

Facile Synthesis and Structure of Heavy Alkali Metal Thiocarboxylates: Structural Comparison with the Selenium and Tellurium Isologues

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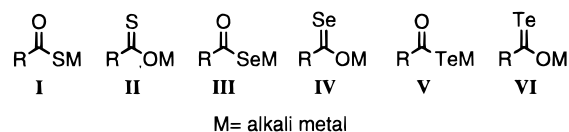
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Potassium, rubidium, and cesium thiocarboxylates were found to be synthesized by the reaction of thiocarboxylic acid or its *O*-trimethylsilyl esters with KF, RbF, and CsF. Tetramethylammonium thiocarboxylates were prepared in good yields by the reaction of sodium thiocarboxylates with tetramethylammonium chloride. The structures of potassium benzene-, 2-methoxybenzene-, and 4-methoxybenzenecarbothioates, rubidium 2-methoxybenzenecarbothioate, tetramethylammonium 2-methoxy- and 2-trifluoromethylbenzenecarbothioates, potassium 2-methoxybenzenecarboxoselenoate, and rubidium 2-methoxybenzenecarboxotelluroate were characterized by X-ray structural analysis. All of these alkali metal salts exhibit a dimeric structure in which the oxygen and/or sulfur atom is associated with the metal of the opposite molecule, while the tetramethylammonium thiocarboxylates are monomeric. In potassium 2-methoxybenzenecarbothioate, the two thiocarboxylate groups chelate to the potassium atoms above and below the plane which involves the thiocarboxylate groups. In potassium 4-methoxybenzenecarbothioate, one thiocarboxylate group chelates to potassium. Without exception, the *o*-methoxy oxygen intermolecularly coordinates to the metal of the opposite molecule. The C–O bond lengths of the thiocarboxylate group are in the range 1.22–1.24 Å, which is slightly longer than those of common thioesters. The C(sp²)–S distances are in the range 1.70–1.72 Å, which is close to that of a typical C–S single bond and suggests that the negative charge may be somewhat localized on the sulfur atom. The interaction number of the metals with oxygen and sulfur atoms was 7 for K and 8 for both Rb and Cs. The dihedral angle between the thiocarboxyl group and the phenyl ring is substantially increased by the introduction of the *o*-methoxy group. In these alkali metal thio-, seleno-, and tellurocarboxylates, only cesium 2-methoxybenzenecarboxotelluroate showed an intermolecular nonbonding interaction between the cesium and the phenyl ring carbons.

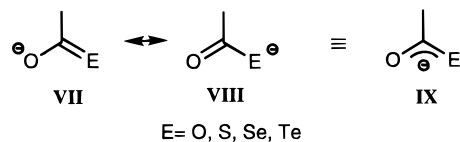
Introduction

There are formally six kinds of alkali metal monochalcogenocarboxylates for each alkali metal in which one of the two oxygen atoms of the carboxyl group has been replaced by a S, Se, or Te atom (Chart 1). In contrast to alkali metal carboxylates, far less is known about the chemistry of these monochalcogeno isologues,¹ although they are considered to be an important class of compounds synthetically, spectroscopically, and theoretically because of a *heteroallylic anion system* (Scheme 1). The study of these salts [especially seleno- (III, IV) and tellurocarboxylates (V, VI)] is frequently complicated by air sensitivity and by contamination of water. The first synthesis of alkali metal thiocarboxylates was reported in 1868 by Engelhardt and Latschinoff, who prepared potassium thiobenzoate by reacting benzoyl chloride with potassium sulfide² or hydrogen sulfide.³

Chart 1



Scheme 1



This method has been shown to be practical for preparing potassium aromatic thiocarboxylates,³ but cannot be applied to heavy rubidium and cesium salts due to the difficulty of preparing and purifying Rb₂S and Cs₂S,⁴ especially with regard to the removal of water and/or solvents. We previously developed a method for preparing water- and solvent-free alkali metal thiocarboxylates by using thiocarboxylic acid with the corresponding metal hydrides or metal acetates.⁵ However, these have not yet been subjected to structural analysis, most likely due to the difficulty of preparing suitable single crystals for X-ray structural analysis. Sodium carboxylates have a structure

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in which the negative charge is delocalized on the carboxyl group⁶ and have been predicted by MO calculation to be highly ionic.⁷ In the case of sulfur analogues, it is unclear whether the negative charge is delocalized on the thiocarboxyl group or localized on the oxygen or sulfur atom. To our knowledge, the first X-ray structural analysis of alkali metal thiocarboxylates was reported in 1976 by Borel and Ledesert, who analyzed potassium⁸ and rubidium thioacetates.⁹ Lithium benzenecarbothioate (PhCOSLi/TMEDA) and cesium thioacetate with crown ether were then reported by Banister et al.¹⁰ and Böttcher et al.,¹¹ respectively. Potassium di- and trithiooxalates have also been documented.¹² Well-characterized examples of molecular compounds with heavy alkali metals are even more scarce. Very recently, we found that aromatic dithiocarboxylic acid potassium, rubidium, and cesium salts exist as dimers in the solid state.¹³ This prompted us to elucidate the structures of the corresponding aromatic thiocarboxylic acid salts. In this paper, we report alternative preparation methods and the structural determination of some heavy alkali metal arenecarbothioates.

Results and Discussion

Synthesis. We previously reported a facile synthesis of *O*-trimethylsilyl thiocarboxylates from the reaction of potassium thiocarboxylates with trimethylsilyl chloride.¹⁴ Recently, *O*-trimethylsilyl seleno- and tellurocarboxylates have been found to react with potassium, rubidium, and cesium fluorides to give the corresponding heavy alkali metal seleno-¹⁵ and tellurocarboxylates in good yields.¹⁶ Using these synthetic conditions, the reactions of *O*-trimethylsilyl thiocarboxylates **1** with rubidium and cesium fluorides were examined. The reactions proceeded smoothly at 25 °C for 5 h in ether to give the corresponding rubidium thiocarboxylates **4** and cesium thiocarboxylates **5** in moderate to good yields, respectively (method A in Scheme 2) (Table 1). The straightforward synthesis using thiocarboxylic acids **2** instead of silyl esters **1** led to analogous yields of the salts (method B). Thiocarboxylic acid and its trimethylsilyl ester appeared to be less reactive toward the metal fluorides than the corresponding dithio acid derivatives.¹³ The reactions with other alkali (LiF, NaF, KF) and alkali earth metal fluorides (MgF₂, CaF₂, SrF₂, BaF₂) and heavy alkali metal

Scheme 2

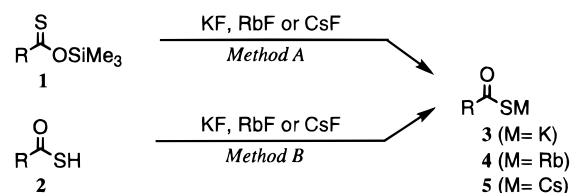


Table 1. Yields of Rubidium Thiocarboxylates **4** and Cesium Thiocarboxylates **5**

no.	RCOSM		method	yield (%)
	R	M		
4a	CH ₃	Rb	A	80
			B	51
4b	<i>t</i> -C ₄ H ₉	Rb	A	100
			B	58
4c	C ₆ H ₅	Rb	A	61
			B	45
4d	2-CH ₃ C ₆ H ₄	Rb	B	63
			A	61
4e	4-CH ₃ C ₆ H ₄	Rb	A	34
			B	34
4f	2-CH ₃ OC ₆ H ₄	Rb	A	44
			B	72
4g	4-CH ₃ OC ₆ H ₄	Rb	A	50
			B	52
4h	4-ClC ₆ H ₄	Rb	A	68
			B	54
5a	CH ₃	Cs	A	71
			B	43
5b	<i>t</i> -C ₄ H ₉	Cs	A	83
			B	75
5c	C ₆ H ₅	Cs	A	67
			B	57
5d	2-CH ₃ C ₆ H ₄	Cs	B	72
			A	71
5e	4-CH ₃ C ₆ H ₄	Cs	A	54
			B	56
5f	2-CH ₃ OC ₆ H ₄	Cs	A	56
			B	56
5g	4-CH ₃ OC ₆ H ₄	Cs	A	71
			B	68
5h	4-ClC ₆ H ₄	Cs	A	74
			B	63

halogenides (RbX and CsX, X = Cl, Br, I) did not occur even under more severe reaction conditions, except that KF led to a 40–50% yield of potassium salts **3**. The formation of **3–5** might be explained by the relatively large affinity of the sulfur atom for these three metals compared with Li, Na, Ca, Sr, and Ba metals and by the low bond energies of KF, RbF, and CsF compared with those of other metal fluorides. For the comparison of structure, the syntheses of quaternary ammonium thiocarboxylates were required. Although the syntheses of primary, secondary, and tertiary ammonium thiocarboxylates have been reported, the quaternary ammonium salts are scarce.¹ Previously we have found that the reaction of rubidium or cesium tellurocarboxylates with tetramethylammonium chloride led to good yields of crystalline tetramethylammonium tellurocarboxylates.^{16b} This method was found applicable to the preparation of tetramethylammonium thiocarboxylates (Scheme 3).

The obtained heavy alkali metal and tetramethylammonium thiocarboxylates are colorless to yellow crystals. They are stable thermally and toward oxygen. Upon exposure to air for 2 weeks no appreciable changes were observed both in the solid state and in solution such as ethanol. They can be stored below 0 °C for over 1 year under oxygen-free conditions. They are soluble in protic and aprotic polar solvents such as methanol and acetonitrile.

