



EurJIC

European Journal of Inorganic Chemistry

 **Chemistry
Europe**

European Chemical
Societies Publishing

Accepted Article

Title: The Alkali Metal Salts of Methyl Xanthic Acid

Authors: Phil Liebing, Marten Schmeide, Marcel Kühling, and Juliane Witzorke

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.202000258

Link to VoR: <https://doi.org/10.1002/ejic.202000258>

WILEY-VCH

FULL PAPER

The Alkali Metal Salts of Methyl Xanthic Acid

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

[a] Dr. P. Liebing, M. Schmeide, M. Kühling, J. Witzorke
 Chemisches Institut der Otto-von-Guericke-Universität Magdeburg
 Universitätsplatz 2, 39106 Magdeburg (Germany)
 E-mail: phil.liebing@ovgu.de; URL: <http://www.ich.ovgu.de/ich/en/Institute.html>

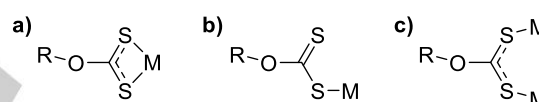
Supporting information for this article is given via a link at the end of the document.

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 ¹³C 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, ¹³C, and alkali metal nuclei) and IR spectroscopy, and most of them were 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 κ²S,S'-chelating, κS-monodentate, and κS:κS'-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 relatively sparingly characterized, and the CSD^[10] contains not more than two sodium xanthates and five potassium xanthates. Lithium xanthates are

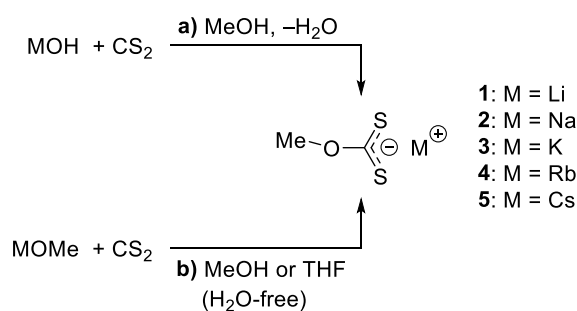
only briefly mentioned in the previous literature^[21] and have never been characterized in detail to the best of our knowledge. Regarding the heavy alkali metals, the literature holds one very brief report on the crystal structure of Rb(SSC-OEt),^[16] and caesium xanthates seem to be entirely unknown 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 herein 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) κ²S,S'-chelating, b) κS-monodentate, and c) κS:κS'-bridging.

Results and Discussion

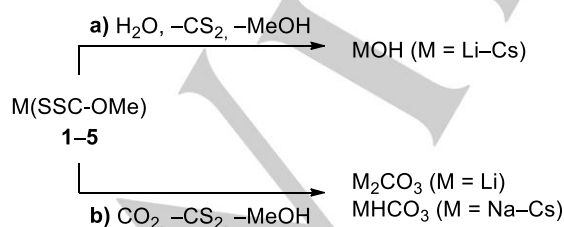
Preparations and properties. All alkali metal methyl xanthates M(SSC-OMe) (M = Li–Cs; **1–5**) are readily available by treatment of a methanolic solution of the corresponding metal hydroxide with excess carbon disulfide (Scheme 2, a). The reactions are easily



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

FULL PAPER

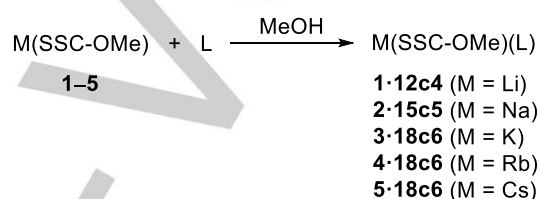
monitored by ^{13}C NMR spectroscopy, showing that the xanthate is the only product, as indicated by a signal at ca. 243 ppm. Moreover, the outcome of the reactions did not depend significantly on whether they were performed in wet methanol or in dry methanol under strict exclusion of air (cf. Figure S1). The anhydrous preparations are not restricted to methanol as a solvent, and solutions of the compounds can be generated by reaction of *in-situ* prepared alkali metal methanollates 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} ($\nu_{\text{as, COC}}$), 1040 cm^{-1} ($\nu_{\text{as, SCS}}$), and 470 cm^{-1} (δ_{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 (δ_{H} ca. 3.9 ppm, δ_{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 MHCO_3 for **2–5** ($\text{M} = \text{Na–Cs}$), 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), $\text{HCO}_3^-/\text{CO}_3^{2-}$ (160 ppm), CS_2 (193 ppm), and unreacted xanthate ($\delta = 233\text{ ppm}$; cf. Figure S4). Addition of HCl results in a clean decomposition to CS_2 and MeOH.



