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## ■ Alkali Metal Compounds

# The Alkali Metal Salts of Methyl Xanthic Acid

Phil Liebing,*[a] Marten Schmeide,[a] Marcel Kühling,[a] and Juliane Witzorke[a]

**Abstract:** Methyl xanthates of the type M(SSC-OMe) (M = Li–Cs) are readily formed when carbon disulfide is reacted with the corresponding alkali metal hydroxides in methanol exposed to air, or with the alkali metal methoxides in dry methanol or THF under exclusion of air. The reactions are easily monitored by $^{13}C$ NMR spectroscopy. The Na, K, Rb, and Cs salt could be isolated in high yields, while the Li salt decomposed upon attempted isolation. All compounds are readily complexed by crown ethers and form isolable 1:1 adducts, including the elusive Li salt. All products were studied by NMR ($^1H$, $^{13}C$, and alkali metal nuclei) and IR spectroscopy, and most of them where structurally characterized by single-crystal X-ray diffraction. Li(SSC-OMe)(12c4) (12c4 = [12]crown-4) and Cs(SSC-OMe)(18c6) (18c6 = [18]crown-6) represent the first structurally characterized lithium and caesium xanthate complexes, respectively.

## Introduction

Xanthates (= *O*-organyl dithiocarbonates) of the general composition RO-CSS⁻ M⁺ are formally the metal salts of the unstable xanthic acids, RO-CSSH. These long-known compounds are readily formed when alcohols are treated with carbon disulfide in alkaline environment.[1] Particularly important on an industrial scale are sodium and potassium xanthates, e.g. in the production of cellulose-derived polymers (cellophane foil,[2] viscose rayon[3]), as flotation agents for the extraction of ores,[4,5] and as herbicides.[6] They are also important intermediates in the field of organic synthesis, including the Barton-McCombie desoxygenation of alcohols[7] and the Chugaev elimination of water from alcohols.[8] In coordination chemistry, the Na and K salts serve as intermediates in the preparation of other metal xanthates.[1] Xanthate anions are ligands which are well-suited for soft metals, including the late transition metals and heavy p-block metals.[9] Many of these compounds have been structurally characterized, and a CSD search for compounds containing the smallest xanthate anion, MeO-CSS⁻, revealed 83 hits (as at Nov 2019).[10] The most important coordination modes of the xanthate moiety are κ²*S,S*′-chelating, κ*S*-monodentate, and κ*S*:κ*S*′-bridging (Scheme 1). Less frequently observed coordination patterns include π-coordination of the CSS fragment (e.g. with Mo(III)[11]) and highly bridging modes (e.g. with Cu,[12,13] Ag,[14,15] K,[16–19] and Ba[20]). In spite of the great industrial importance of alkali metal xanthates, these compounds are rela-

tively sparingly characterized, and the CSD[10] contains not more than two sodium xanthates and five potassium xanthates. Lithium xanthates are only briefly mentioned in the previous literature[21] and have never been characterized in detail to the best of our knowledge. Regarding the heavy alkali metals, the literature holds one very brief report on the crystal structure of Rb(SSC-OEt),[16] and caesium xanthates seem to be entirely unknown so far. This lack of characterization data motivated us to perform a systematic study on the synthesis, properties and molecular structures of the alkali metal methyl xanthate series, M(SSC-OMe) (M = Li–Cs), in order to observe a representative picture of the chemistry of these important compounds. We report here synthetic protocols for the salts under hydrous and anhydrous conditions, their properties, and the preparation of derived crown ether complexes. All products were characterized by spectroscopic methods (IR, NMR) and in most cases by single-crystal structural analysis.
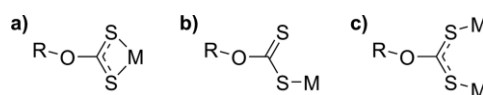


Scheme 1. Frequently observed coordination modes of xanthate ligands in transition metal and main group complexes:[9,10] a) κ²*S,S*′-chelating, b) κ*S*-monodentate, and c) κ*S*:κ*S*′-bridging.
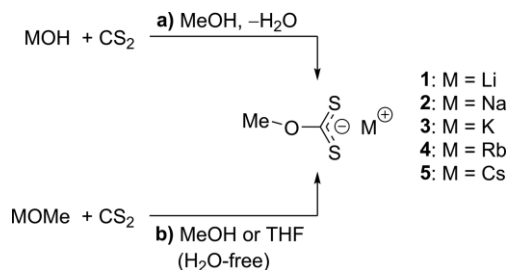
## Results and Discussion

**Preparations and properties.** All alkali metal methyl xanthates M(SSC-OMe) (M = Li–Cs; **1–5**) are readily available by treatment of a methanolic solution of the corresponding metal hydroxide with excess carbon disulfide (Scheme 2, a). The reactions are easily monitored by $^{13}C$ NMR spectroscopy, showing that the xanthate is the only product, as indicated by a signal at ca. 243 ppm. Moreover, the outcome of the reactions did not depend significantly on whether they were performed in wet methanol or in dry methanol under strict exclusion of air (cf. Figure S1). The anhydrous preparations are not restricted to

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000258.

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doi.org/10.1002/ejic.202000258

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Scheme 2. Formation of the alkali metal xanthates **1–5** a) in wet methanol exposed to air and b) under anhydrous conditions.

methanol as a solvent, and solutions of the compounds can be generated by reaction of in-situ prepared alkali metal methoxides with $CS_2$, as it was demonstrated for compounds **1–3** in THF (Scheme 2, b).

