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Heavy Alkali Metal Arenedithiocarboxylates: A Facile Synthesis, Dimeric Structure, and Nonbonding Interaction between the Metals and Aromatic Ring Carbons

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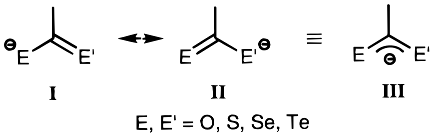
Dithiocarboxylic acids and their trimethylsilyl esters were found to readily react with potassium, rubidium, and cesium fluorides to give the corresponding alkali metal dithiocarboxylates **3**−**5** in moderate to good yields. A series of tetramethylammonium dithiocarboxylates **8** have been prepared in good yields by the reaction of sodium dithiocarboxylates **7** with tetramethylammonium chloride. The structures of potassium (**3b**), rubidium (**4g**), cesium (**5f**), and tetramethylammonium 4-methylbenzenecarbodithioates (**8e)** and tetramethylammonium 2-methoxybenzenecarbodithioate (**8f**) were characterized crystallographically. These heavier alkali metal salts (**3b**, **4g**, **5f**) have a dimeric structure $[(RCSSM)_2$, M = K, Rb, Cs] in which the two dithiocarboxylate groups are chelated to the metal cations which are located on the upper and lower sides of the plane involving the two opposing dithiocarboxylate groups. The K^+ cations interact with the tolyl fragment of a neighboring molecule, while the Rb^+ and Cs^+ cations interact with two neighboring tolyl fragments, in which the ipso and ortho carbons are positioned close to the metals. The interaction number of the metals with surrounding atoms is 8 for K^+ and Rb^+ and 12 for Cs^+. The C−S distances of the dithiocarboxylate group are different for the potassium salt **3b**. In contrast, those of the rubidium salt **4g** and cesium salt **5f** are equal. Similarly, the chelating sulfur−metal bond distances of **3b** are different, while those of **4g** and **5f** are almost equal. The dihedral angles of the phenyl ring and dithiocarboxylate plane increase in the order of the K, Rb, and Cs salts. The structural analysis of sodium 4-methylbenzenecarbodithioate (**7g**) revealed the presence of $4\text{-}CH_3C_6H_4CS_2Na_{0.36}$. In contrast, the tetramethylammonium salts **8** are monomeric where the cation moieties are located out of the dithiocarboxylate plane. The potassium **3**, rubidium **4**, and cesium dithiocarboxylates **5** readily reacted with methyl iodide or triorganotin chlorides at room temperature to give the corresponding methyl **9** and triorganotin dithioesters **10** in good yields. At 0 °C, the reactivity of the rubidium **4** and cesium salts **5** to methyl iodides decreases dramatically compared with those of the sodium salts **7** and potassium salts **3**.

Introduction

Alkali metal carboxylates and chalcogenocarboxylates in which one or two oxygen atoms in the carboxyl group were replaced by a S, Se, or Te atom are considered as a kind of *heteroallylic anion system* (**I**−**III** in Scheme 1). There are 15 possible alkali metal chalcogenocarboxylates for each alkali metal. It is well documented that the C−O bond lengths of alkali metal carboxylates are equal or nearly equal[1,2] and the negative charge is delocalized on the carboxylate group.[1,2] In contrast, little is known about the structure of dithiocarboxylic acid alkali metal salts, which are a very important class of starting compounds for the synthesis of dithiocarboxylic acid derivatives.[3] Houben and Pohl reported in 1907 a valuable method for construction of the dithiocarboxyl moiety by inserting carbon disulfide using a Grignard reagent.[4] In addition, they noted the formation of dithioacetic and dithiobenzoic acids by acidolysis with HCl and of their sodium salts by treatment with aqueous sodium hydroxide.[4] These dithio acids and sodium salts are obtained as oily substances which contain a small amount of water and/or solvents which are difficult to remove.[5] Such water and/or solvent contamination has hampered not only their accurate weighing in stoichiometric reactions but also reactions which use and/or produce water-sensitive compounds. Previously, we developed a convenient method for preparing solid dithiocarboxylic acid alkali metal anhydrous salts by reacting a dithio acid with alkali metal hydrides such as LiH, NaH, and KH or with rubidium and cesium acetates in aprotic nonpolar solvents. However, the use of these metal acetates is somewhat complicated by the removal of the formed acetic acid.[6] Recently, we have found that *O*-trimethylsilyl seleno- and tellurocarboxylates react with rubidium and cesium fluorides to give seleno-[7]

Scheme 1



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[5] Common aromatic dithiocarboxylic acids are oils and cannot be distilled.

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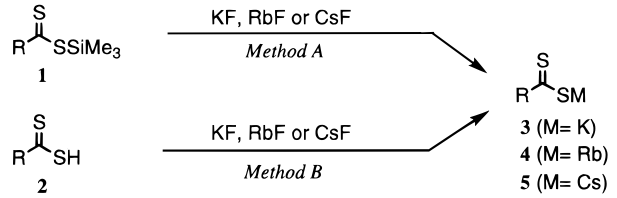
Table 1. Yields of Rubidium Dithiocarboxylates **4** and Cesium Dithiocarboxylates **5**

	RCSSM			
no.	R	M	method	yield[a] (%)
4a	CH_3	Rb	A	72
			B	68[b]
4b	C_2H_5	Rb	A	61
			B	70
4c	i-C_3H_7	Rb	A	85
			B	77
4d	c-C_6H_{11}	Rb	A	90
4e	C_6H_5	Rb	B	49
4f	2-$CH_3C_6H_4$	Rb	B	58
4g	4-$CH_3C_6H_4$	Rb	B	54
4h	4-$CH_3OC_6H_4$	Rb	B	37
4i	4-ClC_6H_4	Rb	B	38
4j	2,4,6-$(CH_3)_3C_6H_2$	Rb	B	55
5a	CH_3	Cs	A	57
			B	75[b]
5b	C_2H_5	Cs	A	54
			B	54
5c	i-C_3H_7	Cs	A	92
			B	77
5d	c-C_6H_{11}	Cs	A	85
5e	C_6H_5	Cs	B	72
5f	4-$CH_3C_6H_4$	Cs	B	58
5g	4-$CH_3OC_6H_4$	Cs	B	55
5h	4-ClC_6H_4	Cs	B	60
5i	2,4,6-$(CH_3)_3C_6H_2$	Cs	B	72

[a] Recrystallization from EtOH/ether. [b] Recrystallization from EtOH/ether/hexane.