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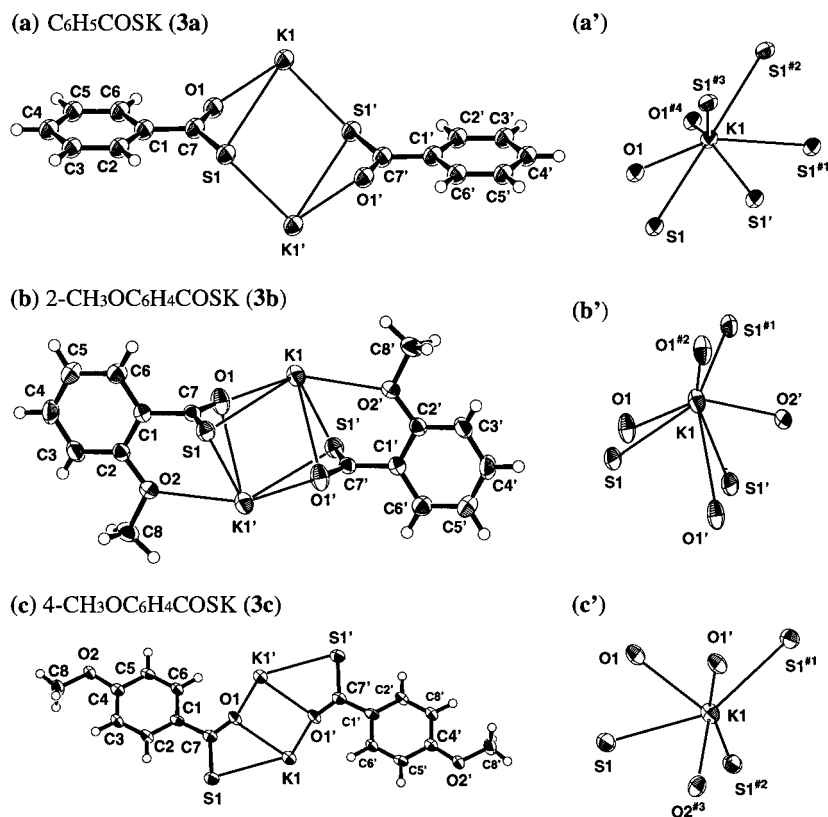
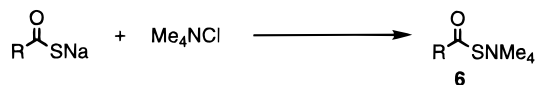


Figure 1. ORTEP drawings and coordination spheres of potassium benzene- (**3a**), 2-methoxybenzene- (**3b**), and 4-methoxybenzenecarbothioates (**3c**). The atoms are drawn with 50% probability ellipsoids.

Scheme 3



	R	%
6a	2-CH ₃ OC ₆ H ₄	79
6b	2-CF ₃ C ₆ H ₄	83

Structure. (a) **Distances.** ORTEP drawings of potassium benzene- (**3a**), 2-methoxybenzene (**3b**), and 4-methoxybenzenecarbothioates (**3c**) are shown in Figure 1 (parts a–c). The final atomic positional parameters are listed in Table 2. Selected bond distances and angles are shown in Tables 3–5. These potassium salts **3** exist fundamentally in the dimer form, in which the O and/or S atom of the chelating thiocarboxylate group is associated with the metal of the opposite molecule, while the ammonium salts **6** (see Figure 3) are monomeric. The average K···K' distances of the potassium salts **3** are over 4.10 Å, indicating no contact between the metals. In **3a**, the C–O and C–S distances of the thiocarboxylate groups are 1.242(3) and 1.715(3) Å, respectively. The C–O bond lengths are slightly longer than those of common esters¹⁷ and thioesters,¹⁸ while the C–S distances are somewhat shorter or close compared with those in common thioesters,^{1f,19,20} suggesting that the negative charge may be localized on the less electronegative sulfur, rather

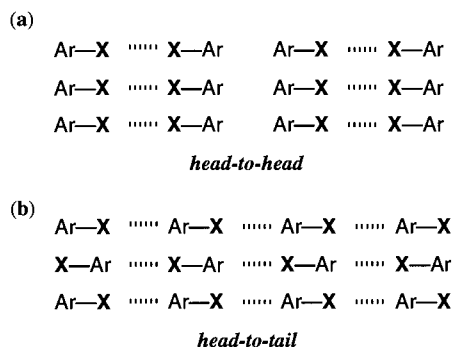


Figure 2. Model of crystal packing (X = COSK).

than on the oxygen atom, although the degree of this localization is likely to be small. The K–S1 and K–O1 distances of the chelating thiocarboxylate group are 3.483(1) and 2.699(4) Å, respectively. The former value is significantly longer than the sum (3.17 Å) of the radii of the potassium and sulfur ions,²¹ while the latter is shorter than the sum (2.85 Å) of the potassium ionic radius and the van der Waals radius of oxygen.²² The intermolecular K1–S1' distance [3.361(1) Å] in the dimer is shorter than the chelating K1–S1 distance, while the intermo-

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Table 2. Crystal Data, and Data Collection and Refinement Parameters for **3a**, **3b**, **3c**, **4f**, **6a**, **6b**, **7** and **8**

	3a	3b	3c	4f	6a	6b	7	8
empirical formula	C ₇ H ₅ KOS	C ₈ H ₇ KO ₂ S	C ₈ H ₇ KO ₂ S	C ₈ H ₇ O ₂ RbS	C ₁₂ H ₁₉ NO ₂ S	C ₁₂ H ₁₆ F ₃ NOS	C ₈ H ₇ KO ₂ Se	C ₈ H ₇ O ₂ RbTe
fw	176.27	206.30	206.30	252.67	241.35	279.32	253.20	348.21
color	colorless	pale yellow	colorless	colorless	colorless	colorless	colorless	red
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
unit-cell dimens								
<i>a</i> (Å)	31.020(8)	8.401(1)	20.858(2)	8.433(3)	11.3264(9)	11.983(2)	8.597(4)	5.546(2)
<i>b</i> (Å)	4.12(1)	7.126(1)	10.880(2)	29.298(3)	13.671(1)	9.064(2)	7.106(4)	7.854(2)
<i>c</i> (Å)	11.907(7)	15.144(1)	7.743(2)	7.395(3)	8.371(1)	12.882(2)	15.104	23.336(8)
β (deg)	97.44(4)	98.866(9)				95.53(1)	100.36(4)	93.18(4)
vol of unit cell (Å ³)	1510(2)	895.8(2)	1757.2(5)	1827.1(8)	1296.1(2)	1392.7(3)	907.7(7)	1014.9(5)
space group	C2/c	P2 ₁ 2 ₁ 2 ₁	Pbca	Pbca	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /a	P2 ₁ /a	P2 ₁ /c
Z value	8	4	8	8	4	4	4	4
<i>D</i> _{calc} (g/cm ³)	1.550	1.530	1.560	1.837	1.237	1.332	1.853	2.279
cryst size (mm)	0.40 × 0.43 × 0.29	0.43 × 0.40 × 0.26	0.17 × 0.17 × 0.11	0.23 × 0.23 × 0.26	0.40 × 0.31 × 0.29	0.31 × 0.29 × 0.17	0.14 × 0.23 × 0.43	0.34 × 0.20 × 0.17
μ (Mo K α) (cm ⁻¹)	9.00	7.79	7.94	55.91	2.36	2.54	45.50	76.46
transm factor for abs correction	0.7238–1.2602			0.8620–1.0921		0.83–1.00	0.8404–1.1623	0.6599–1.5150
temp (°C)	23.0	23.0	–80.0	–80.0	23.0	23.0	–80.0	23.0
$\lambda_{\text{MoK}\alpha}$ (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
$2\theta_{\text{max}}$ (deg)	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.9
no. of measd reflns	2024	2367	2338	2453	1720	3201	2399	2772
no. of unique reflns	1985	2222					2254	2519
<i>R</i> _{int}	0.035	0.021					0.065	0.039
no. of observations (<i>I</i> > 3 σ (<i>I</i>))	1238	1638	1029	1195	1232	1746	1482	1704
no. of variables	111	138	110	109	147	164	138	110
refln/param ratio	11.15	11.87	9.35	10.96	8.38	10.65	10.74	15.49
residuals: <i>R</i> ^a <i>R</i> _w ^b	0.038, 0.038	0.032, 0.041	0.045, 0.048	0.035, 0.036	0.035, 0.036	0.049, 0.058	0.039, 0.041	0.076, 0.167
<i>p</i> value ^b	0.0140	0.0200	0.0200	0.0250	0.0150	0.0300	0.02	0.10
max. and min. of residual electron density (e/Å ³)	0.27, –0.30	0.27, –0.18	0.39, –0.35	0.44, –0.50	0.15, –0.17	0.54, –0.31	0.59, –0.81	2.06, –1.41
goodness of fit indicator	2.86	1.74	1.23	1.11	1.64	1.87	1.83	2.06

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}, \quad w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}.$$

Table 3. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Potassium Benzenecarbothioate (**3a**)^a

Bond Lengths			
O1–C7	1.242(3)	K1–S1	3.483(1)
S1–C7	1.715(3)	K1–S1'	3.361(1)
C1–C7	1.499(4)	K1–S1 ^{#1}	3.422(1)
K1–O1	2.699(2)	K1–S1 ^{#2}	3.377(1)
K1–O1 ^{#4}	2.658(2)	K1–S1 ^{#3}	3.316(1)
K1–O1'	4.22		
Angles			
O1–C7–C1	117.4(3)	K1–O1–C7	108.3(2)
S1–C7–C1	120.4(2)	S1–K1–O1	47.65(4)
S1–C7–O1	122.2(2)	K1–S1–K1'	91.60(3)
K1–S1–C7	69.73(9)	S1–K1–S1'	88.40(3)
Torsion Angles			
O1–C7–C1–C2	174.4(3)	K1–S1–C7–C1	149.3(3)
K1–S1–C7–O1	31.4(2)	K1–S1–K1'–S1'	0.0

^a (') $-x, 1-y, 1-z$. (#1) $-x, -y, 1-z$. (#2) $x, -y, 1/2+z$. (#3) $x, 1-y, 1/2+z$.

lecular K1–O1' distance is very long (4.22 Å), clearly indicating no interaction. The four-membered ring K1, S1, K1', S1' is planar. The two molecules in the dimeric unit are believed to be connected by K \cdots S interaction. In **3b**, however, the chelating K1–S1 and K1–O1 distances are 3.2354(7) and 2.831(2) Å, respectively. The intermolecular K1–S1' and K1–O1' distances in the dimer are 3.4592(8) and 3.091(2) Å, respectively. The latter is close to the sum of the ionic K and O radii. These indicate that the two molecules in the dimer are connected by an interaction of the potassium with the oxygen atom of the opposite molecule, rather than the sulfur. The four-membered ring K1, O1, K1', O1' is planar. The K1–O2' distance is 2.819(2) Å, indicating an interaction of the opposite methoxy oxygen