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.

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 be 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 $78\text{ }^\circ\text{C}$, 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]



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

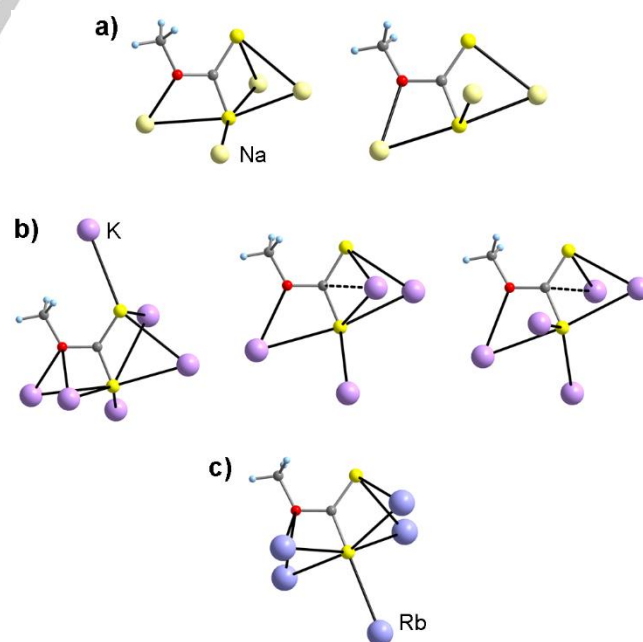


Figure 1. Environment of the MeO-CSS^- anions in the crystal structures of a) **2·0.5THF**, b) **3**, and c) **4** (sulfur = yellow, oxygen = red, carbon = grey).

FULL PAPER

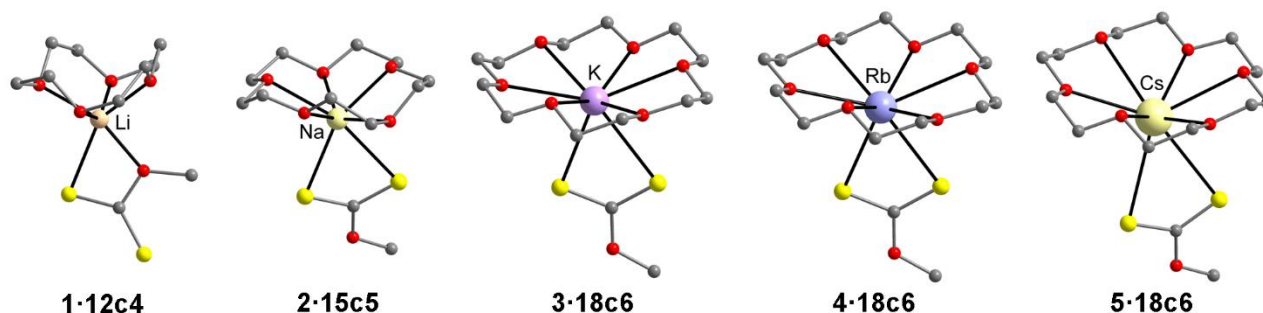


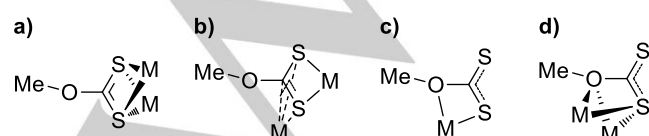
Figure 2. Molecular structures of crown-ether complexes of the alkali metal xanthates **1–5** in the crystal (sulfur = yellow, oxygen = red, carbon = grey). H atoms omitted for clarity.

xanthate counterions adopt highly bridging coordination modes which are formally mixtures of κ^2 -S,S'-chelating, κ^2 S,O-chelating, and κ S-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 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.