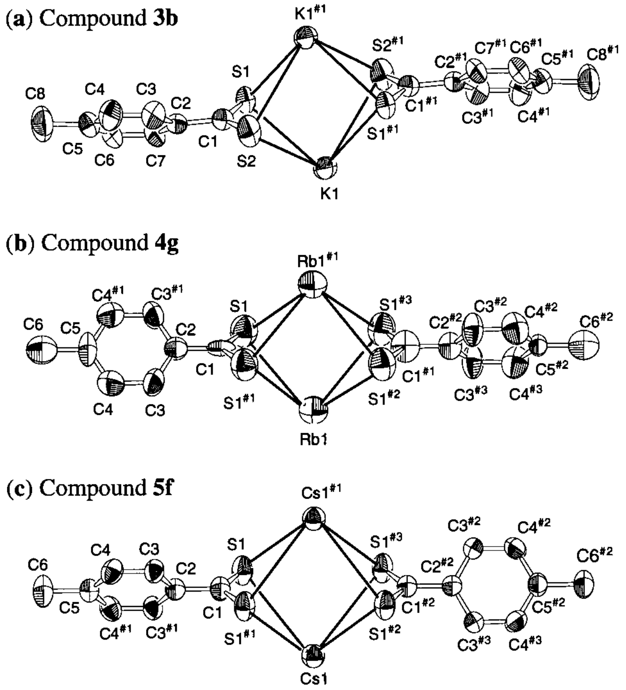
Scheme 2



and tellurocarboxylic acid rubidium and cesium salts.[8] This prompted us to explore the use of the sulfur isologues **5**. We report here a facile synthesis of anhydrous potassium **3**, rubidium **4**, and cesium dithiocarboxylates **5** and X-ray structural analyses of sodium (**7g**), potassium (**3b**), rubidium (**4g**), cesium (**5f**), and tetramethylammonium 4-methylbenzenecarbodithioates (**8e**).

Results and Discussion

Synthesis. Initially, the reaction conditions were examined using trimethylsilyl 1-methylethanecarbodithioate (**1c)** and rubidium and cesium fluorides. In fact, the reaction proceeded readily in ether at 20 °C to give the expected rubidium (**4c**) and cesium 1-methylethanecarbodithioate (**5c)** in yields of 50% and 60%, respectively (method A in Scheme 2). The salts were synthesized in a straightforward manner using the dithiocarboxylic acids themselves (method B in Scheme 1). Table 1 shows the yields of several salts **4** and **5**.



(**a**) Compound **3b**

(**b**) Compound **4g**

(**c**) Compound **5f**

Figure 1. ORTEP drawings of potassium (**3b**), rubidium (**4g**), and cesium 4-methylbenzenecarbodithioates (**5f**). The atoms are drawn with 50% probability thermal ellipsoids. All hydrogen atoms have been omitted.

To extend this reaction, the reactions of **1c** with a variety of alkali (LiF, NaF, KF) and alkali earth metal fluorides (MgF_2, CaF_2, SrF_2, BaF_2) and rubidium and cesium halides (RbX and CsX, X = Cl, Br, I) were examined. However, except for the finding that KF led to a 60% yield of potassium 1-methylethanecarbodithioate (**3a**), no reaction occurred under various conditions. The driving force for the formation of **3**−**5** seems to arise from the relatively large affinity of the sulfur atom for K, Rb, and Cs metals compared with other metals and the low bond energies of KF, RbF, and CsF compared with those of other metal fluorides. The obtained heavy alkali metal dithiocarboxylates are yellow to dark red crystals. They are stable thermally and toward oxygen. Upon exposure to air no appreciable changes were observed for at least 2 weeks both in the solid state and in solution such as ethanol. They are soluble in protic and aprotic polar solvents such as methanol and acetonitrile.

Structure. In general, dithiocarboxylic acid alkali metal salts exist as powders or very thin plates which are unsuitable for X-ray crystallography. To our knowledge, only Borell and Lledesert have documented an example in their analysis of potassium dithioacetate in 1975.[9] The exact nature and structures of alkali metal dithiocarboxylates are still unknown. After several disappointing attempts to obtain single crystals of aromatic dithiocarboxylic acid salts (RCSSM, R = aryl, M = Na, K, Rb, Cs), single needlelike crystals of sodium (**7g**), potassium (**3b**), rubidium (**4g**), and cesium 4-methylbenzenecarbodithioates (**5f**) were obtained from an ethanol/ether solution. Their ORTEP drawings are shown in Figure 1. Final atomic positional parameters are listed in Table 2. Selected bond distances and angles are shown in Table 3.