Table 4. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Potassium 2-Methoxybenzenecarbothioate (**3b**)^a

Bond Lengths			
O1–C7	1.235(3)	K1–O1	2.831(2)
S1–C7	1.708(2)	K1–O1'	3.091(2)
K1–S1	3.2354(7)	K1–O1 ^{#2}	2.715(2)
K1–S1'	3.4592(8)	K1–O2'	2.819(2)
K1–S1 ^{#1}			
Angles			
O1–C7–C1	117.4(2)	S1–K1–O1	50.62(3)
S1–C7–C1	117.6(2)	K1–S1–K1'	81.65(2)
S1–C7–O1	125.0(2)	S1–K1–S1'	98.35(2)
K1–S1–C7	77.72(7)	K1–O1–K1'	95.28(5)
K1–O1–C7	102.3(1)	O1–K1–O1'	84.72(5)
Torsion Angles			
O1–C7–C1–C2	84.0(2)	C3–C2–O2–C8	9.6(3)
K1–S1–C7–C1	112.6(2)	K1–O1–K1'–O1'	0.0
K1–S1–C7–O1	20.8(2)	K1–S1–K1'–S1'	0.0

^a (') $1-x, -y, -z$. (#1) $3/2-x, 1/2+y, -z$. (#2) $3/2-x, -1/2+y, -z$.

with the potassium, and the dimeric structure appears to be enhanced by the coordination of the *o*-methoxy oxygen atom with the potassium ion of the opposite molecule, resulting in the chelation of the two thiocarboxylate groups to the potassium atoms above and below the planes which include the thiocarboxylate groups. The moieties which involve the two metals and the chelating two oxygen and two sulfur atoms in the dimer have distorted bipyramidal configurations. Such a bipyramidal structure is observed for the corresponding selenium isologues (parts a and b in Figure 4) and for the corresponding dithiocarboxylic acid heavy alkali metal salts, such as 4-CH₃C₆H₄-CSSM (M = K, Rb, Cs).¹³ Although **3c** has a space group of

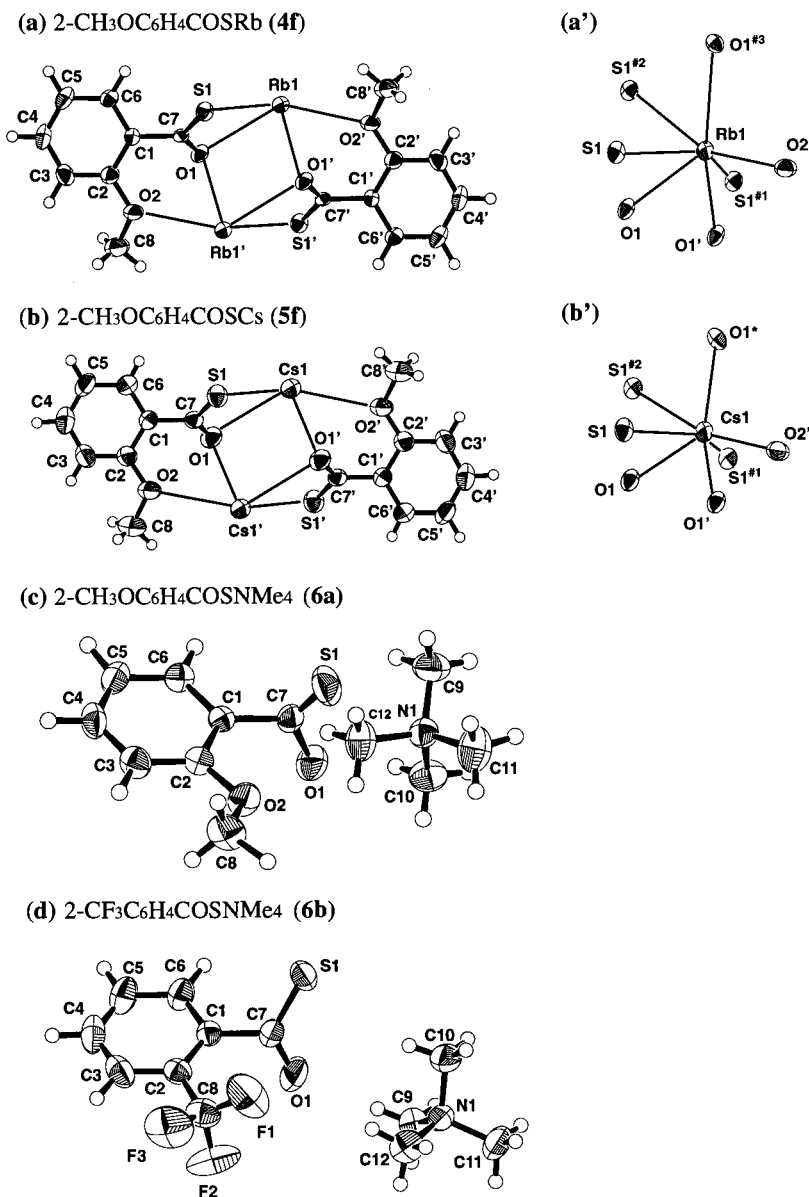


Figure 3. ORTEP drawings and coordination spheres of rubidium 2-methoxybenzenecarbothioate (**4f**), cesium 2-methoxybenzenecarbothioate (**5f**), and tetramethylammonium 2-methoxy- (**6a**) and 2-trifluoromethylbenzenecarbothioates (**6b**). The atoms are drawn with 50% probability ellipsoids.

Table 5. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Potassium 4-Methoxybenzenecarbothioate (**3c**)^a

Bond Lengths			
O1-C7	1.245(5)	K1-S1 ^{#2}	3.251(2)
S1-C7	1.728(5)	K1-O1	2.738(4)
K1-S1	3.267(2)	K1-O1'	2.724(4)
K1-S1 ^{#1}	3.238(2)	K1-O2 ^{#3}	2.796(4)
Angles			
O1-C7-C1	117.7(4)	K1-O1-C7	106.7(3)
S1-C7-C1	119.1(4)	S1-K1-O1	50.90(7)
S1-C7-O1	123.1(4)	K1-O1-K1'	98.2(1)
K1-S1-C7	76.4(2)	O1-K1-O1'	81.8(1)
Torsion Angles			
O1-C7-C1-C2	164.0(4)	K1-S1-C7-O1	15.8(4)
K1-S1-C7-C1	162.0(4)	K1-O1-K1'-O1'	0.0

^a (') 1 - x, -y, 2 - z. (#1) 1 - x, -1/2 + y, 3/2 - z. (#2) 1 - x, -y, 1 - z. (#3) -1/2 + x, y, 3/2 - z.

Pbca, which is different from those (*C2/c* and *P2₁/a*) of **3a** and **3b**, the fundamental unit appears to be a dimer in which the thiocarboxylate oxygen atom is associated with the potassium of the opposite molecule. The four-membered ring K1, O1, K1',

O1' is planar. The thiocarboxylate C=O [1.245(5) Å] and C-S [1.728(5) Å] distances are closer to those of **3a** than to those of **3b**. The *p*-methoxy oxygen coordinates to the potassium of another molecule on the opposite side. The potassium metal of **3c** is surrounded by three oxygen and three sulfur atoms, in which two oxygen atoms and one sulfur atom arise from the chelating thiocarboxyl and methoxy group (Figure 1, part c'). Such coordination of the adjacent *p*-methoxy oxygen appears to be a "head-to-tail" mode (Figure 2, part b), in contrast to that ("head-to-head" mode, Figure 2, part a) in **3a** and **3b**, in which the two thiocarboxyl groups face each other.

The structures of rubidium 2-methoxybenzenecarbothioate (**4f**) and cesium 2-methoxybenzenecarbothioate (**5f**)^{16b} are shown in Figure 3 together with those of tetramethylammonium 2-methoxybenzenecarbothioate (**6a**) and 2-trifluoromethylbenzenecarbothioates (**6b**) (see ref 16b and its supplementary for **5f**). Selected bond lengths and angles of **4f**, **6a**, and **6b** are shown in Tables 6, 7, and 8, respectively. In contrast to **3b**, the space group of **4f** and **5f** is *Pbca*. As expected, the Rb salt **4f** and Cs salt **5f** exhibit similar dimeric structures in which both the

Table 6. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Rubidium 2-Methoxybenzenecarbothioate (**4f**)^a

Bond Lengths			
O1–C7	1.228(6)	Rb1–O1	2.955(3)
S1–C7	1.718(5)	Rb1–O1'	3.070(4)
Rb–S1	3.366(2)	Rb1–O1 ^{#3}	2.868(4)
Rb1–S1 ^{#1}	3.410(2)	Rb1–O2'	3.039(4)
Rb1–S1 ^{#2}	3.572(2)		
Angles			
O1–C7–C1	118.2(4)	Rb1–O1–C7	101.7(3)
S1–C7–C1	116.1(4)	S1–Rb1–O1	48.65(7)
S1–C7–O1	125.7(4)	Rb1–O1–Rb1'	102.2(1)
Rb1–S1–C7	77.2(2)	O1–Rb1–O1'	77.8(1)
Torsion Angles			
O1–C7–C1–C2	52.2(7)	C3–C2–O2–C8	32.8(9)
Rb1–S1–C7–O1	26.1(4)	Rb1–O1–Rb1'–O1'	0.0
Rb1–S1–C7–C1	157.1(4)		

^a (') 2 - x, -y, 1 - z. (#1) 5/2 - x, -y, -1/2 + z. (#2) 1/2 + x, y, 3/2 - z. (#3) 5/2 - x, -y, 1/2 + z.