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-OCH ₂ -4- C ₅ H ₄ N) ·0.5H ₂ O | 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-OPr) | 319.21(5)– 337.53(6) | 317.7(1) | 167.0(2)– 170.0(2) | [27] |
| K(SSC- OCH ₂ CH ₂ OMe) | 318.5(2)– 342.6(2) | 281.5(2)– 316.8(3) | 165.3(2)– 167.0(3) | [17] |
| K(SSC-OCH ₂ CH ₂ - CMe ₂ OMe) | 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 |



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

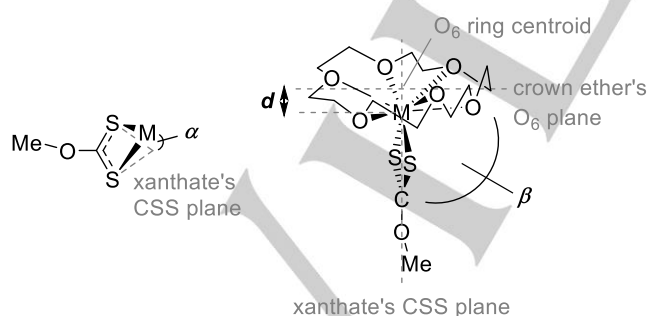
The crown ether complexes of **1–5** contain well-defined monomeric molecules in their crystal structures, in which the metal atom is situated in the center of the crown-ether ring and sterically saturated by a chelating xanthate ligand, resulting in an irregular six- (Li), seven- (Na), or eight-coordination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

FULL PAPER

Table 2. Selected geometric parameters in the crown ether complexes of **1–5** ($M = \text{Li–Cs}$). d denotes the displacement of the M atom from the crown ether's O_n plane, α the coordination angle between the MSX and CSX planes of the xanthate ligand ($X = \text{O}$ for **1** and $X = \text{S}$ for **2–5**), and β 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 | α / deg. | β / 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) |

with $\kappa^2\text{S,O}$ -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 α between the MSX and CSX planes is always $<20^\circ$ ($X = \text{O}$ for **1** and $X = \text{S}$ for **2–5**; Scheme 6). A similar situation has been observed for Na(SSC-O'Pr)(phen)₂ (phen = 1,10-phenanthroline; $\alpha = 0.2(2)^\circ$), which represents the only previously reported alkali metal complex with a $\kappa^2\text{S,S'}$ -chelating xanthate ligand.^[37]



Scheme 6. Definition of the geometric parameters α , β , and d , as exemplified at a complex having a $\kappa^2\text{S,S'}$ -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 β , which is defined as the angle between the xanthate's MSX coordination plane and the crown ether's O_n plane. Comparison of the β values

reveals that the two ligands are arranged almost perfectly perpendicular to each other in **1-12c4** and **2-15c5**, and the xanthate moiety is increasingly bended toward the crown ether plane with rising 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 **3-18c6**. The influence of the rising 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 to 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) ($M = \text{Li–Cs}$; **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

FULL PAPER

table. However, increasing steric saturation of the alkali metal atom by other ligands leads to a reduction of the xanthate coordination to a "normal" $\kappa^2\text{-S,S}'$ -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 $\kappa^2\text{S,O}$ -chelating mode was found to be favored over $\kappa^2\text{S,S}'$ -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; ^1H : 400.1 MHz, ^{13}C : 100.6 MHz; ^7Li : 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. ^1H 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 MeOH-D_4 ($\delta = 193.8$ ppm) or THF-D_8 ($\delta = 193.6$ 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 $\text{Mo-K}\alpha$ 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] CCDC 1989135–1989142 (cf. Table S1 in the SI) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK (Fax: 0044-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