These metal salts consist of discrete dimeric units. The two dithiocarboxylate groups chelate the metal atoms (head to head) located on the upper and lower sides of the planes which include the dithiocarboxylate groups. The moieties involving two metals and four sulfur atoms in the dimer are bipyramidal (Figure 2,

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Table 2. Crystallographic Data for Potassium (**3b**), Rubidium (**4g**), Cesium (**5f**), and Sodium 4-Methylbenzenecarbodithioates (**7g**) and Tetramethylammonium 4-Methylbenzene- (**8e**) and 2-Methoxybenzenecarbodithioates (**8f**)

	3b	**4g**	**5f**	**7g**	**8e**	**8f**
empirical formula	$C_8H_7KS_2$	$C_8H_7RbS_2$	$C_8H_7CsS_2$	$C_8H_7Na_{0.36}S_2$	$C_{12}H_{19}NS_2$	$C_{12}H_{19}NOS_2$
fw	206.36	252.73	300.17	238.29	224.23	258.58
color	red	red	red	red	red	red
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic
unit-cell dimens						
a (Å)	11.398(1)	16.768(2)	17.346(1)	18.727(4)	16.392(2)	10.481(2)
b (Å)	6.7021(9)	21.617(2)	21.891(2)	10.500(2)	9.318(3)	18.243(2)
c (Å)	12.6595(6)	10.929(2)	10.931(2)	4.2192(8)	27.493(2)	7.474(2)
β (deg)	96.022(5)				100.074(9)	
vol of unit cell (Å^3)	961.7(1)	3961.3(8)	4150.7(7)	829.7(3)	4134(1)	1429.0(4)
space group	$P2_1/c$ (No. 14)	*Fddd* (No. 70)	*Fddd* (No. 70)	$P2_12_12$ (No. 18)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
Z value	4	16	16	4	4	4
D_{calc} (g/cm^3)	1.425	1.695	1.921	1.908	1.163	1.196
cryst size (mm)	0.40 × 0.25 × 0.20	0.25 × 0.20 × 0.20	0.35 × 0.25 × 0.25	0.20 × 0.20 × 0.15	0.43 × 0.40 × 0.20	0.23 × 0.20 × 0.17
μ(Mo Kα) (cm^{-1})	9.20	53.46	39.09	6.53	3.58	3.54
temp (°C)	23.0	23.0	23.0	23.0	23.0	23.0
$\lambda_{MoK\alpha}$ (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
$2\theta_{max}$ (deg)	55.0	55.0	55.0	55.0	55.0	55.0
no. of measd reflns	total: 2520	total: 1267	total: 1338	total: 3946	total: 10 018	total: 1921
no. of unique reflns	2405			1405	9861	1920
no. of observations ($I > 3\sigma(I)$)	1607	303	791	513	3324	1035
no. of variables	128	54	54	94	407	145
residuals: R,[a] R_w[b]	0.030; 0.023	0.041; 0.039	0.028; 0.032	0.060; 0.066	0.055; 0.060	0.036; 0.037
goodness of fit indicator	1.84	1.57	1.46	2.71	1.78	1.34

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

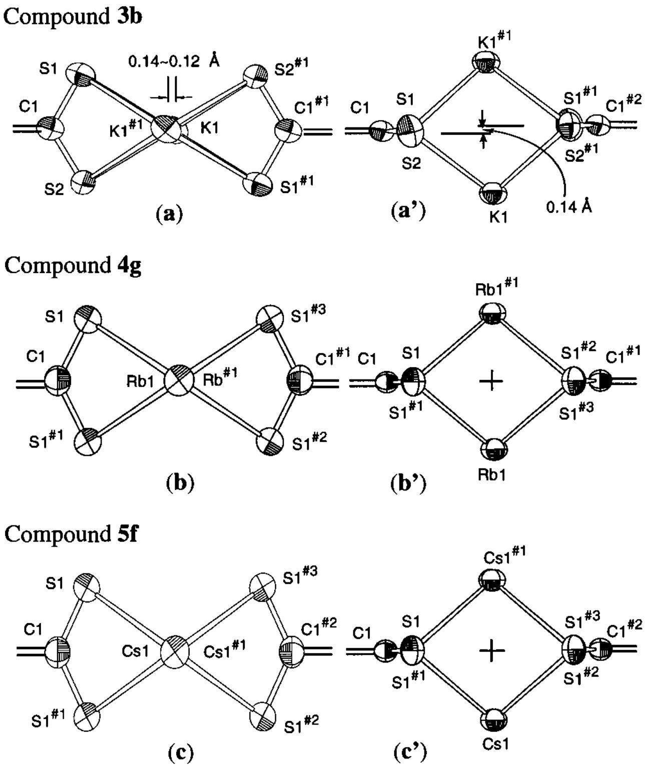

Figure 2. Top views (a−c) and side views (a′−c′) of the CSSM (M = K, Rb, Cs) moieties for potassium (**3b**), rubidium (**4g**), and cesium 4-methylbenzenecarbodithioates (**5f**).

part a′: side view). In the case of the potassium salt **3b**, a dimer unit is around an inversion center. The location of the two potassium metals deviates somewhat from the center of the four sulfur atoms of the two dithiocarboxylate groups (Figure 2, part a: top view), and the planes, which include the dithiocarboxylate group, slip out by ca. 0.14 Å (Figure 2, part a′). The C−S distances in the dithiocarboxylate group of **3b** significantly differ, 1.670(2) and 1.710(3) Å (Table 3). The former is an intermediate of the C−S double (1.63−1.64 Å) and single bonds (1.72−1.74 Å) in common dithioesters,[10] while the latter is comparable to that of the common C(sp^2)−S single bonds. The K−S distances of the chelating dithiocarboxyl group are also different, i.e., 3.2972(9) and 3.354(1) Å.