Table 7. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Tetramethylammonium 2-Methoxybenzenecarbothioate (**6a**)

Bond Lengths			
O1–C7	1.237(4)	N1–C12	1.493(4)
S1–C7	1.704(4)	C1–C7	1.505(4)
N1–C9	1.494(4)	O2–C8	1.420(4)
N1–C10	1.484(4)	C2–O2	1.379(3)
N1–C11	1.484(4)		
Angles			
O1–C7–C1	117.8(3)	C7–C1–C6	121.1(3)
S1–C7–C1	116.7(2)	C1–C2–O2	115.0(3)
S1–C7–O1	125.4(3)	C2–O2–C8	116.5(3)
C7–C1–C2	120.5(3)		
Torsion Angles			
O1–C7–C1–C2	86.5(4)	C3–C2–O2–C8	14.1(4)

Table 8. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Tetramethylammonium 2-Trifluoromethylbenzenecarbothioate (**6b**)

Bond Lengths			
O1–C7	1.225(4)	C1–C7	1.514(4)
S1–C7	1.696(4)	C2–C8	1.499(5)
N1–C9	1.490(4)	C8–F1	1.293(5)
N1–C10	1.493(4)	C8–F2	1.321(5)
N1–C11	1.489(4)	C8–F3	1.334(4)
N1–C12	1.490(4)		
Angles			
O1–C7–C1	116.5(3)	C7–C1–C6	117.6(3)
S1–C7–C1	116.9(2)	C1–C2–C8	122.6(3)
S1–C7–O1	126.6(3)	C3–C2–C8	117.3(3)
C7–C1–C2	124.1(3)		
Torsion Angles			
O1–C7–C1–C2	62.5(4)	C3–C2–C8–F1	146.3(4)

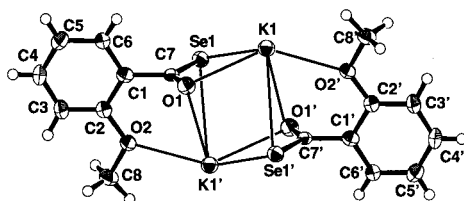
o-methoxy and chelating thiocarboxylate oxygen atoms coordinate to the metal of the opposite molecule, while the ammonium salts are monomeric. The four-membered rings (Rb1, O1, Rb1', O1' and Cs1, O1, Cs1', O1') of both salts are planar. As in **3a** and **3c**, no interaction was observed between the chelating thiocarboxylate sulfur in the dimeric unit and the Rb or Cs metal of the opposite molecule. The Rb and Cs atoms contact four oxygen and three sulfur atoms including one chelating oxygen and sulfur pair (Figure 3, parts a' and b'). The sulfur and oxygen atoms interact with three and four neighboring metals, respectively. The C–O and C–S distances of the COS group are 1.228(6) and 1.718(5) Å for **4f** and 1.231(4) and 1.712(3) Å for **5f**, respectively. These values are almost identical

to those of **3b** and the corresponding tetramethylammonium salt **6a**. The C–O and C–S bond lengths of **6** are 1.237(4) and 1.704(4) Å for **6a** and 1.225(4) Å (C–O) and 1.696(4) Å (C–S) for **6b**, respectively.

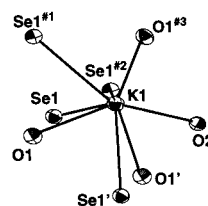
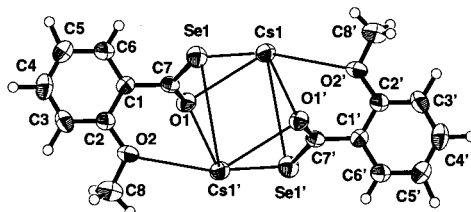
To compare with the selenium and tellurium isologues, potassium 2-methoxybenzenecarboxoselenoate (**7**) and rubidium 2-methoxybenzenecarbotelluroate (**8**) were prepared. Their ORTEP drawings together with those of cesium 2-methoxybenzenecarboxoselenoate (**9**)^{16b} and -telluroate (**10**)^{16b} are shown in Figure 4. The final atomic positional parameters of **7** and **8** are listed in Table 2. Selected bond distances and angles are shown in Tables 9 and 10 (see ref 16b and its supplementary for **9** and **10**). These salts have also been found to consist of similar dimeric units in the solid state. In **7**, two oxygen and two sulfur atoms of the two selenocarboxylate groups contact each metal, while in **8** the tellurocarboxylate oxygen is associated with the metal of the opposite molecule. The Rb...Rb and Cs...Cs distances in the dimeric units are over 4.69 Å for **4f** and **8** and in the range 4.88–5.29 Å for **5f**, **9**, and **10**, respectively, indicating no contact between the metals.²⁰ It is noted that the cesium in **10** interacts with the neighboring phenyl ring, in which the five carbons except for that in the ipso position are relatively close (Figure 4, part d').

(b) Angles. The O–C–S angles of heavy alkali metal arenecarbothioates (ArCOSM, M = K, Rb, Cs) are observed in the range 120–125°, and the ammonium salts show an average of 126.0°; these values are comparable to those for the aliphatic derivatives, CH₃COSK⁸ (124.4°) and CH₃COSRb⁹ (122°). The O–C–Se angles in potassium 2-methoxybenzenecarboxoselenoate (**7**) and cesium 2-methoxybenzenecarboxoselenoate (**9**) and the O–C–Te angles in rubidium 2-methoxybenzenecarbotelluroate (**8**) and cesium 2-methoxybenzenecarbotelluroate (**10**) average 125° and 123°, respectively. The effect of alkali metals on the O–C–E angles (E = S, Se, Te) appears to be minimal, and a general tendency of the magnitude of the angles is not apparent. In the *o*-methoxy derivatives (2-MeOC₆H₄COECs), the C–E–Cs angles are 69–78° and decrease in the order E = S, Se, Te, whereas the O–Cs–E angles are 44–50° and decrease in the order E = S, Se, Te. The effect of alkali metals on the C–E–M angles appears to be minimal. The C–S–M angles in 2-MeOC₆H₄COSM (M = K, Rb, Cs) are the same value of 77°, while the S–M–O angles decrease in the order K, Rb, Cs.

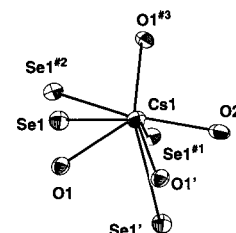
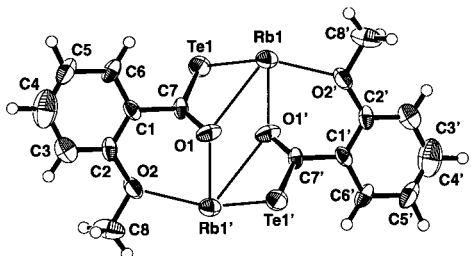
The dihedral angles (θ_1) of the thio-, seleno-, or tellurocarboxyl group and the phenyl ring are shown in Table 11. Since potassium thiobenzoate (**3a**) has the smallest θ_1 value (5.5°), the thiocarboxylate group is nearly coplanar with the benzene ring. The methoxy group in the para position on the phenyl ring results in an increased dihedral angle (17.8°), presumably due to coordination of the methoxy oxygen with the potassium. Compound **3b**, which has an *o*-methoxy group, has a substantially greater angle (84.2°) between the phenyl ring and the thiocarboxylate group. It is noted that a similarly large dihedral angle is observed for the corresponding tetramethylammonium salt **6a**, although that in the 2-trifluoromethyl derivative **6b** is only 63.7°. The rubidium salt **4f** and cesium salt **5f**, which have a methoxy group in the ortho position, show dihedral angles of 56.2° and 58.9°, respectively. Alkali metal cations (K, Rb, Cs) do not show any general tendency regarding the magnitude of their torsion angles. The dihedral angles (θ_1) of the sulfur derivative **5f**, selenium derivative **9** and tellurium derivative **10** increase in the order S, Se, Te. On the other hand, the dihedral angles (θ_2) of the O–M–E plane (C) to the O–C–E plane (B) fall in the range 19–65°.

(a) 2-CH₃OC₆H₄COSeK (7)

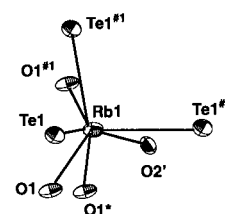
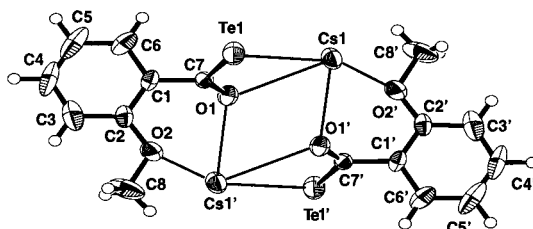
(a')

(b) 2-CH₃OC₆H₄COSeCs (9)

(b')

(c) 2-CH₃OC₆H₄COTeRb (8)

(c')

(d) 2-CH₃OC₆H₄COTeCs (10)

(d')

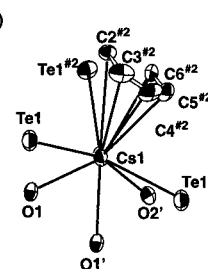


Figure 4. ORTEP drawings and coordination spheres of potassium 2-methoxybenzenecarboselenoate (7), cesium 2-methoxybenzenecarboselenoate (9), rubidium 2-methoxybenzenecarbotelluroate (8), and cesium 2-methoxybenzenecarbotelluroate (10). The atoms are drawn with 50% probability ellipsoids.