The heavier homologs **3–5** could be easily isolated in solvent-free form from the reaction mixtures in high yields, forming air-stable, crystalline solids. The sodium derivative **2** is hygroscopic, but could be isolated in anhydrous form by evaporation of the reaction solution under inert conditions as well. While **3–5** did not show any tendency toward the formation of stable solvates, recrystallization of **2** from THF revealed a crystalline hemisolvate **2·0.5THF**, which was suitable for X-ray structural analysis. The decreasing "solvophilicity" of the alkali metals in going from Li to Cs is well known.[22] The lithium derivative **1**, even though readily obtained in situ similar to **2–5**, always decomposed under $CS_2$ loss upon attempted isolation. The isolated solid contained LiOH (from wet methanol) or LiOMe (from dry methanol or THF).
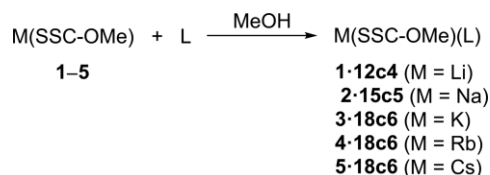
The IR spectra of the isolated compounds **2–4** are very similar and show a number of bands which are typical for xanthate anions,[23,24] of which those at 1180 cm$^{-1}$ ($\nu_{as, COC}$), 1040 cm$^{-1}$ ($\nu_{as, SCS}$), and 470 cm$^{-1}$ ($\delta_{COC}$) are of diagnostic value (cf. Figure S7). Compounds **2–4** are very soluble in methanol and in water, and their $^1H$ and $^{13}C$ NMR spectra in $D_2O$ are virtually identical ($\delta_H$ ca. 3.9 ppm, $\delta_C$ ca. 60 and 234 ppm; cf. Figures S2 and S3). In aqueous solution, small amounts of free methanol were always detected by NMR, indicating that the compounds are in a hydrolysis equilibrium with the respective metal hydroxides (Scheme 3, a). For **2** and **5**, the respective metal nuclei ($^{23}Na$, $^{133}Cs$) gave sharp resonance signals close to 0 ppm, suggesting the presence of fully solvated metal cations in aqueous solution.[25] Solutions of all compounds **1–5** are acid sensitive and absorb $CO_2$ upon prolonged standing exposed to air. The result is the precipitation of the corresponding hydrogen carbonates
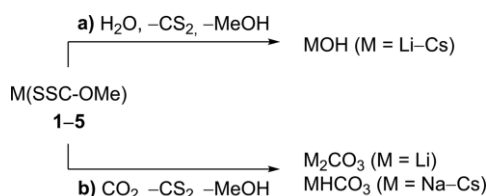
Scheme 3. Typical reactions of the alkali metal xanthates **1–5** in solution: a) hydrolysis, and b) reaction with $CO_2$. For solutions of **2–4** in water, reaction (a) is an equilibrium which is far on the left side, and for **1** the reaction proceeds spontaneously upon attempted isolation.

$MHCO_3$ for **2–5** (M = Na–Cs), or $Li_2CO_3$ for **1** (b). This reaction can be tracked by $^{13}C$ NMR, and methanolic solutions of the compounds treated with dry ice showed signals of $CO_2$ (125 ppm), $HCO_3^-/CO_3^{2-}$ (160 ppm), $CS_2$ (193 ppm), and unreacted xanthate ($\delta$ = 233 ppm; cf. Figure S4). Addition of HCl results in a clean decomposition to $CS_2$ and MeOH.

All compounds **1–5** form well-defined complexes with crown ethers. The so-obtained **1·12c4**, **2·15c5**, **3·18c6**, **4·18c6**, and **5·18c6**, could easily isolated from their methanolic solutions in high yields (Scheme 4). Most remarkable is the high thermal stability of the lithium complex **1·12c4** as compared to the elusive free **1**. This complex melts without decomposition at 78 °C, but different from the heavier alkali metal complexes, shows some tendency towards hydrolysis in aqueous solution. The characteristic xanthate bands in the IR spectra of the complexes appear at similar wavenumbers as for non-complexed **2–4** (ca. 1180, 1040, and 470 cm$^{-1}$), demonstrating that the crown-ether ligand does not exert any strong influence on the bonding situation within the xanthate anion (cf. Figure S8). The $^1H$ and $^{13}C$ NMR shifts of the MeO-CSS$^-$ anion in $D_2O$ resemble those of non-complexed **2–4** (cf. Figures S5 and S6). The NMR shifts of the metal nuclei ($^7Li$, $^{23}Na$, and $^{133}Cs$) are close to 0 ppm. These data confirm the presence of solvent-separated xanthate anions and (crown-ether complexed) metal cations in solution.[25,26]

$$M(SSC\text{-}OMe) + L \xrightarrow{MeOH} M(SSC\text{-}OMe)(L)$$

**1–5**

**1·12c4** (M = Li)
**2·15c5** (M = Na)
**3·18c6** (M = K)
**4·18c6** (M = Rb)
**5·18c6** (M = Cs)

Scheme 4. Preparation of complexes of compounds **1–5** (L = crown ether).

**Crystal structures.** The molecular structures of the title compounds in the crystal are depicted in Figures S9–S16, and experimental details on the structure determinations are summarized in Table S1 in the SI. The crystal structure of **4** is most symmetric having only one equivalent M(SSC-OMe) in the asymmetric unit, while there are two or even three symmetry-independent M(SSC-OMe) units in **2·0.5THF** and **3**, respectively (Figure 1). In order to saturate the alkali metal ions sterically, the xanthate counterions adopt highly bridging coordination modes which are formally mixtures of κ$^2$-S,S'-chelating, κ$^2$S,O-chelating, and κS-monodentate coordinations. In all three compounds, the CSS donor group displays a κ$^2$S,S':κ$^2$S,S'-bridging mode among others, which has been previously observed only in few K,[16–19,27] and in one Pb(II) derivative[28] (Scheme 5, a). However, this rather symmetric dual-chelating mode is switched to a less symmetric variant in two of three formula units in the potassium salt **3**, comprising one K atom in plane with the CSS group and one K atom attached side-on to it (middle and right drawings in Figure 2, b; Scheme 5, b). The bonding situation of the latter two K atoms can be described by π-coordination of the CSS fragment, as it has been previously seen with Mo(III) xanthates[11] and with a related potassium dithiocarbamate.[29] In addition to κ$^2$S,S'-coordination, single- and/or dual-chelation of metal centers is also realized by κ$^2$S,O-modes (Scheme 5, c and d). Contribution of the oxygen donor group in xanthates to

