The First Alkali Metal Selenothioates: Synthesis and Molecular Structure

Osamu Niyomura, Kiyotaka Sakai, Toshiaki Murai,* Shinzi Kato,* Shigehiro Yamaguchi,[†] and Kohei Tamao[†]
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193
[†]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011*

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The reaction of *S*-2-(trimethylsilyl)ethyl selenothioates with KF, CsF, and RbF gave the corresponding alkali metal selenothioates in moderate to good yields. The use of 18-crown-6 ether gave the products in higher yields. The molecular structure analyses of some of metal salts were carried out.

Carboxylic acids and their alkali metal salts have played important roles in organic chemistry and in chemical industries. Sulfur isologues of carboxylic acid metal salts have also been studied in great depth mainly as key starting materials of thioic and dithioic acid esters.[1] During the course of our studies of heavy congeners of carboxylic acid salts, i.e., chalcogenocarboxylic acid salts,[2–4] we have succeeded in the X-ray structural analysis of dithioic acid alkali metal salts.[2] We also reported that monochalcogenocarboxylic acid *O*-trimethylsilyl esters ($RC(E)OSiMe_3$; E = S, Se, Te) were effectively converted to the corresponding heavy alkali metal salts by reacting with RbF and CsF.[4] Very recently, ammonium selenothioates were successfully synthesized by the reaction of selenothioic acid *S*-2-(trimethylsilyl)ethyl esters with ammonium fluorides.[5] We report herein the synthesis of alkali metal selenothioates and their molecular structures.

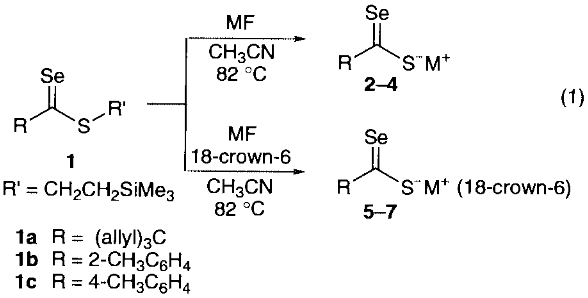

Table 1. Reactions of selenothioic acid *S*-2-(trimethylsilyl)-ethyl esters **1** with KF, RbF, and CsF[a]

Entry	Ester	Product	Product R	Product M	Time /h	Yield[b] /%	^{13}C NMR $\delta_{C=O}$ ppm	^{77}Se NMR ppm
1	**1a**	**2a**	$(allyl)_3C$	K	24	9	277.4	1067.7
2	**1b**	**3b**	$2\text{-}CH_3C_6H_4$	Rb	12	40	259.7	1271.0
3	**1b**	**4b**	$2\text{-}CH_3C_6H_4$	Cs	1.5	77	259.7	1269.7
4	**1a**	**5a**	$(allyl)_3C$	K	3	60	275.2	1097.2
5	**1b**	**5b**	$2\text{-}CH_3C_6H_4$	K	2.5	58	262.9	1257.2
6	**1c**	**5c**	$4\text{-}CH_3C_6H_4$	K	0.16	49	253.6	1197.3
7	**1b**	**6b**	$2\text{-}CH_3C_6H_4$	Rb	0.5	75	262.6	1249.8
8	**1b**	**7b**	$2\text{-}CH_3C_6H_4$	Cs	0.5	68	262.6	1265.2

[a]Selenothioic acid *S*-2-(trimethylsilyl)ethyl esters **1** were treated with 1.3 equiv of KF, RbF, and CsF in CH_3CN (10–15 mL). [b]Isolated yields.