Table 9. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Potassium 2-Methoxybenzenecarboselenoate (7)^a

Bond Lengths			
O1-C7	1.225(6)	K1-Se1 ^{#2}	3.358(2)
Se1-C7	1.861(5)	K1-O1	2.892(4)
K1-Se1	3.309(1)	K1-O1'	3.050(4)
K1-Se1'	3.597(1)	K1-O1 ^{#3}	2.750(4)
K1-Se1 ^{#1}	3.625(2)	K1-O2'	2.810(4)
Angles			
O1-C7-C1	117.6(4)	Se1-K1-Se1'	100.47(3)
Se1-C7-C1	116.7(3)	K1-Se1-K1'	79.53(3)
Se1-C7-O1	125.6(4)	Se1-K1-O1	52.33(7)
K1-Se1-C7	75.7(2)	K1-O1-K1'	96.2(1)
K1-O1-C7	102.3(3)	O1-K1-O1'	83.8(1)
Torsion Angles			
O1-C7-C1-C2	92.2(6)	K1-Se1-C7-O1	20.1(4)
C3-C2-O2-C8	9.2(7)	O1-C7-C1-C6	85.9(6)

^a (') 1 - x, 1 - y, 1 - z. (#1) 1/2 + x, 3/2 - y, z. (#2) 1/2 - x, 1/2 + y, 1 - z. (#3) 1/2 - x, 1/2 + y, 1 - z.

(c) **Packing.** The crystal packings of **3a**, **3b**, **3c**, and **8** are shown in Figures 5-8, respectively. Each sulfur atom in **3a** is

Table 10. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Rubidium 2-Methoxybenzenecarbotelluroate (8)^a

Bond Lengths			
O1-C7	1.25(2)	Rb1-O1	3.02(1)
Te1-C7	2.12(2)	Rb1-O1'	2.86(1)
Rb1-Te1	3.791(2)	Rb1-O1 ^{#1}	3.08(1)
Rb1-Te1 ^{#1}	3.833(2)	Rb1-O2'	3.17(2)
Rb1-Te1 ^{#2}	3.829(2)		
Angles			
O1-C7-C1	122(1)	Rb1-O1-C7	95.7(9)
Te1-C7-C1	117(1)	Te1-Rb1-O1	50.1(2)
Te1-C7-O1	121(1)	Rb1-O1-Rb1'	111.2(4)
Rb1-Te1-C7	62.5(4)	O1-Rb1-O1'	68.8(4)
Torsion Angles			
O1-C7-C1-C2	43(2)	Rb1-Te1-C7-O1	53(1)
C3-C2-O2-C8	3(3)	Rb1-O1-Rb1'-O1'	0.0

^a (') 1 - x, 1 - y, 1 - z. (#1) -1 + x, y, z. (#2) 1 - x, -y, 1 - z.

triple-bridging, resulting in a ladder polymer of square units (K, S, K, S) (Figure 5, part a).²² The phenyl rings are parallel

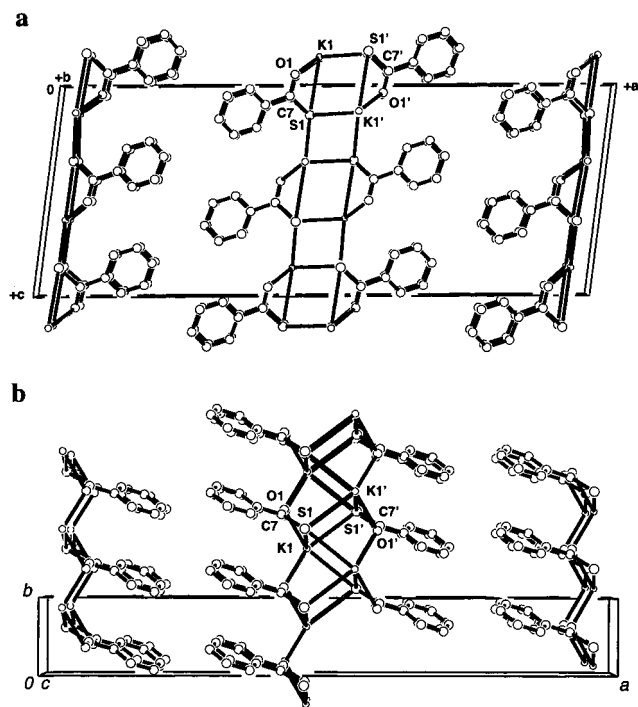


Figure 5. Unit cell of potassium benzenecarbothioate (**3a**) viewed down the *b*-axis (a) and the *c*-axis (b). Hydrogen atoms are omitted for clarity.

Table 11. The Dihedral Angles ($\theta 1$ in a) between the Phenyl Ring Plane (A) and the Thio-, Seleno-, or Tellurocarboxyl Plane (B) and the Dihedral Angles ($\theta 2$ in b) between the O–C–E Plane (B) and the O–M–E Plane (C) in Monochalcogenocarboxylic Acid Salts 3–10

Figure 6 shows the unit cell of potassium 2-methoxybenzenecarbothioate (3b) viewed down the *a*-axis. The structure shows a ladder polymer of square units (K, O, K, O) with phenyl rings parallel to each other. The *b* and *c* axes are indicated.

(a)

(b)

compd no.	X	E	M	$\theta 1$ (deg)	$\theta 2$ (deg)	ref
3a	H	S	K	5.5	39.5	
3b	2-CH ₃ O	S	K	84.2	24.5	
3c	4-CH ₃ O	S	K	17.8	19.1	
4f	2-CH ₃ O	S	Rb	56.2	30.5	
5f	2-CH ₃ O	S	Cs	58.9	32.7	9
6a	2-CH ₃ O	S	NMe ₄	87.2		
6b	2-CF ₃	S	NMe ₄	63.7		
7	2-CH ₃ O	Se	K	86.5	23.7	
8	2-CH ₃ O	Te	Rb	49.2	64.8	
9	2-CH ₃ O	Se	Cs	61.0	32.3	9
10	2-CH ₃ O	Te	Cs	69.5	24.1	9

to each other, but there is no interaction between them (Figure 5, part b). The *o*-methoxy derivative **3b** forms a ladder polymer of square units (K, O, K, O), and the phenyl rings are parallel to each other (Figure 6). In the *p*-methoxy derivative **3c**, the *p*-methoxy oxygen is associated with the potassium, which also coordinates with the thiocarboxylate oxygen and sulfur atoms, resulting in a network polymer (Figure 7). The rubidium telluroate **8** appears to have an analogous ladder structure as observed for **3b** (Figure 8).

Reaction. To our knowledge, there has been no systematic investigation concerning the reactivities of alkali metal thiocarboxylates.^{1a,d} To compare such reactivities, the reactions of alkali metal 4-methylbenzenecarbothioates with alkyl iodide and triphenyltin chloride were carried out. The reactions of the sodium salt **12a** and potassium salt **3d** with methyl iodide readily

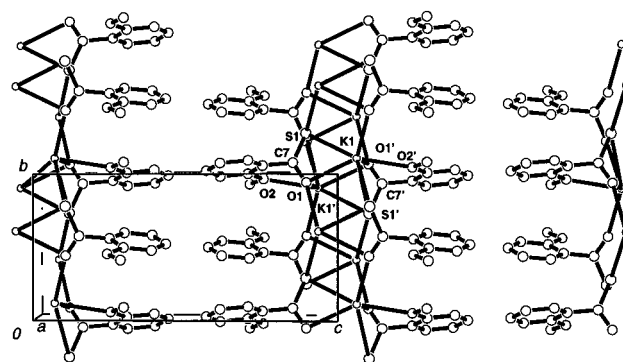


Figure 6. Unit cell of potassium 2-methoxybenzenecarbothioate (**3b**) viewed down the *a*-axis. Hydrogen atoms are omitted for clarity.

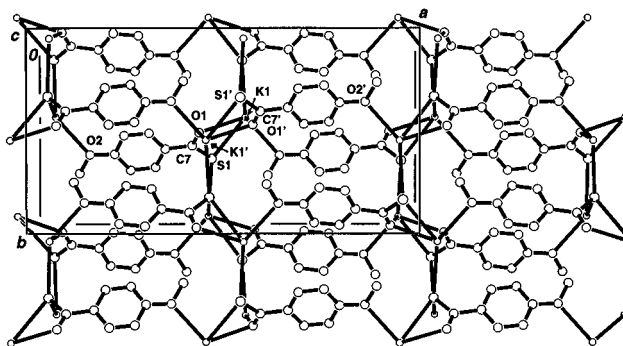


Figure 7. Unit cell of potassium 4-methoxybenzenecarbothioate (**3c**) viewed down the *c*-axis. Hydrogen atoms are omitted for clarity.

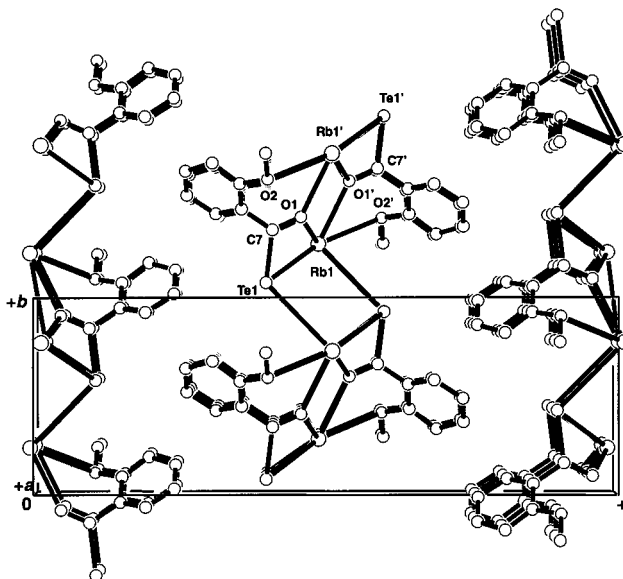


Figure 8. Unit cell of rubidium 2-methoxybenzenecarbotelluroate (**8**) viewed down the *a*-axis. Hydrogen atoms are omitted for clarity.

proceeded at room temperature to give the corresponding methyl esters **13** in quantitative yields, while the reaction with rubidium salt **4e** and cesium salt **5e** resulted in relatively low yields. At 0 °C, however, their reactivity with methyl iodide was substantially lower than the reactivity at room temperature (Scheme 4, Table 12). The reactivity of alkali metal thiocarboxylates to alkyl iodides appears to be roughly in the following order: Na > Cs \approx Rb \approx K > Li. On the other hand, the reaction with triphenyltin chloride gave triphenyltin 4-methylbenzenecarbothioate (**14**) in 45–90% yields. The reactivity of the alkali metal salts to the tin chloride appears to decrease in the order Na \approx