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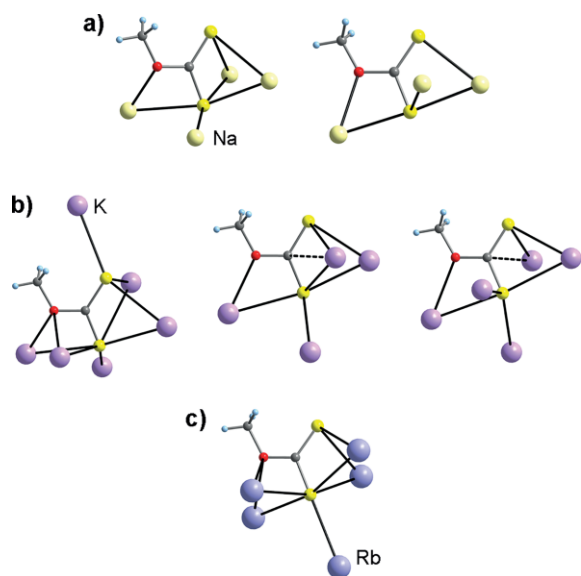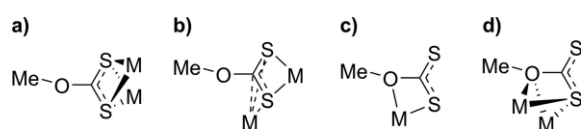European Chemical Societies Publishing

Figure 1. Environment of the MeO-CCS⁻ anions in the crystal structures of a) **2·0.5THF**, b) **3**, and c) **4** (sulfur = yellow, oxygen = red, carbon = grey).



Scheme 5. Repeating xanthate coordination patterns observed in **2·0.5THF**, **3**, and **4**: a) $\kappa^2 S,S':\kappa^2 S,S'$ dual-chelating, b) $\kappa^2 S,S'$-chelating combined with π-coordination, b) $\kappa^2 S,O$-chelating, and d) $\kappa^2 S,O:\kappa^2 S,O$ dual-chelating.

metal coordination is rare and has been reported for few compounds of Na,[30,31] K,[16–19,27,32,33] Ba,[20] Hg(II),[34] and Tl(III).[35] In all three compounds **2·0.5THF**, **3**, and **4**, the metal atoms

adopt irregular coordination spheres, with coordination numbers ranging from seven (**2·0.5THF**) to nine (**4**). In the sodium salt, a μ-bridging THF ligand contributes to steric saturation of the metal atoms. Linkage of the metal atoms and xanthate anions results in two-dimensional polymeric structures for **2·0.5THF** and **4**, and **3** exhibits a three-dimensional structure. The interatomic distances in the compounds resemble the previously observed for related compounds (Table 1).[16,18,19,27,31] The C–S bond lengths within the MeO-CSS⁻ anion are very similar in all three compounds and are in a narrow range of 166–172 pm. These values are between the reference values for C–S single- and double-bonds, respectively, indicating delocalization of the π-electron density over the CSS⁻ fragment.[36] The M–S bond lengths cover much wider ranges, which are within the corresponding ranges observed for other alkali metal compounds with sulfur ligands (ca. 288–326 pm for hepta-coordinated Na, ca. 318–348 pm for octa-coordinated K, and ca. 335–347 pm for octa- and nona-coordinated Rb).[10] The M–O separations are relatively long as compared to database material and fit better with data for neutral R–O-R′ ligating units than for anionic R–O⁻ units (e.g. for octa-coordinated K: ca. 257–323 pm with R–O-R′, 254–298 pm with R–O⁻).[10] Therefore, it can be assumed that the dominant bonding force in the compounds is electrostatic attraction between the M⁺ and CSS⁻ moieties, while the M–O bonding is relatively weak. The caesium salt **5** crystallized as very fine platelets, which did not allow for structure determination.

The crown ether complexes of **1–5** contain well-defined monomeric molecules in their crystal structures, in which the metal atom is situated in the center of the crown-ether ring and sterically saturated by a chelating xanthate ligand, resulting in an irregular six- (Li), seven- (Na), or eight-coordination (K–Cs; Figure 2). In **2·15c5**, **3·18c6**, **4·18c6**, and **5·18c6**, the MeO-CSS⁻
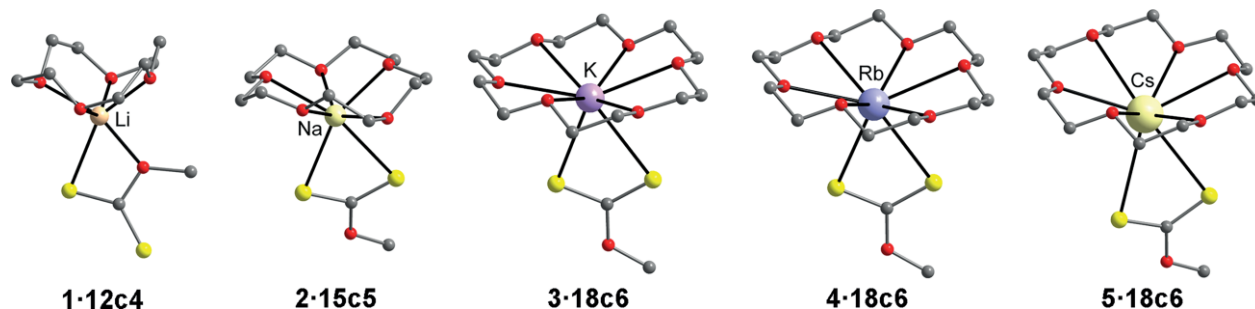


Figure 2. Molecular structures of crown-ether complexes of the alkali metal xanthates **1–5** in the crystal (sulfur = yellow, oxygen = red, carbon = grey). H Atoms omitted for clarity.