To our knowledge, such compounds with a CSSM (M = alkali metal) moiety in which the two C−S and S−M bond lengths differ (anisobidentate) are rare. In analogous compounds such as ionic potassium dithioacetate,[9] dithiocarbamates[3a,b,11] dithioformate, 1,1-dithioxanthates,[13,14] and 1,1,2-trithiooxalate[15] and dithiocarboxylato transition metal complexes $PhCS_2Re(CO)_4$,[16] $(CH_3CS_2)_4Mo$,[17] $(PhCS_2)_4Mo_2(THF)_2$,[18] $(PhCS_2)_2Ni$,[19] $(PhCH_2CS_2)_4Pd_2$,[20] and $[4\text{-}(i\text{-Pr})C_6H_4CS_2]_4Pt_2$,[21] without exception, the lengths of the two C−S and S−M bonds are equivalent in the chelated four-membered rings CSSM. This difference between the C−S bonds seems to indicate a slight localization of negative charge on the dithiocarboxylate group. The difference in the K−S bonds explains the apparent difference in C−S distances involving partial double bonds, and the localization of an electron on the dithiocarboxylate group. In Figure 3, part b, the coordination sphere around potassium is shown. It is noted that the phenyl carbons contact the potassium. The interaction number of potassium is 8 (six sulfur and two carbon atoms)

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Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compounds **3b**, **4g**, **5f**, **8e**, and **8f**

Potassium 4-Methylbenzenecarbodithioate (**3b**)

Bond Lengths

C1−S1	1.710(3)	C3−C4	1.381(4)	C6−C7	1.377(4)	K1−S1$^{\#1}$	3.2555(9)	K1−C2$^{\#2}$	3.209(2)	K1−C5$^{\#2}$	3.93
C1−S2	1.671(2)	C4−C5	1.376(4)	K1−S1	3.2972(9)	K1−S1$^{\#2}$	3.4486(9)	K1−C7$^{\#2}$	3.110(3)	K1−C6$^{\#2}$	3.498(3)
C1−C2	1.488(3)	C5−C6	1.378(4)	K1−S2	3.354(1)	K1−S1$^{\#3}$	3.3448(9)	K1−C3$^{\#2}$	3.69	K1−K1$^{\#1}$	3.872(1)
C2−C3	1.390(3)	C5−C8	1.509(4)	K1−S2$^{\#1}$	3.323(1)	K1−S2$^{\#2}$	5.04	K1−C4$^{\#2}$	4.10		

Bond Angles

S1−C1−S2	123.0(2)	S1−K1−S2$^{\#1}$	84.84(2)	C1−S2−K1	85.92(9)	S2−K1−C2$^{\#2}$	95.25(5)	K1−C2$^{\#2}$−C7$^{\#2}$	73.3(1)
S1−K1−S2	53.07(2)	S2−C1−C2	119.3(2)	S1−C1−C2	117.6(2)	S2−K1−C7$^{\#2}$	100.50(5)	K1−C7$^{\#2}$−C2$^{\#2}$	81.2(1)
S1$^{\#1}$−K1−S2$^{\#1}$	53.69(2)	C1−S1−K1	87.19(8)	S2−K1−S1$^{\#3}$	123.48(3)	K1−S1$^{\#2}$−C1$^{\#2}$	82.47(8)	C2$^{\#2}$−K1−C7$^{\#2}$	25.44(6)
S1−K1−S1$^{\#1}$	107.57(2)								

Torsion Angles

S1−C1−C2−C3	146.9(2)	S2−C1−C2−C3	30.6(3)	K1−S1−C1−C2	148.1(2)	K1−S1−C1−S2	34.4(1)

Rubidium 4-Methylbenzenecarbodithioate (**4g**)

Bond Lengths

C1−S1	1.682(8)	C4−C5	1.37(1)	Rb1−S1$^{\#1}$	3.475(4)	Rb1$^{\#1}$−S1$^{\#1}$	3.458(4)	Rb1−C3$^{\#5}$	3.69(1)	Rb1−Rb1$^{\#1}$	4.376(3)
C1−C2	1.47(2)	C5−C6	1.48(2)	Rb1−S1$^{\#3}$	3.475(4)	Rb1$^{\#1}$−S1$^{\#3}$	3.458(4)	Rb1−C2$^{\#6}$	3.516(4)	Rb1−S1$^{\#4}$	3.94
C2−C3	1.36(1)	Rb1−S1	3.458(4)	Rb1$^{\#1}$−S1$^{\#2}$	3.475(4)	Rb1−C2$^{\#4}$	3.516(4)	Rb1−C3$^{\#7}$	3.69(1)	Rb1−S1$^{\#6}$	3.94
C3−C4	1.38(2)	Rb1$^{\#1}$−S1	3.475(4)	Rb1−S1$^{\#2}$	3.458(4)						

Bond Angles

S1−C1−S1$^{\#1}$	126(1)	S1$^{\#1}$Rb1−S1$^{\#3}$	101.4(1)	Rb1−S1−Rb$^{\#1}$	78.27(8)	Rb1−C2$^{\#4}$−C3$^{\#5}$	86.3(6)
S1−Rb1−S1$^{\#1}$	51.3(1)	S1$^{\#1}$−Rb1−C2$^{\#4}$	101.4(2)	RbI−S1−C1	84.8(4)	Rb1−C3$^{\#5}$−C2$^{\#4}$	80.3(5)
S1−Rb1−S1$^{\#2}$	102.1(1)	S1$^{\#2}$−Rb1−S1$^{\#3}$	51.3(1)	Rb1−S1$^{\#1}$−C1	84.3(4)	C2$^{\#6}$−Rb1−C3$^{\#7}$	22.5(2)
S1−C1−C2	116.9(5)						

Torsion Angles

S1−C1−C2−C3	48.7(6)	Rb1−S1$^{\#2}$−C1$^{\#2}$−C2$^{\#2}$	140.56(6)	Rb1$^{\#1}$−S1−C1−C2	140.74(6)
S1−C1−C2−C3$^{\#1}$	131.3(6)	Rb1−S1−C1−C2	140.56(6)	Rb1−S1−C1−S1$^{\#1}$	39.44(6)

Cesium 4-Methylbenzenecarbodithioate (**5f**)