Scheme 4

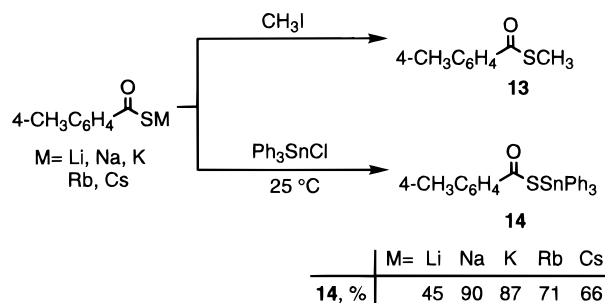


Table 12. Reaction of Alkali Metal Thiocarboxylates $4\text{-CH}_3\text{C}_6\text{H}_4\text{COSM}$ with Methyl Iodide

run	M	reactn condits		yield of 13 (%)
		temp ($^\circ\text{C}$)	time (min)	
1	Li (11)	0	30	5
2	Na (12b)	0	30	25
3	K (3d)	0	30	10
4	Rb (4e)	0	30	12
5	Cs (5e)	0	30	17
6	Li (11)	30	30	12
7	Na (12b)	30	30	100
8	K (3d)	27	30	54
9	Rb (4e)	28	30	49
10	Cs (5e)	30	30	64

Table 13. Spectral Data of Alkali Metal Thiobenzoates $\text{C}_6\text{H}_5\text{COSM}$

M	IR (cm^{-1}) ^a	^{13}C NMR ^b	ref
	$\nu\text{C=O}$	$\delta\text{C=O}$	
Li	1509 ⁵	215.2	5
Na	1525 ⁵	214.6	5
K	1523 ⁵	214.5	5
Rb	1520 ⁵	214.5 ^{16b}	5, 16b
Cs	1526 ⁵	214.2 ^{16b}	5, 16b

^a KBr. ^b CD_3OD .

Table 14. Spectral Data of Potassium Benzenecarbochalcogenoates $\text{C}_6\text{H}_5\text{COEK}$

E	IR (cm^{-1}) ^a	NMR [δ] ^b		ref
		$\nu\text{C=O}$	$^{13}\text{C=O}$	
O	1552	174.2		
S	1523 ⁵	214.5		5
Se	1538 ^c	215.9	363.0 (^{77}Se) ^d	15b
Te	1548 ^c	208.9	220.0 (^{125}Te) ^e	23

^a KBr. ^b CD_3OD . ^c Nujol. ^d Standard: $(\text{CH}_3)_2\text{Se}$. ^e Standard: $(\text{CH}_3)_2\text{Te}$.

$\text{K} > \text{Rb} \cong \text{Cs} > \text{Li}$ and is lower than that of the corresponding dithio salts.¹³

Spectra. The carbonyl carbon chemical shifts of the thiocarboxylates are observed in the narrow region δ 213–217. The signals of *o*-methoxy derivatives **3b**, **4f**, and **5f** show slightly downfield shifts compared with those of the unsubstituted and para-substituted forms. As shown in Table 13, the alkali metal cation appears to have very little effect on the carbonyl carbon chemical shift. Their C=O bond distances are also nearly the same. Table 14 shows the carbonyl stretching frequencies and carbonyl carbon chemical shifts for potassium benzenecarbochalcogenoates.^{5,15b,23} The carbonyl stretching frequencies show a tendency of high frequency shift in the order E = S, Se, and Te. The carbonyl carbon chemical shifts show a downfield shift in the order E = O, S, and Se. However, the tellurium isologue

shows a more upfield shift than those of the sulfur and selenium isologues, presumably reflecting the large metallic (electron-donating) property of tellurium compared with those of sulfur and selenium.

Conclusions

The structures of a series of alkali metal arenecarbothioates, -selenoates, and -telluroates were for the first time characterized by X-ray analysis. The overall conformations of these salts are similar to each other as described above. The similarity of the structures of these heavy alkali metal salts suggests the coordination requirement of the K, Rb, and Cs to be similar. Their fundamental unit in these structures is a dimer which is connected in a head-to-head mode and enhanced by the introduction of an *o*-methoxy group to the phenyl ring, due to coordination of the methoxy oxygen to the potassium of the opposite molecule. The dimeric units are further connected by the interaction of the metal cation with the oxygen and/or sulfur atoms, which results in a ladder polymer. The methoxy oxygen in the para position on the phenyl ring coordinates to the metal of another adjacent molecule on the opposite site, leading to a network polymer structure. These findings may serve for understanding the complexation properties of the ion carrier not only in biological membranes but also for the design of many electric materials which will be developed in the future.

Experimental Section

IR spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer. ^1H , ^{13}C , and ^{119}Sn NMR were recorded on a JEOL JNM- α 400 instrument at 399.7, 100.4, and 149.0 MHz, respectively. CD_3OD was employed as a solvent with tetramethylsilane as internal standard for ^1H NMR. CD_3OD was used as an internal standard for ^{13}C NMR. Me_4Sn was used as an external standard for ^{119}Sn NMR.

Materials. Rubidium fluorides (Aldrich) and other alkali and alkali earth metal fluorides (Nacalai Tesque Co., Kyoto, Japan) were purchased. They were dried under reduced pressure at > 120 $^\circ\text{C}$ before use. Lithium thiocarboxylate **11**, sodium thiocarboxylates **12**, and potassium thiocarboxylates **3** were prepared by the reaction of acyl chlorides with the corresponding alkali metal sulfides as described in the literature.^{3,5} Thiocarboxylic acids were prepared by acidolysis of the corresponding potassium salts with hydrogen chloride. *O*-Trimethylsilyl thiocarboxylates were prepared by the reaction of potassium thiocarboxylates with trimethylsilyl chloride.¹⁴ Potassium selenide was prepared by the reaction of potassium metal with selenium in liquid ammonia.²⁴ Rubidium 2-methoxybenzenecarbotelluroate (**8**) was prepared by according to the literature.^{16b} Additional spectral data of these salts are shown below. The following solvents were purified under nitrogen and dried as indicated: diethyl ether and hexane, refluxed with sodium metal using benzophenone as indicator and distilled before use; acetonitrile, distilled over phosphorus pentoxide, after refluxing for 5 h. All manipulations were carried out under argon.

Lithium 4-Methylbenzenecarbothioate (11).⁵ IR (KBr): 1508 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.33 (s, 3H, CH_3), 7.11 (d, J = 8.2 Hz, 2H, Ar), 8.03 (d, J = 8.2 Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 21.4 (CH_3), 128.8, 129.3, 141.6, 143.0 (Ar), 214.5 (C=O).

Sodium Benzenecarbothioate (12a).⁵ IR (KBr): 1525 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 7.29–7.36 (br, 2H, Ar), 8.12–8.14 (br, 2H, Ar). ^{13}C NMR (CD_3OD): δ 128.2, 129.1, 131.2, 145.5 (Ar), 214.6 (C=O).

Sodium 4-Methylbenzenecarbothioate (12b).⁵ IR (KBr): 1528 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.33 (s, 3H, CH_3), 7.11 (d, J = 8.1 Hz, 2H, Ar), 8.05 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 21.4 (CH_3), 128.7, 129.3, 141.6, 142.7 (Ar), 214.3 (C=O).

Sodium 2-Trifluoromethylbenzenecarbothioate (12c). IR (Nujol): 1534 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 7.36 [t, J = 7.6 Hz, 1H, Ar (5-H)], 7.49 [t, J = 7.6 Hz, 1H, Ar (4-H)], 7.54 [d, J = 7.6 Hz, 1H, Ar (6-H)], 7.67 [d, J = 7.6 Hz, 1H, Ar (3-H)]. ^{13}C NMR (CD_3OD):

(23) Kato, S.; Niyomura, O.; Nakaiida, S.; Kawahara, Y.; Kanda, T.; Yamada, R.; Hori, S. *Inorg. Chem.* **1999**, *38*, 519–530.

(24) Reference 4, p 421.

OD): δ 124.6 [q, $^2J_{C-F}$ = 31.4 Hz, Ar (2-C)], 125.4 (q, $^1J_{C-F}$ = 273.3 Hz, CF₃), 126.4, 128.3, 129.1, 132.2, 148.7 (Ar), 216.5 (C=O).

X-Ray Structure Analysis. The measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo K α radiation (λ = 0.710 69 Å). All of the structures were solved and refined using the teXsan crystallographic software package on an IRIS Indigo computer. The crystals were cut from the grown crystals. The crystals were mounted on a glass fiber. Because these samples were unstable in air, the crystals were coated with an epoxy resin. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and showed no significant intensity variations during the data collection. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [DIFABS²⁵ (**3a**, **4f**, **7**, and **8**)] were also applied. The structures were solved by direct methods using SHELXS86²⁶ and expanded using DIRDIF94.²⁷ Scattering factors for neutral atoms were from Cromer and Waber,²⁸ and anomalous dispersion²⁹ was used. The function minimized was $\sum w(|F_{obs}| - |F_{calc}|)^2$, and the weighting scheme employed was $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. Crystal data and the measurement description are summarized in Table 2.

Preparation of Single Crystals. Potassium benzenecarbothioate (**3a**) (0.212 g) was single-crystallized from acetonitrile (5 mL), hexane (2 mL), and ether (0.5 mL) at room temperature for 2 months. Potassium 2-methoxybenzenecarbothioate (**3b**) (0.195 g) was single-crystallized from acetonitrile (5 mL), hexane (2 mL), and ether (2 mL) at room temperature for 13 days. Potassium 4-methoxybenzenecarbothioate (**3c**) (0.099 g) was single-crystallized from methanol (1 mL), hexane (0.5 mL), and ether (0.2 mL) at room temperature for 13 days. Rubidium 2-methoxybenzenecarbothioate (**4f**) was single-crystallized by allowing to stand a solution of **4f** (0.040 g) in acetonitrile (0.5 mL), hexane (0.2 mL), and ether (0.8 mL) at room temperature for 4 days. Tetramethylammonium 2-methoxybenzenecarbothioate (**6a**) was single-crystallized by allowing to stand a solution of **6a** (0.4 g) in acetonitrile (5 mL) and ethyl acetate (3 mL) at room temperature for 3 days and then -20 °C for 2 days. Tetramethylammonium 2-trifluoromethylbenzenecarbothioate (**6b**) was single-crystallized by allowing to stand a solution of **6b** (0.096 g) in acetonitrile (1.3 mL), hexane (0.2 mL), and ether (1.0 mL) in limited amounts at room temperature for 50 days. Potassium 2-methoxybenzenecarbothioate (**7**)²⁹ was single-crystallized by allowing to stand a solution of **7** (0.135 g) in acetonitrile (3 mL), hexane (2 mL), and ether (2 mL) at room temperature for 4 days. Rubidium 2-methylbenzenecarbothioate (**8**) (0.506 g)^{16b} was single-crystallized from acetonitrile (2 mL) and ether (12 mL) at room temperature for 5 days.