Table 1. Selected interatomic distances [pm] in the crystal structures of **2·0.5THF** (M = Na), **3** (M = K), **4** (M = Rb), and related compounds.

| Compound | M–S | M–O | C-S | Ref. |
|---|---|---|---|---|
| Na(SSC-OMe) (**2**)·0.5THF | 288.4(1)–319.1(1) | 245.9(2)–277.1(2) | 166.4(2)–170.2(2) | this work |
| Na(SSC-OCH₂-4-C₅H₄N)·0.5H₂O | 293.06(6)–303.57(6) | 247.61(9)–254.25(9) | 168.1(1)–168.8(1) | [31] |
| [K](SSC-OMe) (**3**) | 316.7(1)–344.8(1) | 272.2(2)–308.0(2) | 167.5(3)–169.6(2) | this work |
| [K](SSC-OEt) | 324(2)–354(2) | 284(3)–286(3) | 166(5)–172(5) | [16] |
| [K](SSC-O*i*Pr) | 319.21(5)–337.53(6) | 317.7(1) | 167.0(2)–170.0(2) | [27] |
| [K](SSC-OCH₂CH₂OMe) | 318.5(2)–342.6(2) | 281.5(2)–316.8(3) | 165.3(2)–167.0(3) | [17] |
| [K](SSC-OCH₂CH₂-CMe₂OMe | 321.7(2)–353.8(2) | 299.0(4) | 167.7(6)–170.3(6) | [19] |
| Rb(SSC-OMe) (**4**) | 337.1(3)–348.3(8) | 313(1)–325(1) | 168(2)–172(1) | this work |

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Table 2. Selected geometric parameters in the crown ether complexes of **1–5** (M = Li–Cs). $d$ denotes the displacement of the M atom from the crown ether's $O_n$ plane, $\alpha$ the coordination angle between the MSX and CSX planes of the xanthate ligand (X = O for **1** and X = S for **2–5**), and $\beta$ the angle between the xanthate's MSX plane and the crown ether's $O_n$ plane (cf. Scheme 6).

| | M–S / pm | M–O / pm | C–S / pm | $d$ / pm | $\alpha$ / deg. | $\beta$ / deg. |
|---|---|---|---|---|---|---|
| Li(SSC-OMe) (**1**)·12c4 | 251(4)–258(4) | 207(4)–217(4) | 164(2)–170(2) | 97(3)–104(4) | 1(1)–11(1) | 84.4(8)–88.5(8) |
| Na(SSC-OMe) (**2**)·15c5 | 284.5(1), 306.6(1) | – | 166.8(2), 169.1(2) | 93.3(1) | 17.0(1) | 85.56(4) |
| [K](SSC-OMe) (**3**)·18c6 | 323.0(2)–343.0(2) | – | 167.2(6)–168.6(6) | 82.1(1)–84.2(1) | 2.6(3)–6.9(2) | 81.58(6)–83.94(4) |
| Rb(SSC-OMe) (**4**)·18c6 | 337.5(1), 344.1(1) | – | 167.9(2), 168.8(3) | 99.02(3) | 13.22(1) | 80.04(2) |
| Cs(SSC-OMe) (**5**)·18c6 | 349.1(2), 353.6(2) | – | 167.6(6), 169.1(6) | 125.44(4) | 18.80(4) | 76.08(6) |

ligand adopts a typical $\kappa^2S,S'$-chelating coordination, while it is an unusual $\kappa^2S,O$ mode in **1·12c4**. In contrast, in the previously reported Na and K xanthate complexes, the molecular units are aggregated through additional S- and O-coordinations alongside with $\kappa^2S,O$-chelation.[30,32,33] As compared to the non-complexed salts, the reduced xanthate coordination does not influence the M–S bond lengths significantly, and the respective values for **2·15c5**, **3·18c6**, and **4·18c6** are close to those in **2·0.5THF**, **3**, and **4**. (Table 2). Similar as for the Na, K, and Rb compounds, the respective M–S separations in **1·12c4** and **5·18c6** are in agreement with the typical ranges observed for other Li–S and Cs–S compounds, respectively (ca. 250–289 pm for hexa-coordinated Li, and around 360 pm for octa-coordinated Cs).[10] The Li–O(xanthate) bond length in **1·12c4** is within the typical range for neutral oxygen donors coordinated to Li. The C–S distances are in a narrow range of 164–170 pm, which is virtually identical with those in non-complexed xanthates and indicates delocalization of the π-electron density over the CSS fragment. Interestingly, this includes the Li complex **1·12c4**, in which only one S atom is coordinated to the metal atom and the formulation of one distinct C–S single bond and one C=S double bond would be reasonable. Regarding the orientation of the xanthate ligand relative to the metal center, the M atom is almost in plane with the respective chelating unit in all five crown ether complexes, as the angle $\alpha$ between the MSX and CSX planes is always <20° (X = O for **1** and X = S for **2–5**; Scheme 6). A similar situation has been observed for Na(SSC-O*i*Pr)(phen)₂ (phen = 1,10-phenanthroline; $\alpha$ = 0.2(2)°), which represents the only previously reported alkali metal complex with a $\kappa^2S,S'$-chelating xanthate ligand.[37]
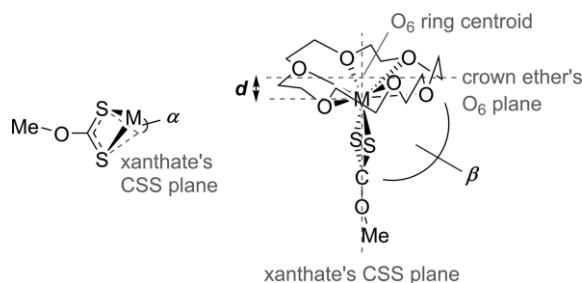


Scheme 6. Definition of the geometric parameters $\alpha$, $\beta$, and $d$, as exemplified at a complex having a $\kappa^2S,S'$-xanthate ligand and a [18]crown-6 ligand.