Bond Lengths

C1−S1	1.688(3)	C4−C5	1.378(6)	Cs1−S1$^{\#1}$	3.594(2)	Cs1−S1$^{\#6}$	3.964(2)	Cs1−C2$^{\#4}$	3.529(2)	Cs1−C4$^{\#4}$	3.84
C1−C2	1.486(9)	C5−C6	1.50(1)	Cs1−S1$^{\#2}$	3.581(2)	Cs1−C2$^{\#6}$	3.529(2)	Cs1−C3$^{\#4}$	3.675(5)	Cs1−C4$^{\#5}$	3.76
C2−C3	1.390(5)	Cs1−S1	3.581(2)	Cs1−S1$^{\#3}$	3.594(2)	Cs1−C3$^{\#6}$	3.675(2)	Cs1−C3$^{\#5}$	3.561(5)	Cs1−C5$^{\#4}$	3.91
C3−C4	1.379(7)	Cs1$^{\#1}$−S1	3.594(2)	Cs1−S1$^{\#4}$	3.964(2)	Cs1−C3$^{\#7}$	3.561(5)	Cs1−Cs1$^{\#1}$	4.5932(9)		

Bond Angles

S1−C1−S1$^{\#1}$	125.9(4)	S1−Cs1−S1$^{\#4}$	86.889(6)	Cs1−S1−C1	85.6(2)	Cs1−Cs$^{\#5}$−C2$^{\#4}$	73.0(2)
S1−Cs1−S1$^{\#1}$	49.53(4)	S1−Cs−S1$^{\#6}$	135.61(1)	C1−S1−Cs1$^{\#1}$	85.2(2)	C2$^{\#4}$−Cs1−C3$^{\#4}$	22.13(8)
S1−Cs1−S1$^{\#2}$	100.63(5)	S1−C1−C2	117.1(2)	Cs1−C2$^{\#4}$−C1$^{\#4}$	104.9(1)	C2$^{\#4}$−Cs1−C3$^{\#5}$	22.61(9)
S1−Cs1−S1$^{\#3}$	80.18(4)	Cs1−S1−Cs1$^{\#1}$	79.61(3)	Cs1−C2$^{\#4}$−C3$^{\#5}$	84.8(2)		

Torsion Angles

S1−C1−C2−C3	130.0(3)	Cs1−S1$^{\#2}$−C1$^{\#2}$−C2$^{\#2}$	139.97(2)	Cs1$^{\#1}$−S1−C1−C2	140.11(2)
S1$^{\#1}$−C1−C2−C3	50.0(3)	Cs1−S1−C1−C2	139.97(2)	Cs1−S1−C1−S1$^{\#1}$	40.03(2)

Tetramethylammonium 4-Methylbenzenecarbodithioate (**8e**)

Bond Lengths

C1−S1	1.669(6)	[C1−S	1.675(6)][a]	[C1−C2	1.486(8)][a]	C3−C4	1.391(8)	C5−C6	1.387(9)	C2−C7	1.402(7)
C1−S2	1.675(5)	C1−C2	1.485(7)	C2−C3	1.388(7)	C4−C5	1.392(8)	C6−C7	1.377(8)	N−C9	1.481(6)

Bond Angles

S1−C1−S2	124.8(4)	[S1−C1−S2	125.4(4)][a]	S1−C1−C2	117.7(4)	S2−C1−C2	117.5(4)	[S1−C1−C2	117.8(5)][a]

Torsion Angles

S1−C1−C2−C3	43.3(7)

Tetramethylammonium 2-Methoxybenzenecarbodithioate (**8f**)

Bond Lengths

C1−S1	1.675(4)	C1−C2	1.496(6)	C3−C4	1.393(7)	C5−C6	1.358(8)	C2−C7	1.374(6)
C1−S2	1.671(4)	C2−C3	1.394(6)	C4−C5	1.373(7)	C6−C7	1.385(7)	N−C9	1.495(5)

Bond Angles

S1−C1−S2	125.2(3)	S1−C1−C2	116.5(3)	S2−C1−C2	118.1(3)

Torsion Angles

S1−C1−C2−C3	71.6(5)

[a] The values in square brackets represent the average of the three independent molecules.

(Figure 3, parts a and b). The two carbons are the ipso and ortho carbons of the phenyl ring of a neighboring molecule (K^+-η^2) [K1−C2$^{\#2}$ = 3.209(2) Å and K1−C7$^{\#2}$ = 3.110(3) Å, respectively] (Figure 3, part a; Figure 6, part a).[22,23] Such interaction between an aromatic carbon and alkali metals is the first example for the compounds having both carboxylate and chalcogenocarboxylate groups, although the following have been reported: η^2 and η^3 interactions between $Ph_2P(PhCH)K$ (K−

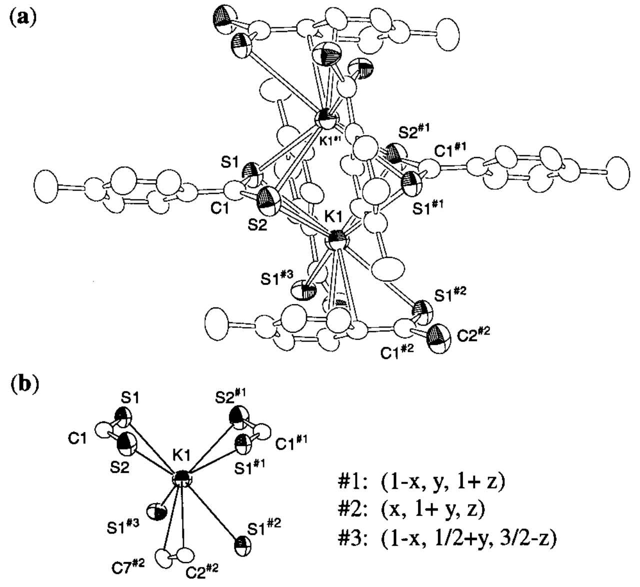

Figure 3. Packing (a) of potassium 4-methylbenzenecarbodithioate (**3b**) and coordination sphere (b) around the potassium. The atoms are drawn with 50% probability thermal ellipsoids. All hydrogen atoms have been omitted.