The reaction of *S*-2-(trimethylsilyl)ethyl selenothioates **1** with KF, RbF, and CsF was examined (eq 1). The results are shown in Table 1.[6] The ester **1a** was reacted with KF in CH_3CN at 82 °C for 24 h. The reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts, and the solvent was removed under reduced pressure. To this was added hexane, and the mixture was stirred for 10 min. The resulting precipitates were collected by filtration to give 9% of potassium selenothioate **2a** as green microcrystals along with 77% of the starting ester **1a** (entry 1). A similar reaction of esters **1** with RbF gave the corresponding metal salts in moderate yields (entry 2), and the use of CsF substantially increased the yields of the corresponding salts (entry 3). However, running the reaction with RbF and CsF for a longer time decreased the yields of the salts **3** and **4** probably because of the partial decomposition of the salts formed in situ. The synthesis of the alkali metal salts in better yields was attained by using 18-crown-6 ether (18-c-6) as an additive. For example, the reaction of aromatic selenothioates **1b** and **1c** with KF in the presence of 18-c-6 gave the products in 58 and 49% yields, respectively (entries 5 and 6). This result is in a marked contrast to the reaction in the absence of 18-c-6 where only the starting materials were recovered even after the reaction for 38 h. Similarly, the reaction of esters **1** with RbF and CsF in the presence of 18-c-6 proceeded smoothly in CH_3CN to give the corresponding selenothioic acid alkali metal salts involving one equiv of 18-c-6 as green to brown microcrystals in good yields (entries 7 and 8). The obtained metal salts were relatively stable toward oxygen and water. For example, upon exposure of **6b** to the air for 5 h, appreciable change of **6b** was not observed.

The alkali metal selenothioates **2**–**7** were characterized by ^{1}H, ^{13}C, and ^{77}Se NMR spectra, and UV–visible spectra. In the ^{13}C NMR spectra of aromatic derivatives the signals due to the CSSe group were observed at δ 253–263, and the chemical shifts of aromatic derivatives were shifted to higher fields compared with those of aliphatic salts. In the ^{77}Se NMR spectra the signals due to **2**–**7** were observed in the region of δ 1067–1266, and the chemical shifts of aliphatic salts were observed in the higher fields than those of aromatic ones. In visible spectra, alkali metal salts **2**–**7** showed maximum absorptions at 520–580 nm due to the n–π* transitions of the selenothiocarboxyl group.

The single crystals of **5b**,[7] **6b**, and **7b** were obtained from THF/hexane solution and their structures were analyzed by X-ray crystallography. These metal salts are isostructural, and the selected bond lengths and angles of **5b** are shown in Table 2. The ORTEP drawing of **5b** is shown in Figure 1. The 18-c-6

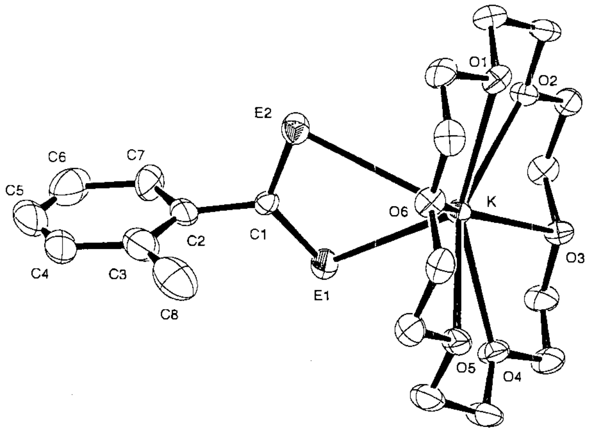

Figure 1. ORTEP Drawing of **5b**. Hydrogen atoms are omitted for clarity. The atoms E1 and E2 represent selenium or sulfur atom.