For the crown ether complexes of **1–5**, the relative arrangement of the two ligands can be quantified by an angle $\beta$, which is defined as the angle between the xanthates's MSX coordination plane and the crown ether's $O_n$ plane. Comparison of the $\beta$ values reveals that the two ligands are arranged almost per-

fectly perpendicular to each other in **1·12c4** and **2·15c5**, and the xanthate moiety is increasingly bent toward the crown ether plane with increasing size of the metal center. Due to the xanthate coordination, the metal atom is significantly displaced from the coordination plane of the macrocyclic ligand. As quantified by the distance $d$ between the M atom and the $O_n$ ring centroid, the displacement depends not only on the metal ionic radius, but also on the crown ether's ring size, and decreases in going from **1·12c4** to **2·15c5** to **3·18c8**. The influence of the increasing metal ion radius is clearly seen for the [18]crown-6 complexes of **3–5**, resulting in an increasing displacement in going from K to Rb to Cs. The observed $d$ values are comparable with those observed in crown ether complexes with bidentate anionic ligands other than xanthate, e.g. Li(S-2-C₅H₄N)(12c4) (99.6(4) pm),[38] Na(S-2-C₅H₄N)(15c5) (102.1(1) pm),[38] K(S-2-C₅H₄N)(18c6) (77.27(6) pm),[38] K(OAc)(18c6) (77.98(4) pm),[39] Rb(SO₃CF₃)(18c6) (95.53(8) pm),[40] and Cs(SO₃CF₃)(18c6) (129.14(6) pm).[40]

## Conclusion

In summarizing the results reported here, we investigated the synthesis, properties and molecular structures of the compounds of the alkali metal methyl xanthate series, M(SSC-OMe) (M = Li–Cs; **1–5**). We provide synthetic protocols for the straightforward in-situ preparation of the compounds under hydrous and anhydrous conditions, which could be potentially useful for various progressive preparations of other metal compounds with MeO-CSS⁻ ligands. The increasing "softness" and therefore enhanced thiophilicity of the alkali metals in going from Li to Cs is reflected in the properties of compounds **1–5**. While the K, Rb, and Cs derivatives **3–5** are easily isolated in solvent-free form and bench-stable, the Na salt **2** is hygroscopic and the Li salt **1** is unstable at normal conditions. However, we showed that the reactivity of **1** and **2** can be significantly decreased by complexation with crown ethers, as **2·15c5** is non-hygroscopic and **1·12c2** is at least bench-stable under exclusion of moisture. Crystal structure elucidation of **2–4** revealed that the xanthate moiety displays different coordination patterns than frequently seen with late transition metals and p-block metals, being governed by highly bridging modes under contribution of the oxygen donor group. This finding can be addressed to the fact that for the alkali metals steric saturation is more important than well-defined coordination polyhedra, and a similar behavior can be expected for the group 2 and group 3 elements of the periodic table. However, increasing steric saturation of the alkali metal atom by other ligands leads

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to a reduction of the xanthate coordination to a "normal" $\kappa^2$-$S,S'$-chelating mode, as it has been demonstrated at the example of crown ether complexes of **2–5**. Herein, the corresponding complex of the lithium xanthate **1** marks again an interesting exception, as the untypical $\kappa^2 S,O$-chelating mode was found to be favored over $\kappa^2 S,S'$-chelation. The methyl xanthates may be representative model compounds for alkali metal xanthates in general, and our findings on synthesis, properties and molecular structures could probably be transferred to derivatives with substituents other than methyl.

## Experimental Section

**General.** Unless otherwise noted, all operations were performed under atmospheric conditions without exclusion of air. All starting materials were obtained from commercial suppliers. Fresh alkali metal hydroxides with minimum carbonate content were used, and the hygroscopic crown ethers were stored under nitrogen in order to avoid accumulation of moisture. For preparations under air- and moisture-free conditions, carbon disulfide was cold-distilled from $P_4O_{10}$ under nitrogen prior to use. *Caution: Carbon disulfide is very volatile (boiling point 46 °C) and extremely flammable (autoignition temperature <100 °C).*[41] *Therefore, all operations with $CS_2$ should be performed in a well-ventilated fume hood in the strict absence of any hot surfaces.* NMR spectra were recorded on a Bruker AVIII 400 machine (5 mm BBO; $^1$H: 400.1 MHz; $^{13}$C: 100.6 MHz; $^7$Li: 155.5 MHz; $^{23}$Na: 105.8 MHz; $^{133}$Cs: 52.5 MHz) at 295(2) K. For isolated products, $D_2O$ was used as solvent. $^1$H and $^{13}$C shifts are referenced to tetramethylsilane ($\delta = 0$ ppm), and the shifts of the alkali metal nuclei to external samples of 9.7 mol/L LiCl, 0.1 mol/L NaCl, or 0.1 mol/L $CsNO_3$ in $D_2O$ ($\delta = 0$ ppm each). $^{13}$C NMR shifts of crude reaction mixtures (non-deuterated solvents) were referenced vs. samples of $CS_2$ in [$D_4$]MeOH ($\delta = 193.8$ ppm) or [$D_8$]THF ($\delta = 193.6$ ppm), respectively. IR spectra were measured on a Bruker Vertex V70 FTIR spectrometer equipped with a diamond ATR unit. Elemental analyses (C, H, S) were performed using a VARIO EL cube and melting/decomposition temperatures were determined in closed, evacuated glass capillaries with a Büchi Melting Point B-540 apparatus. The single-crystal X-ray intensity data were collected on a STOE IPDS 2T diffractometer equipped with a 34cm image-plate detector, using Mo-$K_\alpha$ radiation, at $T = 133(2)$ K. The crystal structures were solved with SHELXT-2018/3[42] and refined by full-matrix least-squares methods on $F^2$ using SHELXL-2018/3,[43] using the Olex 1.2 environment.[44] Numerical absorption correction has been applied to the intensity data.[45] Deposition Numbers 1989135–1989142 (cf. Table S1 in the SI) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Synthesis of Li(SSC-OMe) (1): Procedure A)** Carbon disulfide (3.65 mL, 60 mmol) was added to a solution of lithium hydroxide monohydrate (1.26 g, 30 mmol) in methanol (50 mL) at ambient temperature. After decay of the exothermic reaction, the flask was tightly closed in order to avoid contact to atmospheric carbon dioxide, and the yellow solution was allowed to stir for 1 h. Subsequently, solid material was allowed to settle if necessary, and a $^{13}$C NMR spectrum of the solution was recorded, indicating the formation of **1** ($\delta = 234.1$ ppm; MeO-$C$SSLi) as the only product. All attempts to isolate the product led to decomposition to LiOH besides undefined yellow, malodorous, sulfur-containing material. **Procedure B)** Under an inert atmosphere of nitrogen, a solution of

