0.25thf]_x and [K(SR)(thf)]_x (thf = tetrahydrofuran)

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[Na(OR)(thf)₂]₂ **1**, [K(OR)(thf)₂(μ-thf)]₂ **2**, [Na(SR)(thf)₂·0.25thf]_x **3** and [K(SR)(thf)]_x **4** were formed by the reaction of the appropriate combinations of 2,4,6-tris(trifluoromethyl)phenol (ROH) or 2,4,6-tris(trifluoromethyl)benzenethiol (RSH) with NaH or KH; compounds **1–4** have been characterised by NMR spectroscopy and single crystal X-ray structure analysis, both phenoxides being dimeric whereas two distinct polymeric structural types are observed for the thiolates.

Sterically and/or electronically demanding ligands can stabilise compounds with unusual oxidation states, unusual coordination numbers and other unusual structural features. There is currently much interest in ligands containing the 1,3,5-tris(trifluoromethyl)benzene (RH) fragment.^{1–6} We have now extended our studies to 2,4,6-tris(trifluoromethyl)phenol (ROH) and 2,4,6-tris(trifluoromethyl)benzenethiol (RSH) and report here the preparation and crystal structures of their sodium and potassium derivatives. The Cambridge Structural Database⁷ reveals that surprisingly few structures of sodium or potassium alkoxides, aryloxides or siloxides have been reported, and, to our knowledge, no monodentate sodium or potassium thiolate salts have been structurally characterised.⁸

[Na(OR)(thf)₂]₂ **1** and [K(OR)(thf)₂(μ-thf)]₂ **2** were formed by reactions of NaH and KH, respectively, with ROH in thf. In each case suitable crystals for X-ray structural analysis were

obtained by recrystallisation from thf. NaSR and KSR can be synthesised by the reaction of RSH with stoichiometric amounts of NaH or KH in thf or with NaN(SiMe₃)₂ or KN(SiMe₃)₂ in toluene.⁹ Huge rod-like crystals of [Na(SR)(thf)₂·0.25thf]_x **3** formed on cooling the filtered thf reaction solution. Block-like crystals of [K(SR)(thf)]_x **4** were crystallised from a THF–hexane (10 : 90) solution. The crystals of **3** and **4** melt rapidly at room temperature; however, by cooling the microscope slide with dry ice and using an inert mounting oil we were able to isolate and mount suitable crystals.¹⁰ These were transferred immediately to the low-temperature gas stream of the diffractometer. The crystals were stable under these conditions and their structures have been determined.†

The structures of **1** and **2** are shown in Figs. 1 and 2, respectively. The most striking feature is the bridging thf ligands found in **2**. Bridging thf has only been observed in two

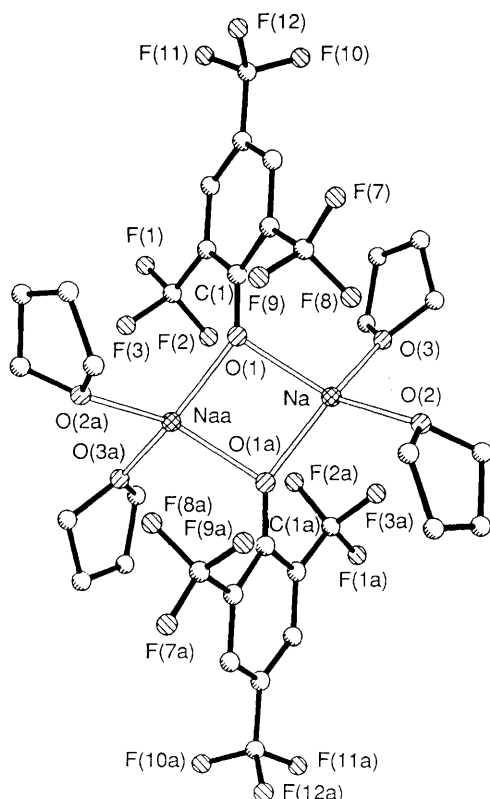


Fig. 1 Perspective view of [Na(OR)(thf)₂]₂ **1**; selected interatomic distances (Å) and angles (°): Na–O(1) 2.296(7), Na–F(8) 2.664(7), Na–O(2) 2.313(6), Na–O(3) 2.306(6), Na–O(1a) 2.231(6), Na(a)–O(1) 2.231(6), O(1)–C(1) 1.289(12), O(1)–Na–O(2) 136.5(2), O(1)–Na–O(3) 100.4(3), O(2)–Na–O(3) 99.3(2), O(1)–Na–O(1a) 85.0(3), O(2)–Na–O(1a) 103.5(3), O(3)–Na–O(1a) 140.1(2), Na–O(1)–C(1) 121.6(3), Na–O(1)–Na(a) 94.6(3), C(1)–O(1)–Na(a) 140.8(4)