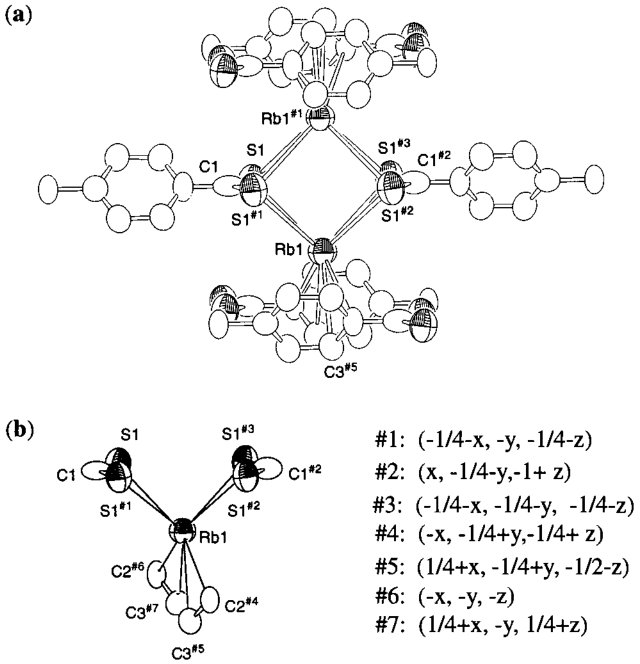

Figure 4. Packing (a) of rubidium 4-methylbenzenecarbodithioate (**4g**) and coordination sphere (b) around the rubidium. The atoms are drawn with 50% probability thermal ellipsoids. All hydrogen atoms have been omitted.

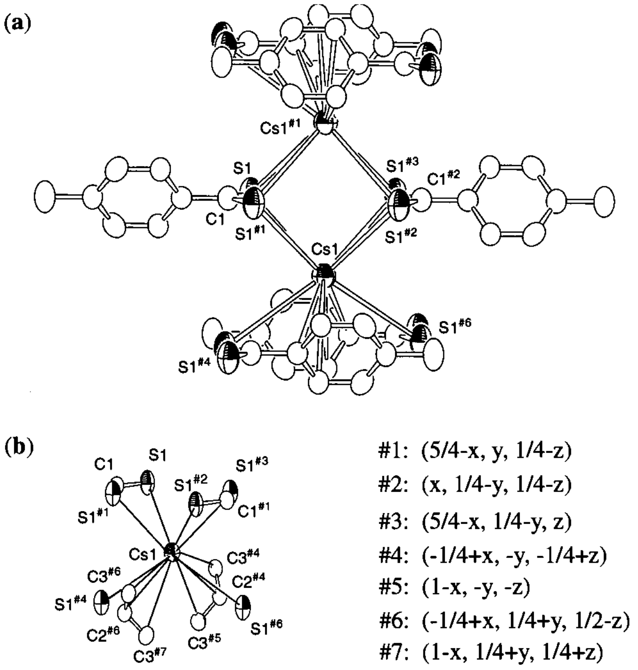

Figure 5. Packing (a) of cesium 4-methylbenzenecarbodithioate (**5f**) and coordination sphere (b) around the cesium. The atoms are drawn with 50% probability thermal ellipsoids. All hydrogen atoms have been omitted.

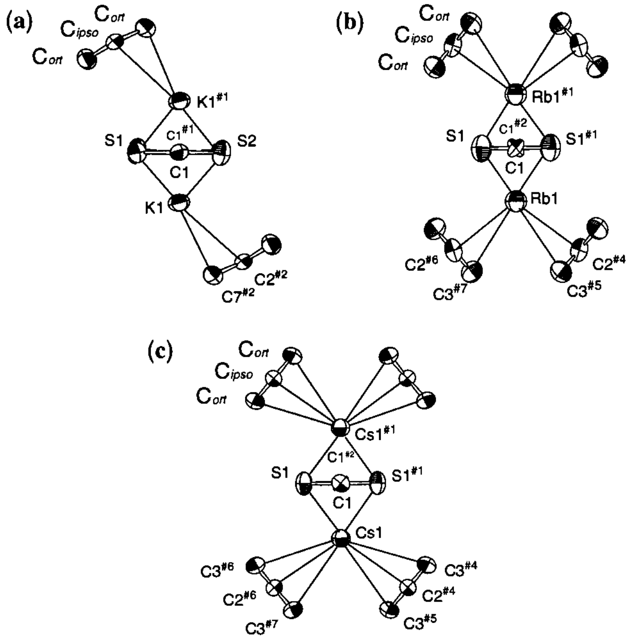

Figure 6. Front views (a, b, c) of the coordination of the ipso and ortho carbons to the potassium, rubidium, and cesium in the salts **3b**, **4g**, and **5f**, respectively. The phenyl rings which are bonded to the central dithiocarboxylate carbons (C1 and C1$^{\#1}$ or C1$^{\#2}$) are omitted.

C, 3.01∼3.25 Å);[24] (2-C_5H_4N)($Ph_2CHPh_2CHK\cdot 2THF$);[25] Ph_2-(2-C_5H_4N)CK·PMDTA·THF (K−C, 3.14−3.46 Å);[26] η^5 = dianion triple salt where K^+ interacts η^5 to the ring (K−C, 3.02−3.12 Å) which was obtained by reduction of tetraphenylbutadiene with potassium; η^6 = $Ph_3CK\cdot THF\cdot PMDTA$ (K−C, 3.14−3.25 Å);[27] $[(Ph_3P)_2(Ph_2PC_6H_4)RuH_2]_2C_{10}H_8\cdot Et_2O$ (K−C, 2.61−2.97 Å),[28] $(PhMe_2P)OsH_3K$ (K−C, 3.12−3.60 Å),[29] $[(2,6\text{-}i\text{-}Pr_2C_6H_3O)_4Nd]K$ (K−C, 3.12−3.47 Å),[30] η^6-benzene contacts,[31]