*n*Butyllithium in hexanes (18.8 mL, 1.6 mol/L, 30 mmol) was carefully added to dry methanol (50 mL), or an equivalent amount of dry methanol (1.21 mL, 30 mmol) in dry THF (50 mL), with vigorous stirring at 0 °C. After decay of the gas formation and exothermic reaction, the mixture was warmed to ambient temperature and carbon disulfide (3.65 mL, 60 mmol) was added. Stirring was continued overnight, during which time the thick white precipitate (MeOLi) has dissolved and a clear yellow solution has formed. A $^{13}$C NMR spectrum of the solution was recorded, indicating the formation of **1** ($\delta = 234.1$ ppm in MeOH, 234.2 ppm in THF; MeOCSSLi) as the only product. All attempts to isolate the product led to decomposition to MeOLi besides undefined yellow, malodorous, sulfur-containing material.

**Synthesis of Na(SSC-OMe) (2): Procedure A)** In a round-bottom Schlenk flask, carbon disulfide (3.65 mL, 60 mmol) was added to a solution of sodium hydroxide (1.20 g, 30 mmol) in methanol (50 mL) at room temperature. After decay of the exothermic reaction, the flask was tightly closed in order to avoid contact to atmospheric carbon dioxide, and the yellow solution was allowed to stir for 1 h. The solution was filtered under an inert atmosphere of nitrogen and subsequently evaporated to dryness in vacuo. The residue was washed with dry diethyl ether several times and dried in vacuo, affording an analytically pure product, which was stored under exclusion of air and moisture. Yield: 3.20 g (82 %). Light yellow, hygroscopic, microcrystalline solid, Dec. 152 °C. A characteristic malodor of the product indicated the presence of small amounts of sulfur-containing decomposition products. Very soluble in water, methanol and THF, soluble in acetone, poorly soluble in diethyl ether. Recrystallization from a minimum amount dry THF under nitrogen at room temperature revealed single crystals of **2·0.5 THF** which were suitable for X-ray structure determination. Anal. calcd. for $C_2H_3NaOS_2$ ($M = 130.15$ g mol$^{-1}$): C 18.46, H 2.32, S 49.26 %; found C 18.43, H 2.38, S 49.16 %. $^1$H NMR: $\delta = 3.89$ (s) ppm. $^{13}$C NMR: $\delta = 60.3$ (s; $CH_3$), 233.6 (s; $CSS$) ppm. $^{23}$Na NMR: $\delta = -0.3$ (s) ppm. IR: $\nu$ 3022(w), 3000(w), 2941(m), 2820(w), 1448(w), 1429(m), 1421(sh), 1240(w), 1184(s), 1160(w), 1107(s), 1096(s), 1042(s br), 1023(sh), 936(s), 581(w), 473(s), 427(w), 335(m), 300(m br), 228(sh) cm$^{-1}$. **Procedure B)** In order to produce an anhydrous solution of **2**, metallic sodium (0.69 g, 30 mmol) was dissolved in dry methanol (50 mL) under an inert atmosphere of nitrogen at 0 °C.* The clear solution was warmed to room temperature, carbon disulfide (3.65 mL, 60 mmol) was added and subsequently stirred for 1 h. $^{13}$C NMR spectroscopy of the solution indicated the formation of **2** ($\delta = 234.1$ ppm; MeO-$C$SSNa) as the only product. *An anhydrous THF solution of **2** could be prepared by evaporating the solution of sodium in methanol to dryness and suspending the MeONa residue in dry THF (50 mL). After addition of carbon disulfide, the mixture was stirred overnight, affording a clear yellow solution of **2** ($^{13}$C NMR: $\delta = 234.0$ ppm; MeO-$C$SSNa).

**Synthesis of M(SSC-OMe) (M = K, Rb, Cs; 3–5): Procedure A)** Carbon disulfide (3.65 mL, 60 mmol) was added to a solution of potassium hydroxide, rubidium hydroxide monohydrate, or caesium hydroxide monohydrate (30 mmol) in methanol (50 mL) at ambient temperature. After decay of the exothermic reaction, the flask was tightly closed in order to avoid contact to atmospheric carbon dioxide, and the yellow solution was allowed to stir overnight. The solution was filtered if necessary, and the solvents evaporated to dryness on a rotary evaporator at 40 °C. The residue was washed with diethyl ether several times and dried in vacuo, affording analytically pure products.