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** (δ 234.1 ppm; MeO-CSSLi) 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 allowed to warm 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** (δ 234.1 ppm in MeOH, 234.2 ppm in THF; MeO-CSSLi) 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 $\text{C}_2\text{H}_3\text{NaOS}_2$ ($M = 130.15$ g mol $^{-1}$): C 18.46, H 2.32, S 49.26 %; found: C 18.43, H 2.38, S 49.16 %. ^1H NMR: δ 3.89 (s) ppm. ^{13}C NMR: δ 60.3 (s; CH_3), 233.6 (s; CSS) ppm. ^{23}Na NMR: δ -0.3 (s) ppm. IR: ν 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 allowed to warm 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** (δ 234.1 ppm; MeO-CSSNa) 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: δ 234.0 ppm; MeO-CSSNa).

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 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 methanol, 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 $\text{C}_2\text{H}_3\text{KOS}_2$ ($M = 146.26$ g mol $^{-1}$): C 16.42, H 2.07, S 43.84 %; found: C 16.40, H 2.10, S 43.78 %. ^1H NMR: δ 3.93 (s) ppm. ^{13}C NMR: δ 60.4 (s; CH_3), 233.6 (s; CSS) ppm. IR: ν 3011(w), 2999(w), 2990(w), 2933(w), 1449(w), 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, air-stable 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 $\text{C}_2\text{H}_3\text{ORbS}_2$ (M

FULL PAPER

= 192.63 g mol⁻¹): C 12.47, H 1.57, S 33.29 %; found: C 12.42, H 1.59, S 33.26 %. ¹H NMR: δ 3.95 (s) ppm. ¹³C NMR: δ 61.8 (s; CH₃), 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, air-stable crystalline solid, Dec. 160 °C. Very soluble in water and methanol, soluble in THF and acetone, poorly soluble in diethyl ether. Anal. calcd. for C₂H₃CsOS₂ (*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 %. ¹H NMR: δ 3.88 (s) ppm. ¹³C NMR: δ 60.3 (s; CH₃), 233.6 (s; CSS) ppm. ¹³³Cs NMR: δ 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 (¹³C NMR: (δ 234.1 ppm in MeOH, 234.1 ppm in THF; MeOCSSK).

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 C₁₀H₁₉LiO₅S₂ (*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 %. ¹H NMR: δ 3.62 (s, 16H; CH₂), 3.89 (s, 3H; CH₃) ppm. ¹³C NMR: δ 60.2 (s; CH₃), 69.5 (s; CH₂), 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 C₁₀H₂₃NaO₆S₂ (*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 %. ¹H NMR: δ 3.70 (s, 20H; CH₂), 4.00 (s, 3H; CH₃) ppm. ¹³C NMR: δ 60.3 (s; CH₃), 69.2 (s; CH₂), 233.6 (s; CSS) ppm. ²³Na NMR: δ -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 **3-18c6** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for C₁₂H₂₇KO₇S₂ (*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 %. ¹H NMR: δ 3.59 (s, 24H; CH₂), 3.91 (s, 3H; CH₃) ppm. ¹³C NMR: δ 60.3 (s; CH₃), 69.7 (s; CH₂), 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(w), 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 **4-18c6** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for C₁₂H₂₇O₇RbS₂ (*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 %. ¹H NMR: δ 3.60 (s, 24H; CH₂), 3.91 (s, 3H; CH₃) ppm. ¹³C NMR: δ 60.3 (s; CH₃), 69.5 (s; CH₂), 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 **5-18c6** suitable for X-ray structure determination were obtained by slow evaporation of a methanol solution at room temperature. Anal. calcd. for C₁₂H₂₇CsO₇S₂ (*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 %. ¹H NMR: δ 3.56 (s, 24H; CH₂), 3.87 (s, 3H; CH₃) ppm. ¹³C NMR: δ 60.4 (s; CH₃), 61.6 (s; CH₂), 235.7 (s; CSS) ppm. ¹³³Cs NMR: δ 4.0 (s) ppm. IR: ν 2969(w), 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 CO₂: In contact with atmospheric CO₂, solutions of **1** and **2** decomposed within several hours under precipitation of Li₂CO₃ or NaHCO₃, 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 MHCO₃ (*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. ¹³C NMR spectroscopy indicated immediate formation of carbonate (δ 161.2 ppm), together with gradual decrease of the MeO-CSS⁻ signal intensity.