† *Crystal data for 1*: C₃₄H₃₆F₁₈Na₂O₆, colourless, crystal dimensions 0.2 × 0.3 × 0.4 mm, monoclinic, *a* = 29.524(6), *b* = 8.720(2), *c* = 21.059(6) Å, β = 131.06(1)°, *V* = 4088(2) Å³, space group *C2/c*, *Z* = 4, *F*(000) = 1888, 3771 reflections collected with 8 < 2θ < 47° at 153 K; of these 3008 were unique and the 1618 which had *F* > 3σ(*F*) were used in the structural analysis. The refinement converged with *R* = 7.95% and *R_w* = 8.26%.

Crystal data for 2: C₄₂H₅₂F₁₈K₂O₈, colourless, crystal dimensions 0.3 × 0.3 × 0.4 mm, triclinic, *a* = 9.835(4), *b* = 10.548(4), *c* = 12.897(5) Å, α = 78.54(3)°, β = 74.81(2)°, γ = 83.03(3)°, *V* = 1262(1) Å³, space group *P1̄*, *Z* = 1, *F*(000) = 568, 3626 reflections collected with 8 < 2θ < 45° at 153 K; of these 3282 were unique and the 2721 which had *F* > 3σ(*F*) were used in the structural analysis. The refinement converged with *R* = 5.92% and *R_w* = 7.94%.

Crystal data for 3: C₃₄H₃₆F₁₈Na₂O₄S₂C₂H₄O_{0.5}, colourless, crystal dimensions 0.4 × 0.5 × 0.7 mm, triclinic, *a* = 9.200(2), *b* = 10.354(2), *c* = 23.541(4) Å, α = 99.36(2)°, β = 95.34(1)°, γ = 91.59(1)°, *V* = 2200.9(7) Å³, space group *P1̄*, *Z* = 2, *F*(000) = 1016, 8433 reflections collected with 8 < 2θ < 50° at 153 K; of these 7693 were unique and the 5803 which had *F* > 3σ(*F*) were used in the structural analysis. The refinement converged with *R* = 6.32% and *R_w* = 7.49%.

Crystal data for 4: C₁₃H₁₀F₉KOS, colourless, crystal dimensions 0.4 × 0.6 × 0.7 mm, monoclinic *C*-lattice, *a* = 25.199(4), *b* = 4.851(1), *c* = 27.239(4) Å, β = 93.78(1)°, *V* = 3322.4(9) Å³, space group *C2/c*, *Z* = 8, *F*(000) = 1696, 7454 reflections collected with 8 < 2θ < 50° at 153 K; of these 3799 were unique and the 3184 which had *F* > 3σ(*F*) were used in the structural analysis. The refinement converged with *R* = 6.31% and *R_w* = 7.35%.

The data were collected on a Siemens-Stoe AED diffractometer using Mo-Kα radiation. 2θ–ω scans, with online profile fitting²¹ and variable scan speeds were employed. Each structure was solved by direct methods (SHELXS-86)²² and refined by full-matrix least-squares techniques (SHELX-76, modified by the author). Rotational disorder of some of the *para*-CF₃ groups was apparent in each structure. This was modelled by the insertion of a second component, and the fluorine atoms 'opposite' each other were constrained to have equal *U_{ij}* values. Atomic coordinates, bond lengths, bond angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