**K(SSC-OMe) (3):** Yield: 3.55 g (81 %). Pale yellow, odorless, air-stable crystalline solid, Dec. 156 °C. Very soluble in water and meth-

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doi.org/10.1002/ejic.202000258

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anol, soluble in THF and acetone, poorly soluble in diethyl ether. Slow evaporation of a methanol solution at room temperature afforded single crystals of **3** suitable for X-ray structure determination. Anal. calcd. for $C_2H_3KOS_2$ ($M$ = 146.26 g mol$^{-1}$): C 16.42, H 2.07, S 43.84 %; found C 16.40, H 2.10, S 43.78 %. $^1$H NMR: $\delta$ = 3.93 (s) ppm. $^{13}$C NMR: $\delta$ = 60.4 (s; $CH_3$), 233.6 (s; $CSS$) ppm. IR: ν 3011(w), 2999(w), 29990(w), 2933(w), 1449(m), 1430(m), 1420(sh), 1186(s), 1155(w), 1103(s), 1087(s), 1043(s br), 1023(sh), 944(m br), 580(w), 473(s), 334(m), 288(m br) cm$^{-1}$.

**Rb(SSC-OMe) (4):** Yield: 4.91 g (85 %). Pale yellow, odorless, airstable crystalline solid, Dec. 170 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether. Slow evaporation of a methanol solution at room temperature afforded single crystals of **4** suitable for X-ray structure determination. Anal. calcd. for $C_2H_3ORbS_2$ ($M$ = 192.63 g mol$^{-1}$): C 12.47, H 1.57, S 33.29 %; found C 12.42, H 1.59, S 33.26 %. $^1$H NMR: $\delta$ = 3.95 (s) ppm. $^{13}$C NMR: $\delta$ = 61.8 (s; $CH_3$), 235.1 (s; $CSS$) ppm. IR: ν 2999(w), 2940(w), 2812(w), 1443(w), 1420(m), 1414(sh), 1240(w), 1178(s), 1112(sh), 1097(m), 1076(s), 1040(s), 1003(sh), 936(m), 833(w), 701(w), 577(m), 468(s), 329(m), 297(m br) cm$^{-1}$.

**Cs(SSC-OMe) (5):** Yield: 5.04 g (70 %). Pale yellow, odorless, airstable crystalline solid, Dec. 160 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether. Anal. calcd. for $C_2H_3CsOS_2$ ($M$ = 240.07 g mol$^{-1}$): C 10.01, H 1.26, S 26.71 %; found C 9.94, H 1.31, S 26.62 %. $^1$H NMR: $\delta$ = 3.88 (s) ppm. $^{13}$C NMR: $\delta$ = 60.3 (s; $CH_3$), 233.6 (s; $CSS$) ppm. $^{133}$Cs NMR: $\delta$ = 2.6 (s) ppm. IR: ν 2992(w), 2936(w), 2810(w), 1443(w), 1417(m), 1391(sh), 1351(w br), 1238(w), 1176(s), 1106(sh), 1095(sh), 1078(s), 1040(s), 1024(sh), 992(sh), 935(m), 830(m), 694(m), 661(w), 576(m), 467(s), 326(m), 288(m br), 250(w br), 243(sh) cm$^{-1}$.

**Synthesis of K(SSC-OMe) (3): Procedure B)** Anhydrous solutions of **3** in methanol or THF were prepared similarly as described for **2**, using potassium hydride (1.20 g, 30 mmol) instead of metallic sodium ($^{13}$C NMR: ($\delta$ = 234.1 ppm in MeOH, 234.1 ppm in THF; MeO$C$SSK).

**Synthesis of 1·12c4:** A solution of compound **1** (10 mmol) in dry methanol (20 mL) was prepared in situ under an inert atmosphere of nitrogen as described above, followed by addition of dry [12]crown-4 (1.62 mL, 10 mmol). Stirring was continued for 30 min and the solution was subsequently evaporated to dryness in vacuo. The rosiny residue was washed with dry diethyl ether (3 × 10 mL) and then dried in vacuo, upon which the product solidified. The product was stored under exclusion of air and moisture. Yield: 2.71 g (93 %). Pale yellow, hygroscopic, crystalline solid, M.p. 78 °C. A characteristic malodor of the product indicated the presence of small amounts of sulfur-containing decomposition products. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether. Single crystals of **1·12c4** suitable for X-ray structure determination were obtained from a concentrated THF solution at 5 °C. Anal. calcd. for $C_{10}H_{19}LiO_5S_2$ ($M$ = 290.32 g mol$^{-1}$): C 41.37, H 6.60, S 22.09 %; found C 41.50, H 6.61, S 22.08 %. $^1$H NMR: $\delta$ = 3.62 (s, 16H; $CH_2$), 3.89 (s, 3H; $CH_3$) ppm. $^{13}$C NMR: $\delta$ = 60.2 (s; $CH_3$), 69.5 (s; $CH_2$), 233.4 (s; $CSS$) ppm. IR: ν 2963(w), 2931(m), 2918(sh), 2874(m), 1491(w), 1474(w), 1448(m), 1440(sh), 1417(w), 1359(m), 1344(sh), 1308(sh), 1284(m), 1258(sh), 1244(m), 1233(sh), 1180(m), 1132(s), 1100(sh), 1083(s), 1067(sh), 1054(sh), 1041(s), 1016(s), 932(sh), 921(s), 858(s), 815(w), 779(w), 565(m), 555(w), 537(w), 507(w), 478(m), 372(s br), 330(s), 307(m br), 287(w), 275(w), 242(sh), 205(sh) cm$^{-1}$.

**Synthesis of 2·15c5, 3·18c6, 4·18c6, and 5·18c6:** The respective crown ether (10 mmol) was added to a solution of the respective xanthate salt **2–5** (10 mmol)* in methanol (30 mL), and the mixture was stirred for 30 min at room temperature. The solution was then reduced in vacuo until the product began to crystallize, and subsequently diethyl ether (100 mL) was added. The precipitate was isolated by vacuum filtration, washed with diethyl ether (3 × 20 mL) and dried in vacuo. *In-situ preparation of **2–5** instead of using the isolated solids led to comparable results.