Acknowledgements

General financial support by Otto von Guericke Universität Magdeburg is gratefully acknowledged.

Keywords: xanthate • dithiocarbonate • crown ether • alkali metal • crystal structure elucidation

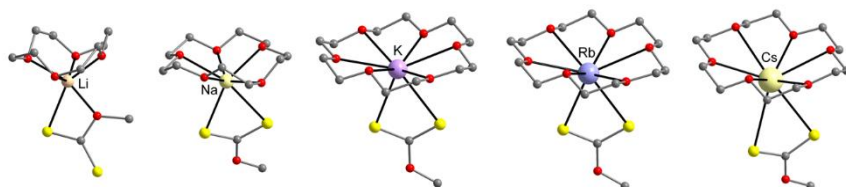
[1] R. J. Magee, *Rev. Anal. Chem.* **1973**, *1*, 335–377.

FULL PAPER

- [2] E. Wellisch, *Sci. Technol. Polym. Film.* **1968**, *1*, 139–172.
- [3] G. B. Kauffman, *J. Chem. Educ.* **1993**, *70*, 887–893.
- [4] C. H. Keller, *US 1554216*, **1925**.
- [5] M. F. Meso, A. A. Adeleke, P. Mendonidis, M. O. Adeoye, *J. Phys. Sci.* **2016**, *27*, 13–21.
- [6] A. H. Roberts, W. Bond, A. Walker, E. R. Page, *Ann. Appl. Biol.* **1981**, *98*, 121–129.
- [7] D. H. R. Barton, S. W. McCombie, *J. Chem. Soc., Perkin Trans. I* **1975**.
- [8] L. Tschugaeff, *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 3332–3335.
- [9] I. Haiduc, *Compr. Coord. Chem. II* **2003**, *1*, 349–376.
- [10] C. R. Groom, F. H. Allen, *Angew. Chem. Int. Ed.* **2014**, *53*, 662–671.
- [11] F. A. Cotton, M. W. Extine, R. H. Niswander, *Inorg. Chem.* **1978**, *17*, 692–696.
- [12] C. Wycliff, D. S. Bharathi, A. G. Samuelson, M. Nethaji, *Polyhedron* **1999**, *18*, 949–958.
- [13] K. Tang, X. Jin, Y. Ling, P. Cui, Y. Tang, *J. Chem. Res.* **2000**, 452.
- [14] X. Jiang, W. Zhang, Y. Zhong, S. Wang, *Collect. Czech. Chem. Commun.* **2002**, *67*, 1629–1634.
- [15] I. Ara, F. El Bahij, M. Lachkar, *Acta Crystallogr.* **2003**, *C59*, m265–m267.
- [16] F. Mazzi, C. Tadini, *Z. Krist.* **1963**, *118*, 378–392.
- [17] N. A. Frolova, T. I. Malinovskii, V. K. Kravtsov, Y. M. Chumakov, S. B. Leonov, *Dokl. Akad. Nauk SSSR* **1991**, 316.
- [18] M. Al-Shakban, P. D. Matthews, G. Deogratias, P. D. McNaughten, J. Raftery, I. Vitorica-Yrezabal, E. B. Mubofu, P. O'Brien, *Inorg. Chem.* **2017**, *56*, 9247–9254.
- [19] M. Al-Shakban, P. D. Matthews, X. L. Zhong, I. Vitorica-Yrezabal, J. Raftery, D. J. Lewis, P. O'Brien, *Dalton Trans.* **2018**, *47*, 5304–5309.
- [20] I. K. Bezougli, A. Bashall, M. Mcpartlin, D. Mingos, Michael, *J. Chem. Soc., Dalt. Trans.* **1998**, 2671–2677.
- [21] K. Yamaguchi, O. Sonoda, Y. Minoura, *J. Polym. Sci. Part A-1 Polym. Chem.* **1972**, *10*, 63–76.
- [22] N. S. Poonia, A. V. Bajaj, *Chem. Rev.* **1979**, *79*, 389–445.
- [23] L. H. Little, G. W. Poling, J. Leja, *Can. J. Chem.* **1961**, *39*, 745–754.
- [24] G. W. Watt, B. J. McCormick, *Spectrochim. Acta* **1965**, *21*, 753–761.