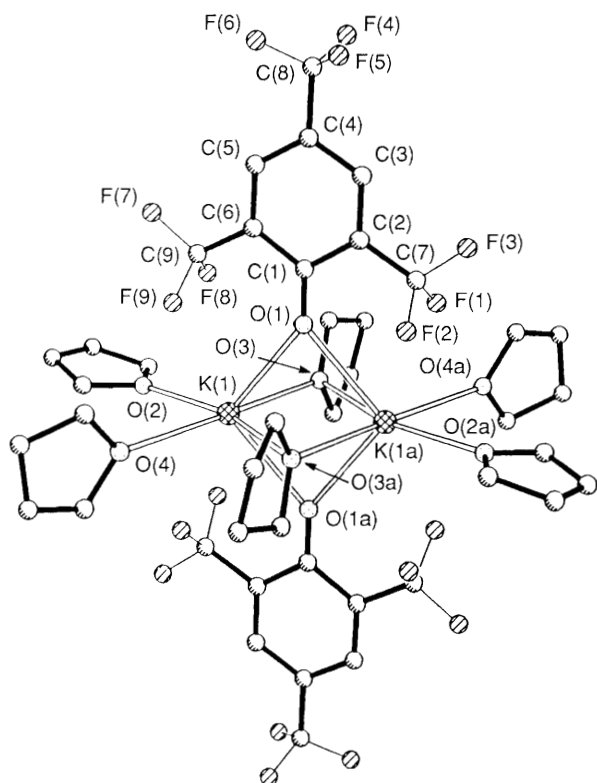


Fig. 2 Perspective view of $[\text{K}(\text{OR})(\text{thf})_2(\mu\text{-thf})]_2$ **2**; selected interatomic distances (Å) and angles ($^\circ$): K(1)–O(1) 2.752(3), K(1)–O(2) 2.753(3), K(1)–O(3) 2.882(4), K(1)–O(3a) 2.888(3), K(1)–O(4) 2.963(4), K(1)–O(1a) 2.833(3), K(1)–F(1a) 2.867(3), K(1)–F(2a) 3.217(3), K(1)–F(8) 3.250(3), K(1)–F(9) 2.980(3), O(1)–C(1) 1.267(4), O(1)–K(1)–O(2) 121.2(1), O(1)–K(1)–O(3) 68.5(1), O(2)–K(1)–O(3) 92.2(1), O(1)–K(1)–O(1a) 102.7(1), O(2)–K(1)–O(1a) 120.4(1), O(3)–K(1)–O(1a) 67.3(1), O(1)–K(1)–O(4) 115.4(1), O(3)–K(1)–O(4) 174.9(1), O(4)–K(1)–O(1a) 113.9(1), O(2)–K(1)–O(4) 82.9(1), O(1)–K(1)–O(3a) 68.2(1), O(3)–K(1)–O(3a) 105.6(1), O(1a)–K(1)–O(3a) 67.3(1), O(2)–K(1)–O(3a) 162.1(1), O(4)–K(1)–O(3a) 79.2(1), K(1)–O(1)–C(1) 142.7(2), K(1)–O(1)–K(1a) 77.3(1), C(1)–O(1)–K(1a) 140.0(2), K(1)–O(3)–K(1a) 74.4(1)

structures, to our knowledge.¹¹ Both **1** and **2** are dimeric; in each case the RO^- group bridges the two metal atoms, forming an M_2O_2 core. Each metal atom is also bound by two terminal thf molecules. In **1** there are two weak Lewis acid–base interactions between the sodium and *ortho*-fluorine atoms [$\text{Na}–\text{F}(3a)$ 2.720(7), $\text{Na}–\text{F}(8)$ 2.664(7) Å].^{5,6,12} The RO^- aromatic ring is tilted at 57.9° to the nearly planar Na_2O_2 ring. In contrast to the weak interactions in the sodium salt, two strong Lewis acid–base interactions occur between potassium and fluorine in **2** [K(1)–F(1a) 2.867(3), K(1)–F(9) 2.980(3) Å], bringing the coordination number of potassium to eight. The angle between the OR^- aromatic ring and the planar $\text{K}_2\text{O}(3)\text{O}(3a)$ ring is 88.1° .

In contrast to these dimeric phenolates two distinct polymeric structural types are observed for the thiolates **3** and **4** (Figs. 3 and 4). In **3** alternating six-coordinate sodium atoms and doubly bridging sulphur atoms form the backbone of a zigzag 'chain' polymer.¹³ The asymmetric unit contains two sodium atoms, two thiolate and four thf ligands, and a half occupancy, uncoordinated thf molecule. The polymer is built up by translation of this unit. Two sulphur donors from the thiolates and two oxygen donors from the thf molecules are coordinated to each sodium atom. In addition there are two strong Lewis acid–base interactions between sodium and fluorine atoms within *ortho*- CF_3 groups [$\text{Na}(1)–\text{F}(3)$ 2.434(3), $\text{Na}(1)–\text{F}(12a)$ 2.436(3), $\text{Na}(2)–\text{F}(18)$ 2.486(3), $\text{Na}(2)–\text{F}(9)$ 2.571(3) Å]. The diversity of bonding to sodium leads to a distorted octahedral coordination geometry.