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alkali metal graphite intercalates (K−C, 3.05 Å),[32] [(PMDTA)-$PhCH_2M$] [M = K (M−C, 3.15−3.29 Å), M = Rb (Rb−C, 3.35−3.64 Å)],[33] *N*-rubidiocarbazole·PMDTA (Rb−C, 3.42−3.68 Å),[33] and $Ph_3CRb·M(PMDTA)_n$ (Rb−C, 3.35−3.64 Å).[26]

In the rubidium salt **4g** a dimer unit is around the 222 site. A 2-fold axis is through the rubidium atoms, and another is through the dithiocarboxylate groups of which C1, C2, C5, and C6 are on the axis. In contrast to the potassium salt **3b**, the two dithiocarboxylates groups of the rubidium salt **4g** are in the same plane and the two metals on the upper and lower sides are located almost in the center of the four sulfur atoms of the opposing dithiocarboxylate groups (Figure 2, parts b and b′). The C−S bond distances [1.682(8) and 1.682(8) Å] of the dithiocarboxyl group are equal, indicating electronic delocalization overall for the CSS group. The eight Rb−S distances [3.458(4) Å for Rb1−S1, Rb1−S1$^{\#2}$, Rb1$^{\#1}$−S1$^{\#1}$, and Rb1$^{\#1}$−S1$^{\#3}$; 3.475(4) Å for Rb1−S1$^{\#1}$, Rb1−S1$^{\#3}$, Rb1$^{\#1}$−S1, and Rb1$^{\#1}$−S1$^{\#2}$] of **4g** are very similar and do not differ from accepted values 3.442−3.494 Å which were found for rubidium thioacetate.[34] The interaction number of Rb with surrounding atoms is 8 (Figure 4, part b), Rb being surrounded by four sulfur and four carbon atoms which are ipso and ortho carbon atoms of the neighboring two phenyl rings which are close to the metal [Rb1−C2$^{\#4}$ = 3.516(4) Å, Rb1−C3$^{\#5}$ = 3.69(1) Å, Rb1−C2$^{\#6}$ = 3.516(4) Å, Rb1−C3$^{\#7}$ = 3.69(1) Å, respectively (Rb^+-η^2)] (Figures 4, and 6, part b). The cesium salt **5f** is isostructural with **4g**, and the geometries of both salts are very similar (Figure 2, parts c and c′). The interaction number of the cesium is 12 (Figure 5, parts a and b), Cs being surrounded by six sulfur atoms, four of which are those in the same plane involving two-faced dithiocarboxyl groups, and by six carbon atoms of two tolyl groups of the neighboring molecules, in which one ipso and two ortho carbon atoms are close to the metal [Cs1−C2$^{\#4}$ = 3.529(2) Å, Cs1−C3$^{\#4}$ = 3.675(5) Å, and Cs1−C3$^{\#5}$ = 3.561(5) Å, and Cs1−C2$^{\#6}$ = 3.529(2) Å, Cs1−C3$^{\#6}$ = 3.675(5) Å, and Cs1−C3$^{\#7}$ = 3.561(5) Å, respectively (Cs^+-η^3)] (Figures 5 and 6, part c). The distances of Cs−C_{ipso} are shorter than those of Cs−C_{ortho}. It is noted that the distances between meta or para carbons and cesium (Cs1−C4$^{\#4}$, Cs1−C4$^{\#5}$, Cs1−C5$^{\#4}$, Cs1−C4$^{\#6}$, Cs1−C4$^{\#7}$, Cs1−C5$^{\#6}$) are 3.76−3.91 Å, suggesting a weak interaction.[31d,f] The four Cs−S distances (Cs1−S1, Cs1−S1$^{\#1}$, Cs1−S1$^{\#2}$, Cs1−S1$^{\#3}$) are equivalent [3.581(2)−3.594(2) Å], which agrees with the values for cesium 1,1-dithiooxalate,[35] and are shorter than the values calculated from the sum of the ionic radii of sulfur[36] and cesium atoms,[37] respectively. In contrast, the distances of Cs1−S1$^{\#4}$ [3.964(2) Å] and Cs1−S1$^{\#6}$ [3.964(2) Å] are much longer. The interaction (coordination?) number of these ipso and ortho carbons with hydrogen, carbons, and metals is 4. The coordination number of the sulfur atom is 3 (two potassiums and one carbon) and 5 (four potassiums and one carbon) for **3b**, 3 (two rubidiums and one carbon) for **4g**, and 4 (three cesiums and one carbon) for **5f**, respectively.

Table 4. Deviation of the Metal Cations from the CSS Plane in Alkali Metal Dithiocarboxylates

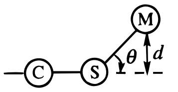
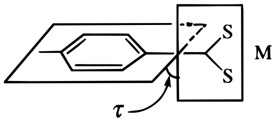
$4\text{-}MeC_6H_4CSSM$	M	θ (°)	d (Å)
	Na (**7g**)	<14.7 (?)	0.448
	K (**3b**)	38.8	1.863
	Rb (**4g**)	44.4	2.188
	Cs (**5f**)	44.8	2.297

Table 5. Dihedral Angles between the Phenyl Ring and the CSS Plane in Alkali Metal 4-Methylbenzenecarbodithioates

$4\text{-}MeC_6H_4CSSM$	M	τ (°)
	Na (**7g**)	< 21.6
	K (**3b**)	31.2
	Rb (**4g**)	48.7
	Cs (**5f**)	50.0
	NMe_4 (**8e**)	49.3^a
	$2\text{-}MeOC_6H_4CSSNMe_4$ (**8f**)	70.9

^{a}The average value of three independent molecules.