Preparation of Alkali Metal Thiocarboxylates. Reaction of *O*-Trimethylsilyl Thiocarboxylates (Method A) or Thiocarboxylic Acids (Method B) with Alkali Metal Fluoride. Typical procedures are described for rubidium 2-methoxybenzenecarbothioate (**4f**) and cesium 4-methylbenzenecarbothioate (**5e**).

Potassium Benzenecarbothioate (3a). IR (KBr): 1525 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 7.30–8.16 (m, 5H, Ar). ¹³C NMR (CD₃OD): δ 128.2, 129.1, 131.3, 145.4 (Ar), 214.5 (C=O).

(25) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

(26) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: 1985; pp 175–189.

(27) The DIRDIF-94 program system was used: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. In *Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1994.

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(29) Creagh, D. C.; McAuley, W. J. In *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219–222.

Potassium 2-Methoxybenzenecarbothioate (3b). IR (Nujol): 1522 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 3.69 (s, 3H, CH₃O), 6.76–7.42 (m, 4H, Ar). ¹³C NMR (CD₃OD): δ 56.2 (CH₃O), 112.7, 120.9, 129.4, 130.0, 139.8, 155.3 (Ar), 217.0 (C=O).

Potassium 4-Methoxybenzenecarbothioate (3c). IR (Nujol): 1510 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 3.80 (s, 3H, CH₃O), 6.83 (d, J = 8.9 Hz, 2H, Ar), 8.31 (d, J = 8.9 Hz, 2H, Ar). ¹³C NMR (CD₃OD): δ 55.8 (CH₃O), 113.2, 131.2, 138.2, 163.1 (Ar), 213.1 (C=O).

Potassium 4-Methylbenzenecarbothioate (3d). IR (KBr): 1523 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 2.64 (s, 3H, CH₃), 7.11 (d, J = 7.8 Hz, 2H, Ar), 8.06 (d, J = 7.8 Hz, 2H, Ar). ¹³C NMR (CD₃OD): δ 21.5 (CH₃), 129.0, 129.3, 141.8, 143.0 (Ar), 214.2 (C=O).

Potassium 2-Trifluoromethylbenzenecarbothioate (3e). IR (Nujol): 1537 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 7.36 [t, J = 7.8 Hz, 1H, Ar (5-H)], 7.49 [t, J = 7.8 Hz, 1H, Ar (4-H)], 7.54 [d, J = 7.8 Hz, 1H, Ar (6-H)], 7.65 [d, J = 7.8 Hz, 1H, Ar (3-H)]. ¹³C NMR (CD₃OD): δ 124.6 [q, $^2J_{C-F}$ = 31.2 Hz, Ar (2-C)], 125.5 (q, $^1J_{C-F}$ = 272.4 Hz, CF₃), 129.2 [q, $^3J_{C-F}$ = 2.6 Hz, Ar (3-C)], 126.5, 128.3, 132.3 [Ar (4, 5, 6-C)], 148.9 [q, $^3J_{C-F}$ = 2.3 Hz, Ar (1-C)], 216.5 (C=O).

Rubidium Thioacetate (4a). IR (KBr): 1541 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 2.45 (s, CH₃). ¹³C NMR (CD₃OD): δ 39.0 (CH₃), 220.2 (C=O).

Rubidium 1,1-Dimethylethanecarbothioate (4b). IR (KBr): 1523 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 1.21 (s, CH₃). ¹³C NMR (CD₃OD): δ 30.0 (CH₃), 49.1 (C-CO), 229.4 (C=O).

Rubidium Benzenecarbothioate (4c). IR (KBr): 1531 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 7.27–8.13 (m, 5H, Ar). ¹³C NMR (CD₃OD): δ 128.2, 129.1, 131.2, 145.7 (Ar), 214.5 (C=O).

Rubidium 2-Methylbenzenecarbothioate (4d). IR (KBr): 1523 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 2.38 (s, 3H, CH₃), 7.06–7.13 (m, 3H, Ar), 7.46–7.48 (m, 1H, Ar). ¹³C NMR (CD₃OD): δ 19.9 (CH₃), 125.9, 127.4, 128.4, 131.0, 132.9, 150.0 (Ar), 219.7 (C=O).

Rubidium 4-Methylbenzenecarbothioate (4e). IR (KBr): 1520 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 2.33 (s, 3H, CH₃), 7.12 (d, J = 8.1 Hz, 2H, Ar), 8.03 (d, J = 8.1 Hz, 2H, Ar). ¹³C NMR (CD₃OD): δ 21.4 (CH₃), 128.9, 129.3, 141.7, 143.0 (Ar), 214.2 (C=O).

Rubidium 2-Methoxybenzenecarbothioate (4f). Method A. A solution of *O*-trimethylsilyl 2-methoxybenzenecarbothioate (0.514 g, 2.14 mmol) in ether (3 mL) was added to a suspension of rubidium fluoride (0.156 g, 1.49 mmol) in the same solvent (9 mL), and the mixture was stirred at 26 °C for 5 h. The precipitates were filtered off by a glass filter (G4), followed by washing with hexane (3 mL), and dissolved in methanol (10 mL). The insoluble parts (white precipitates) were filtered off, followed by removal of the solvent under reduced pressure to give a white solid. The solid was dissolved in acetonitrile (2 mL) to give a yellow solution. Ether (2 mL) and then hexane (1 mL) were added slowly at room temperature. Removal of the resulting precipitates by filtration gave 0.165 g (44%) of rubidium 2-methoxybenzenecarbothioate (**4f**) as colorless microcrystals. IR (Nujol): 1520 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 3.81 (s, 3H, CH₃O), 6.87 (t, J = 7.8 Hz, 1H, Ar), 6.93 (d, J = 7.8 Hz, 1H, Ar), 7.21 (t, J = 7.8 Hz, 1H, Ar), 7.50 (d, J = 7.8 Hz, 1H, Ar). ¹³C NMR (CD₃OD): δ 56.2 (CH₃O), 112.7, 121.0, 129.3, 123.0, 139.9, 155.2 (Ar), 217.1 (C=O).

Method B. A solution of 2-methoxybenzenecarbothioic acid (1.968 g, 11.7 mmol) in ether (5 mL), was added to a suspension of rubidium fluoride (0.827 g, 7.92 mmol) in the same solvent (5 mL) and the mixture was stirred at 27 °C for 5 h. The precipitates were filtered off by a glass filter (G4) and dissolved in methanol (30 mL). The insoluble parts (white precipitates) were filtered off, followed by removal of the solvent under reduced pressure to give a white solid. The solid was dissolved in acetonitrile (15 mL) to give a yellow solution. To the solution were added ether (20 mL) and hexane (7 mL) slowly at room temperature to give 1.437 g (72%) of **4f** as colorless microcrystals.

Rubidium 4-Methoxybenzenecarbothioate (4g). IR (KBr): 1512 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 3.82 (s, 3H, CH₃O), 6.84 (d, J = 8.8 Hz, 2H, Ar), 8.13 (d, J = 8.8 Hz, 2H, Ar). ¹³C NMR (CD₃OD): δ 55.8 (CH₃O), 113.3, 131.3, 138.3, 163.2 (Ar), 212.9 (C=O).

Rubidium 4-Chlorobenzenecarbothioate (4h). IR (KBr): 1525 (C=O) cm⁻¹. ¹H NMR (CD₃OD): δ 7.28 (d, J = 8.5 Hz, 2H, Ar), 8.10 (d, J = 8.5 Hz, 2H, Ar). ¹³C NMR (CD₃OD): δ 128.2, 130.7, 137.3, 144.2 (Ar), 212.6 (C=O).

Cesium Thioacetate (5a). IR (KBr): 1542 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.43 (s, CH_3). ^{13}C NMR (CD_3OD): δ 39.0 (CH_3), 220.1 (C=O).

Cesium 1,1-Dimethylethanecarbothioate (5b). IR (KBr): 1525 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 1.22 (s, CH_3). ^{13}C NMR (CD_3OD): δ 29.8 (CH_3), 49.1 (C-CO), 227.3 (C=O).

Cesium Benzenecarbothioate (5c). IR (KBr): 1526 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 7.28–8.14 (m, 5H, Ar). ^{13}C NMR (CD_3OD): δ 128.3, 128.9, 131.3, 145.6 (Ar), 214.2 (C=O).

Cesium 2-Methylbenzenecarbothioate (5d). IR (KBr): 1523 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.39 (s, 3H, CH_3), 7.08–7.14 (m, 3H, Ar), 7.46–7.48 (m, 1H, Ar). ^{13}C NMR (CD_3OD): δ 19.9 (CH_3), 126.0, 127.4, 128.4, 131.0, 132.9, 150.1 (Ar), 219.7 (C=O).