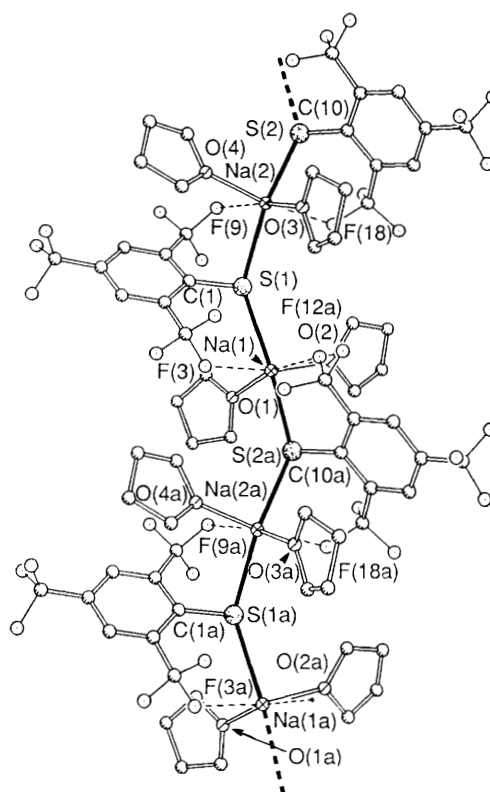


Fig. 3 Perspective view of $[\text{Na}(\text{SR})(\text{thf})_2]_x$ **3**, lattice thf omitted for clarity; selected interatomic distances (Å) and angles ($^\circ$): Na(1)–S(1) 2.838(2), Na(1)–O(1) 2.263(4), Na(1)–O(2) 2.277(3), Na(1)–S(2a) 2.833(2), Na(2)–S(2) 2.835(2), Na(2)–O(3) 2.312(4), Na(2)–O(4) 2.317(3), Na(2)–S(1) 2.825(2), S(1)–C(1) 1.732(4), S(2)–C(10) 1.732(4), S(1)–Na(1)–O(1) 98.4(1), S(1)–Na(1)–O(2) 96.5(1), O(1)–Na(1)–O(2) 96.5(1), S(1)–Na(1)–S(2a) 160.4(1), O(1)–Na(1)–S(2a) 93.0(1), O(2)–Na(1)–S(2a) 97.3(1), S(1)–Na(2)–S(2) 140.4(1), S(1)–Na(2)–O(3) 102.3(1), S(2)–Na(2)–O(3) 106.5(1), S(1)–Na(2)–O(4) 104.4(1), S(2)–Na(2)–O(4) 100.6(1), O(3)–Na(2)–O(4) 93.0(1), Na(1)–S(1)–C(1) 114.1(1), Na(1)–S(1)–Na(2) 141.8(1), C(1)–S(1)–Na(2) 97.5(1), Na(2)–S(2)–C(10) 95.9(1), Na(2)–S(2)–Na(1b) 144.2(1), C(10)–S(2)–Na(1b) 113.2(1)

Each sulphur atom in **4** is triply bridging and a 'ladder' polymer results.^{13a} Each potassium atom is coordinated by three sulphurs and one oxygen of a thf molecule. Several potassium–fluorine interactions are also observed [K(1)–F(7a) 3.087(2), K(1)–F(1) 2.944(2), K(1)–F(2) 3.094(2), K(1)–F(9b) 2.920(2) Å], and a very distorted geometry at potassium results.

In **3** and **4** two sets of aromatic rings can be identified. Within each set, the aromatic rings are stacked parallel to one another. In **4** the repeat distance (along the M–S–M backbone) is half that observed for **3** and leads to a separation of 4.0 Å between parallel aromatic rings. In comparison **3** has a more open structure with the aromatic rings alternating up and down, and a distance of 6.3 Å between parallel rings. Compound **4** can be thought of as resulting from the joining of two single zigzag chains¹⁴ similar to those found in **3**, but with the aromatic groups lined up with each other rather than alternating up and down along the chain. As the chains come together each potassium atom forms a new KS bond rather than binding a second thf molecule.

The differences between the sodium and potassium structures (**1** vs. **2** and **3** vs. **4**) can be attributed to the differences in the ionic radii (Na^+ 0.95, K^+ 1.33 Å).¹⁵ In **2** the larger potassium cation binds two more thf molecules and forms more interactions with fluorine than does the smaller sodium cation in **1**. The difference between **3** and **4** is more dramatic because the potassium cation coordinates a third RS^- forming a 'ladder' polymer.