**2·15c5:** Yield: 2.21 g (63 %). Pale yellow, odorless, air-stable crystalline solid, M.p. 120 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether as well as in chlorinated and non-chlorinated hydrocarbons. Single crystals of **2·15c5** suitable for X-ray structure determination were obtained by layering a concentrated methanol solution with excess diethyl ether within several days at room temperature. Anal. calcd. for $C_{10}H_{23}NaO_6S_2$ ($M$ = 350.42 g mol$^{-1}$): C 41.13, H 6.62, S 18.30 %; found C 41.08, H 6.68, S 18.26 %. $^1$H NMR: $\delta$ = 3.70 (s, 20H; $CH_2$), 4.00 (s, 3H; $CH_3$) ppm. $^{13}$C NMR: $\delta$ = 60.3 (s; $CH_3$), 69.2 (s; $CH_2$), 233.6 (s; $CSS$) ppm. $^{23}$Na NMR: $\delta$ = –1.2 (s) ppm. IR: ν 2991(w), 2971(w), 2961(w), 2928(sh), 2912(m), 2894(w), 2873(m), 2864(sh), 2818(w), 1472(m), 1453(w), 1425(m), 1348(m), 1288(m), 1276(sh), 1252(m), 1239(w), 1229(sh), 1180(m), 1142(w), 1119(sh), 1112(s), 1093(sh), 1084(s), 1071(sh), 1045(s), 1036(s), 952(sh), 946(s), 926(sh), 861(m), 840(w), 829(m), 804(w), 574(w), 553(w), 542(w), 524(m), 473(s), 330(sh), 320(m br), 306(sh), 238(s br), 201(s br) cm$^{-1}$.

**3·18c6:** Yield: 3.65 g (89 %). Pale yellow, odorless, air-stable crystalline solid, Dec. 160 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether as well as in chlorinated and non-chlorinated hydrocarbons. Single crystals of **3·18c8** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for $C_{12}H_{27}KO_7S_2$ ($M$ = 410.58 g mol$^{-1}$): C 40.96, H 6.63, S 15.62 %; found C 40.97, H 6.62, S 15.60 %. $^1$H NMR: $\delta$ = 3.59 (s, 24H; $CH_2$), 3.91 (s, 3H; $CH_3$) ppm. $^{13}$C NMR: $\delta$ = 60.3 (s; $CH_3$), 69.7 (s; $CH_2$), 233.5 (s; $CSS$) ppm. IR: ν 2965(w), 2930(sh), 2901(m), 2966(w), 2926(w), 1472(m), 1455(m), 1436(w), 1428(w), 1370(w), 1350(m), 1285(m), 1251(m), 1236(m), 1182(m), 1135(w), 1096(s), 1082(sh), 1044(s), 1009(w), 960(s), 835(s), 531(w), 474(m), 255(m br), 228(m br) cm$^{-1}$.

**4·18c6:** Yield: 3.56 g (78 %). Pale yellow, odorless, air-stable crystalline solid, Dec. 180 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether as well as in chlorinated and non-chlorinated hydrocarbons. Single crystals of **4·18c8** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for $C_{12}H_{27}O_7RbS_2$ ($M$ = 456.95 g mol$^{-1}$): C 36.80, H 5.96, S 14.03 %; found C 36.72, H 6.08, S 13.95 %. $^1$H NMR: $\delta$ = 3.60 (s, 24H; $CH_2$), 3.91 (s, 3H; $CH_3$) ppm. $^{13}$C NMR: $\delta$ = 60.3 (s; $CH_3$), 69.5 (s; $CH_2$), 233.5 (s; $CSS$) ppm. IR: ν 2966(w), 2930(w), 2902(m), 2869(w), 2856(sh), 2822(w), 1474(m), 1455(m), 1430(w), 1349(m), 1285(m), 1249(m), 1233(w), 1182(m), 1135(m), 1094(s), 1077(sh), 1041(s), 1017(sh), 955(s), 834(s), 527(w br), 473(m), 295(w), 254(m), 230(m) cm$^{-1}$.

**5·18c6:** Yield: 3.38 g (67 %). Pale yellow, odorless, air-stable crystalline solid, M.p. 144 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether as well as in chlorinated and non-chlorinated hydrocarbons. Single crystals of **5·18c8** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for $C_{12}H_{27}CsO_7S_2$ ($M$ = 504.39 g mol$^{-1}$): C 33.34, H 5.40, S 12.71 %; found C 33.29, H 5.50, S 12.67 %. $^1$H NMR: $\delta$ = 3.56 (s, 24H; $CH_2$), 3.87 (s, 3H; $CH_3$) ppm. $^{13}$C NMR: $\delta$ = 60.4 (s; $CH_3$), 61.6 (s; $CH_2$), 235.7 (s; $CSS$) ppm. $^{133}$Cs NMR: $\delta$ = 4.0 (s) ppm. IR: ν 2969(w),

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doi.org/10.1002/ejic.202000258

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2931(w), 2900(m), 2877(w), 2863(sh), 2851(sh), 2819(w), 1475(m), 1454(m), 1430(w), 1348(m), 1283(m), 1247(m), 1233(w), 1182(m), 1132(m), 1093(s), 1041(s), 1017(sh), 953(s), 940(sh), 925(sh), 864(w), 831(s), 523(w), 475(m), 296(w br), 247(m br), 230(sh) $cm^{-1}$.

**Reaction with $CO_2$:** In contact with atmospheric $CO_2$, solutions of **1** and **2** decomposed within several hours under precipitation of $Li_2CO_3$ or $NaHCO_3$, respectively. For **3–5**, this reaction proceeded significantly slower. However, samples of **3–5**, which were isolated from solutions that were exposed to air for a prolonged period of time, were always contaminated with significant amounts of $MHCO_3$ (M = K, Rb, Cs). In a representative series of test reactions, excess dry ice was added to solutions of **1**, **2**, or **3** in methanol. $^{13}C$ NMR spectroscopy indicated immediate formation of carbonate ($\delta$ = 161.2 ppm), together with gradual decrease of the MeO-$CSS^-$ signal intensity.

## Acknowledgments

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