Cesium 4-Methylbenzenecarbothioate (5e). **Method A.** A solution of *O*-trimethylsilyl 4-methylbenzenecarbothioate (0.745 g, 3.18 mmol) in ether (5 mL) was added to a suspension of cesium fluoride (0.217 g, 1.43 mmol) in the same solvent (10 mL), and the mixture was stirred at 25 °C for 5 h. The precipitates were filtered off by a glass filter (G4), followed by washing with hexane (3 mL), and dissolved in methanol (5 mL). The insoluble parts (white precipitates) were filtered off, followed by removal of the solvent under reduced pressure to give a white solid. The solid was dissolved in acetonitrile (10 mL) to give a yellow solution. Ether (10 mL) and then hexane (8 mL) were added slowly at room temperature. Filtration of the resulting precipitates gave 0.289 g (71%) of cesium 4-methylbenzenecarbothioate (**5e**) as colorless microcrystals. IR (KBr): 1526 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.34 (s, 3H, CH_3), 7.13 (d, $J = 7.8$ Hz, 2H, Ar), 8.02 (d, $J = 7.8$ Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 21.4 (CH_3), 128.9, 129.3, 141.9, 142.6 (Ar), 213.5 (C=O).

Method B. A solution of 4-methylbenzenecarbothioic acid (0.641 g, 4.21 mmol) in ether (5 mL) was added to a suspension of cesium fluoride (0.410 g, 2.70 mmol) in the same solvent (3 mL), and the mixture was stirred at 27 °C for 5 h. The precipitates were filtered off by a glass filter (G4) and dissolved in ethanol (22 mL). The insoluble parts (white precipitates) were filtered off, followed by removal of the solvent under reduced pressure to give a white solid. The solid was dissolved in acetonitrile (16 mL) to give a yellow solution. Ether (15 mL) and then hexane (14 mL) were added slowly at room temperature. Removal of the resulting precipitates by filtration gave 0.414 g (54%) of **5e** as colorless microcrystals.

Cesium 2-Methoxybenzenecarbothioate (5f). IR (KBr): 1522 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 3.83 (s, 3H, CH_3O), 6.90 (m, 2H, Ar), 7.21–7.24 (m, 1H, Ar), 7.47–7.49 (m, 1H, Ar). ^{13}C NMR (CD_3OD): δ 56.3 (CH_3O), 112.9, 121.2, 129.1, 130.0, 140.0, 155.0 (Ar), 216.8 (C=O).

Cesium 4-Methoxybenzenecarbothioate (5g). IR (KBr): 1517 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 3.82 (s, 3H, CH_3O), 6.84 (d, $J = 8.7$ Hz, 2H, Ar), 8.13 (d, $J = 8.7$ Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 55.8 (CH_3O), 113.4, 131.2, 137.9, 163.3 (Ar), 212.3 (C=O).

Cesium 4-Chlorobenzenecarbothioate (5h). IR (KBr): 1526 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 7.29 (d, $J = 8.8$ Hz, 2H, Ar), 8.10 (d, $J = 8.8$ Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 128.2, 130.7, 137.4, 144.0 (Ar), 212.5 (C=O).

Preparation of Tetramethylammonium Thiocarboxylates (6). Typical procedures are described for tetramethylammonium 2-trifluoromethylbenzenecarbothioate (**6b**).

Tetramethylammonium 2-Methoxybenzenecarbothioate (6a). Yield: 79%; pale yellow crystals [recrystallization from ether/acetonitrile (1:1) at –20 °C]. Mp: 164–165 °C dec. IR (KBr): 1533 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 3.16 (s, 12H, NMe), 3.77 (s, 3H, CH_3O), 6.84–7.44 (m, 4H, Ar). ^{13}C NMR (CD_3OD): δ 55.9 (t, $J = 4.3$ Hz, NCH_3), 56.1 (CH_3O), 112.6, 120.9, 129.0, 129.8, 140.4, 155.2 (Ar), 216.3 (C=O).

Tetramethylammonium 2-Trifluoromethylbenzenecarbothioate (6b). To an acetonitrile solution (15 mL) of sodium 2-trifluoromethylbenzenecarbothioate (1.072 g, 4.70 mmol) was added tetramethylammonium chloride (0.540 g, 4.93 mmol), and the mixture was stirred at 27 °C for 5 h. Filtration of the insoluble parts (NaCl and excess Me_4NCl) and evaporation of the solvent under reduced pressure (32 °C, 0.3 Torr) gave 1.090 g (83%) of crude **6b** as an orange solid (wet), followed by washing with ether (10 mL) and then acetonitrile (1.5 mL).

The solid was dissolved in acetonitrile (4 mL) to give an orange solution. Ether (4 mL) and then hexane (2 mL) were added slowly. Removal of the precipitates by filtration gave 0.381 g (29%) of chemically pure **6b** as colorless microcrystals. IR (Nujol): 1531 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 3.16 (d, 12H, NMe), 7.36 [t, $J = 7.7$ Hz, 1H, Ar (5-H)], 7.50 [t, $J = 7.7$ Hz, 1H, Ar (4-H)], 7.54 [d, $J = 7.7$ Hz, 1H, Ar (6-H)], 7.60 [d, $J = 7.7$ Hz, 1H, Ar (3-H)]. ^{13}C NMR (CD_3OD): δ 55.9 (NMe), 124.5 [q, $^2J_{\text{C-F}} = 31.2$ Hz, Ar (2-C)], 125.6 (q, $^1J_{\text{C-F}} = 273.3$ Hz, CF_3), 126.6 [q, $^3J_{\text{C-F}} = 4.9$ Hz, Ar (3-C)], 128.1, 129.1, 132.5 [Ar (4, 5, 6-C)], 149.5 [Ar (1-C)], 215.5 (C=O).

Preparation of Alkali Metal Selenocarboxylates.³⁰ Potassium 2-Methoxybenzenecarboxoselenoate (7). All manipulations were carried out under argon. An acetonitrile solution (13 mL) containing 2-methoxybenzoyl chloride (0.325 g, 1.91 mmol) was added to a suspension of potassium selenide (0.425 g, 2.70 mmol) in the same solvent (10 mL). The mixture was stirred at room temperature for 1.5 h (the color quickly changed from white to yellow brown). The insoluble part (KCl and excess K_2Se) was filtered off, and the solvent was removed under reduced pressure. The residue was washed with ether (15 mL) to give a yellow solid. The solid was dissolved in acetonitrile (2 mL), and then ether (5 mL) was slowly added. Filtration of the resulting precipitates gave 0.264 g (55%) of potassium 2-methoxybenzenecarboxoselenoate (**7**) as pale yellow microcrystals. Anal. Calcd: C, 37.95; H, 2.87; Found: C, 38.14; H, 2.87.

Reaction of Alkali Metal 4-Methylbenzenecarbothioates with Methyl Iodide. Typical procedures are described for the reaction of potassium 4-methylbenzenecarbothioate (**3d**). Potassium 4-methylbenzenecarbothioate (**3d**) (0.195 g, 1.02 mmol) and methyl iodide (5 mL, 80 mmol) were stirred at room temperature for 30 min. Filtration and evaporation of an excess of the methyl iodide under reduced pressure gave 0.091 g (54%) of *S*-methyl 4-methylbenzenecarbothioate (**13**) as a pale yellow oil. The IR and ^1H and ^{13}C NMR spectra were exactly consistent with those of an authentic sample prepared by the reaction of rubidium 4-methylbenzenecarbothioate (**4e**) with methyl iodide: pale yellow oil; IR (neat) 1662 (C=O) cm^{-1} . ^1H NMR (CD_3OD): δ 2.38 (s, 3H, CH_3Ar), 2.44 (s, 3H, SCH_3), 7.22 (d, $J = 8.2$ Hz, 2H, Ar), 7.85 (d, $J = 8.2$ Hz, 2H, Ar). ^{13}C NMR (CD_3OD): δ 11.5 (CH_3S), 21.6 (CH_3Ar), 127.1, 129.2, 134.5, 144.0 (Ar), 191.9 (C=O).

Reaction of Thiocarboxylic Acids with Alkali and Alkali Earth Metal Chlorides, Bromides, and Iodides or with Lithium and Sodium Fluorides. General Procedures. 4-Methylbenzenecarbothioic acid (7 mmol) and alkali metal halogenides (LiF, NaF, KF, KCl, KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr, CsI) (4 mmol) or alkali earth metal fluorides (CaF_2 , SrF_2 , BaF_2) (3 mmol) were stirred in ether (1 mL) at 20 °C for 2 h or refluxed for 30 min. By removal of the insoluble part by filtration followed by washing with ether (3 \times 3 mL), the alkali metal except for KF and alkali earth metal halogenides were recovered in quantitative yield, respectively.

Reaction of Alkali Metal 4-Methylbenzenecarbothioates with Triphenyltin Chloride. Typical Procedures.³¹ Rubidium 4-methylbenzenecarbothioate (**4e**) (0.241 g, 1.02 mmol) and triphenyltin chloride (0.385 g, 1.0 mmol) were stirred in ether (20 mL) at 25 °C for 15 h. The reaction mixture was poured onto water and extracted with dichloromethane (150 mL). The organic layer was washed with water (100 mL \times 4), dried over anhydrous sodium sulfate, and then concentrated under reduced pressure. Crystallization of the resulting pale yellow oil with ether (1 mL) and hexane (1 mL) gave 0.355 g (71%) of triphenyltin 4-methylbenzenecarbothioate (**14**) as pale yellow crystals. The IR and ^1H NMR spectra were consistent with those of an authentic sample prepared by the reaction of other alkali metal 4-methylbenzenecarbothioates with triphenyltin chloride. Mp: 234–235 °C. IR (KBr): 1621 (C=O) cm^{-1} . ^1H NMR (CDCl_3): δ 2.28 (s, 3H,

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CH₃), 7.11 (d, $J = 7.9$ Hz, 2H, Ar), 7.35–7.37 (m, 9H, Ar), 7.68–7.73 (m, 19H, Ar), 7.96 (d, $J = 7.9$ Hz, 2H, Ar). ¹³C NMR (CDCl₃): δ 21.6 (CH₃), 128.8, 129.7, 128.8, 129.7, 135.1, 136.8, 138.3, 144.3 (Ar), 196.0 (C=O). ¹¹⁹Sn NMR (CDCl₃): δ -97.7 ($^1J_{^{13}\text{C}-^{119}\text{Sn}} = 594$ Hz).

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Supporting Information Available: X-ray structural information for the compounds **3a–c**, **4f**, **6a,b**, **7**, and **8** in Table 2 including atomic coordinates, isotropic thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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