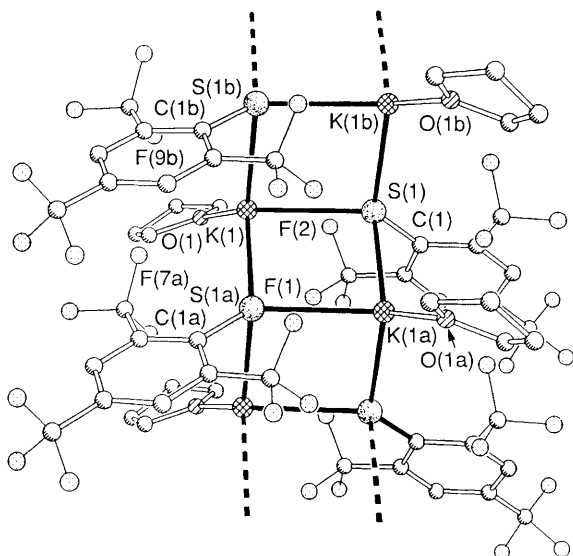


Fig. 4 Perspective view of $[K(SR)(thf)]_x$ **4**; selected interatomic distances (Å) and angles ($^\circ$): K(1)–S(1) 3.159(1), K(1)–O(1) 2.676(3), K(1)–S(1a) 3.166(1), K(1)–S(1b) 3.171(1), S(1)–C(1) 1.729(3), S(1)–K(1)–O(1) 130.9(1), S(1)–K(1)–S(1a) 78.2(1), O(1)–K(1)–S(1a) 124.0(1), O(1)–K(1)–S(1b) 129.0(1), S(1)–K(1)–S(1b) 78.1(1), S(1a)–K(1)–S(1b) 99.9(1), K(1)–S(1)–C(1) 124.4(1), K(1)–S(1)–K(1a) 101.8(1), C(1)–S(1)–K(1a) 88.4(1), K(1b)–S(1)–C(1) 130.2(1), K(1)–S(1)–K(1b) 101.9(1), K(1a)–S(1)–K(1b) 99.9(1)

The increased aggregation observed for the thiolates (compared to the phenolates) probably reflects a reduction in *ortho*-CF₃ crowding about the metal owing to the larger size of the sulphur donor.

Dimers such as **1** and **2** have not been seen for sodium and potassium alkoxy compounds¹⁶ although there are many examples in lithium chemistry.¹⁷ In the lithium dimers the lithium is usually three-coordinate, with only one solvent molecule bound to lithium. As substantial changes in structure and degree of aggregation are often observed as one goes down Group 1,¹⁵ it is interesting that **1** and **2** adopt a dimeric form similar to that of lithium, but with extra solvent molecules bound to satisfy the increased coordination number requirements of the larger cations.

Compounds **3** and **4** are the first structurally characterised sodium and potassium salts of a monodentate thiolate.⁸ Interestingly, the closely related lithium thiolate, $[Li(thf)_3(SC_6H_2Bu^t-2,4,6)]$, is monomeric with three coordinated thf molecules.¹⁸ Dimeric¹⁹ and polymeric^{13a} structures have been observed for less hindered lithium thiolates.

Sodium and potassium interactions with fluorine substituted ligands are uncommon so these structures are valuable examples of this phenomenon.¹² In each compound, despite these fluorine interactions, the ¹⁹F NMR spectrum shows only two fluorine signals, even at low temperatures.‡

‡ NMR data in $[^2H_8]thf$ (standards: C₆F₆ for ¹⁹F, SiMe₄ for ¹H; room temperature unless specified): **1**, ¹⁹F at $-100^\circ C$ δ +102.7 (*p*-CF₃) and +98.1 (*o*-CF₃); ¹H δ 7.5 (s, C₆H₂), 3.6 (br., OCH₂) and 1.7 (br., OCH₂CH₂), ratio 1:4:4. **2**, ¹⁹F at $-100^\circ C$ δ +107.9 (*p*-CF₃) and +103.3 (*o*-CF₃); ¹H δ 7.6 (s, C₆H₂), 3.6 (m, OCH₂) and 1.7 (m, OCH₂CH₂). **3**, ¹⁹F δ +102.1 (*p*-CF₃) and +99.9 (*o*-CF₃); ¹H δ 7.5 (s, C₆H₂), 3.6 (m, OCH₂) and 1.7 (m, OCH₂CH₂), ratio 1:4:4. **4**, ¹⁹F δ +102.1 (*p*-CF₃) and +100.0 (*o*-CF₃); ¹H at $-80^\circ C$ δ 7.6 (s, C₆H₂), 3.6 (br., OCH₂) and 1.7 (br., OCH₂CH₂), ratio 1:2:2.

The synthesis of other unusual compounds is possible employing **1–4** as starting materials.²⁰

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