- [25] R. E. Richards, B. A. Yorke, *Mol. Phys.* **1963**, *6*, 289–300.
- [26] J. W. Akitt, A. J. Downs, *Chem. Ind. (London, United Kingdom)*, **1967**, *22*, 199–206.
- [27] M. A. Buntine, M. J. Cox, Y. X. Lim, T. C. Yap, E. R. T. Tiekink, *Zeitschrift für Krist.* **2003**, *218*, 56–61.
- [28] J. M. Clark, G. Kociok-Köhn, N. J. Harnett, M. S. Hill, R. Hill, K. C. Molloy, H. Saponia, D. Stanton, A. Sudlow, *Dalton Trans.* **2011**, *40*, 6893–6900.
- [29] P. Liebing, *Acta Crystallogr.* **2017**, *E73*, 1375–1378.
- [30] M. S. Hill, G. Kociok-Köhn, K. C. Molloy, D. C. Stanton, *Main Gr. Met. Chem.* **2015**, *38*, 61–67.
- [31] R. F. Semeniuc, T. J. Reamer, K. A. Hammock, H. B. Jones, M. D. Smith, K. A. Wheeler, *Inorg. Chim. Acta* **2017**, *475*, 161–171.
- [32] S. P. Nair, T. Mirkovic, G. D. Scholes, A. J. Lough, *Acta Crystallogr.* **2006**, *E62*, m1317–m1319.
- [33] P. D. Beer, A. R. Cowley, J. C. Jeffery, R. L. Paul, W. W. H. Wong, *Polyhedron* **2003**, *22*, 795–801.
- [34] G. Rajput, M. K. Yadav, T. S. Thakur, M. G. B. Drew, N. Singh, *Polyhedron* **2014**, *69*, 225–233.
- [35] J. S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, R. F. Semeniuc, J. Sordo, *J. Mol. Struct.* **2003**, *656*, 225–230.
- [36] F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *Int. Tables Crystallogr.* **2006**, *C*, 790–811.
- [37] F. Li, *Acta Crystallogr.* **2008**, *E64*, m27.
- [38] S. Chadwick, K. Ruhlandt-Senge, *Chem. Eur. J.* **1998**, *4*.
- [39] P. Liebing, A. Zaeni, F. Olbrich, F. T. Edelman, *Acta Crystallogr.* **2016**, *E72*, 1757–1761.
- [40] M. Gjikaj, A. Adam, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2475–2480.
- [41] www.acros.com, Safety Data Sheet of Carbon Disulfide, accessed on Feb 24, 2020.
- [42] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
- [43] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.
- [44] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [45] Stoe & Cie, *X-Area and X-Red*, Darmstadt, Germany, **2002**.

FULL PAPER

Entry for the Table of Contents

Key Topic: Alkali Metal Compounds

The preparation, properties, and molecular structures of Methyl xanthates of the type $M(\text{SSC-OMe})$ ($M = \text{Li-Cs}$) as well as their crown ether complexes are reported. $\text{Li}(\text{SSC-OMe})(12\text{c}4)$ ($12\text{c}4 = [12]\text{crown-4}$) and $\text{Cs}(\text{SSC-OMe})(18\text{c}6)$ ($18\text{c}6 = [18]\text{crown-6}$) represent the first structurally characterized lithium and caesium xanthate complexes, respectively.