Table 2. Selected bond lengths (Å), angles (deg) and torsion angles (deg) of **5b**

Bond lengths		Angles		Torsion angles	
K–E1	3.355(2)	E1–K–E2	56.83(3)	K–E1–C1–C2	162.3(7)
K–E2	3.290(2)	E1–C1–E2	126.6(4)	K–E2–C1–C2	161.9(3)
C1–E1	1.776(8)	E1–C1–C2	116.9(6)	E1–C1–C2–C3	102.2(10)
C1–E2	1.764(8)	E2–C1–C2	116.3(6)		
K–O (av)	2.87	K–E1–C1	85.0(2)		

complex **5b** was monomeric, and intermolecular interactions were not observed. Although the sulfur and selenium atoms of the CSSe group in the complexes could not be defined,[8] the bond lengths between the potassium and oxygen atoms were 2.87 Å, and they were within the sum of the ionic radius of the potassium ion (1.44 Å)[9] and the van der Waals radius of the oxygen atom (1.50 Å).[10] Thus, the coordination number around the potassium ion was eight from six oxygen atoms of 18-c-6 and from sulfur and selenium atoms of selenothiocarboxyl group.

In summary, the alkali metal selenothioates were synthesized as stable green to red brown microcrystals for the first time. The X-ray structural analyses of crown ether complexes were also successful. Further studies on the application of the present metal salts are in progress.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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6 Typical experimental procedure for the synthesis of alkali metal selenothioates: In a 20-mL two-necked flask, a solution of *S*-2-(trimethylsilyl)ethyl 2-methylbenzenecarboselenothioate **1b** (0.236 g, 0.748 mmol) in CH_3CN (10 mL) was added to a suspension of KF (0.201 g, 1.323 mmol) and 18-crown-6 ether (0.086 g, 0.322 mmol) in CH_3CN (2 mL) at 20 °C. The mixture was stirred at 82 °C for 2.5 h. The insoluble parts were removed by filtration, and the solvent was evaporated under reduced pressure (20 °C / 0.4 mmHg). To the residue was added hexane (10 mL) at 20 °C, followed by stirring for 10 min. The resulting precipitates were collected by filtration to give 0.313 g (68%) of potassium 2-methylbenzenecarboselenothioate 18-crown-6 ether complex **5b** as brown microcrystals. To a solution of **5b** in THF (7 mL), hexane (5 mL) was added. The mixture was allowed to stand at –20 °C for 1 day. The resulting precipitates were collected by filtration with glass filter (G4) to give 0.033 g (58%) of **5b** as a deep red crystal: mp 110–113 °C dec; IR (KBr) 3854, 3004, 2887, 1654, 1560, 1542, 1508, 1474, 1453, 1434, 1350, 1284, 1270, 1251, 1108, 1044, 1013, 981, 960, 912, 890, 878, 836, 747, 718, 651, 634, 528 cm^{-1}; ^1H NMR (CD_3CN) δ 2.31 (s, 3H, CH_3), 3.56 (s, 24H, 18-crown-6), 6.93–6.99 (m, 4H, Ar); ^{13}C NMR (CD_3CN) δ 19.5, 70.9, 118.2, 123.8, 125.0, 125.4, 128.8, 130.4, 262.9; ^{77}Se NMR (CD_3CN) δ 1257.2; UV/vis (THF) λ_{max} (log ε) 529 (2.41), 384 (3.83), 256 (3.99), 250 (4.00). Anal. Calcd for $C_{20}H_{31}O_6KSSe$: C, 46.41; H, 6.04%. Found: C, 46.41; H, 6.00%.

7 Crystal data of **5b**: $C_{20}H_{31}KO_6SSe$, fw = 517.58, monoclinic, space group $C2/c$, $a = 25.363(1)$ Å, $b = 8.9403(3)$ Å, $c = 22.607(1)$ Å, $\beta = 111.302(2)°$, $V = 4776.3(4)$ Å^3, $Z = 8$, $D_{calc} = 1.439$ g·cm^{-3}, $T = 173$ K, $R = 0.062$, $R_w = 0.093$, 3449 reflections ($I > 3\sigma(I)$).

8 The selenium or sulfur atom appeared at the position [E1] or at the position [E2] shown in Figure 1. The occupancy of the selenium atom is 0.59 in [E1] and 0.41 in [E2], respectively, and the reverse results are obtained for the sulfur atom.

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