The angles (θ) between the dithiocarboxylate plane [CSS] and the plane [SSM] and the distances (d) between the [CSS] plane and the alkali metal (M) of the salts **7g**, **3b**, **4g**, and **5f** are listed in Table 4. The angle of the potassium is small compared with those of the rubidium **4g** and cesium **5f**. The significantly longer K−K [3.872(1) Å], Rb−Rb [4.376(4) Å], and Cs−Cs distances [4.593(1) Å] in the dimeric units of **3b**, **4g**, and **5f** related to the values (3.04 Å for K, 3.32 Å for Rb, and 3.62 Å for Cs)[37] calculated from the sum of the ionic radii of these metals clearly indicate the absence of bonding between the two metals. Table 5 shows the dihedral angles (τ) of the dithiocarboxyl and the aromatic ring planes. The angles increase in the order K, Rb, and Cs. The magnitude of these angles might be influenced by coordination of the aromatic ring to the metals.

The successful single crystallization of potassium, rubidium, and cesium salts prompted us to prepare the single crystals of the corresponding lithium salt **6b** and sodium salt **7g**. Despite extensive attempts to crystallize a variety of lithium dithiocarboxylates **6** and sodium dithiocarboxylates **7**, it was difficult to obtain single crystals suitable for X-ray crystallography. Due to the poor crystal quality, the X-ray structure analysis of sodium 4-methylbenzenecarbodithioate **(7g)** revealed the presence of $CH_3C_6H_4CS_2Na_{0.36}$ at the level of R/R_w = 0.060/0.066. Therefore, we could not discuss the geometry in detail, although **7g** appeared to be a monomer and there appeared the possibility of some localization of the negative charge on the dithiocarboxyl group, which was also suggested from the structure of **3b**.

To our knowledge, no crystal analysis of ammonium dithiocarboxylates has been reported. Since the first isolation of crystalline ammonium dithiocarboxylates in 1972,[38] a variety of ammonium dithiocarboxylates have been prepared.[39−41] However, quaternary ammonium dithiocarboxylate has been limited to only tetramethylammonium 2-methylpropanecarbodithioate and benzenecarbodithioate[42] and tetraethylammonium 2-hydroxybenzenecarbodithioate[43] and tetrathiooxalates,[44]

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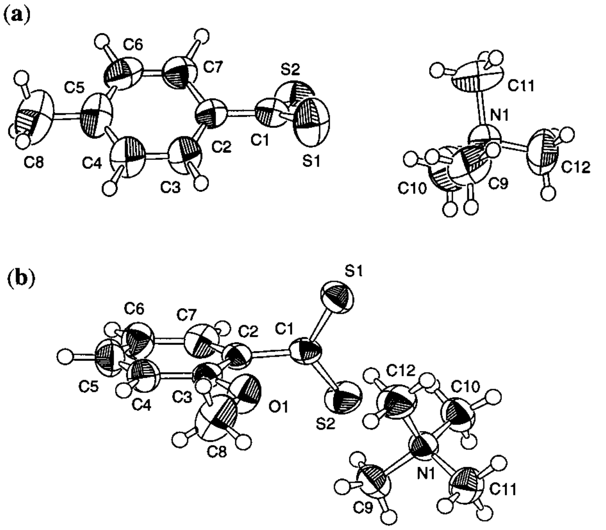
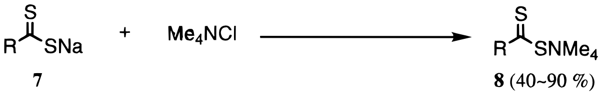


Figure 7. ORTEP drawings of tetramethylammonium 4-methyl- (**8e**) (a) and 2-methoxybenzenecarbodithioates (**8f**) (b). The atoms are drawn with 50% probability thermal ellipsoids.

Scheme 3



No.	R	No.	R
8a	C_2H_5	**8e**	$4\text{-}CH_3C_6H_4$
8b	*i*-C_3H_7	**8f**	$2\text{-}CH_3OC_6H_4$
8c	C_6H_5	**8g**	$4\text{-}CH_3OC_6H_4$
8d	$2,4,6\text{-}(CH_3)_3C_6H_2$	**8h**	$4\text{-}ClC_6H_4$

most likely due to the difficulty of preparation and purification. Their X-ray structural analyses have not been described. Recently, we have found that alkali metal tellurocarboxylates readily react with tetramethylammonium chloride to give the corresponding ammonium arenecarbotelluroates.[8b] This prompted us to prepare tetramethylammonium dithiocarboxylates. After several attempts, we succeeded in preparing a series of tetramethylammonium dithiocarboxylates **8** in 40−90% yields (Scheme 3). The obtained tetramethylammonium salts **8** are stable thermally and toward oxygen. Upon exposure to air, no appreciable changes were observed for at least 1 week, and they can be stored at 0 °C under nitrogen for over 6 months. The ORTEP drawings of tetramethylammonium 4-methyl- (**8e**) and 2-methoxybenzenecarbodithioate (**8f**) are shown in Figure 7. Final atomic positional parameters are listed in Table 2. Selected bond distances and angles are shown in Table 3. For **8e**, three independent molecules were present in one asymmetric unit. As opposed to the above-mentioned heavy alkali metal salts, **8e** and **8f** exist as monomers, in which the tetramethylammonium cation is located outside the plane of the dithiocarboxyl group (Figure 7). The C−S bond lengths of the dithiocarboxylate groups of both salts are almost equal, 1.672(4)−1.678(5) Å, indicating the localization of negative charge on the dithiocarboxyl group. The dihedral angles of the dithiocarboxyl plane and the aromatic ring in **8e** and **8f** are 49.3° and 70.9°, respectively, larger than those of the corresponding alkali metal salts.

Table 6. IR and ^{13}C NMR Spectra of Alkali Metal Dithiocarboxylates

RCSSM			
R	M	$\nu_{\mathrm{asym}}CS_2$[a] (cm^{-1})	$^{13}C{=}S$[b] (δ)
i-C_3H_7	Li (**6a**)	952	275.8
	Na (**7a**)	956	275.6
	K (**3a**)	949	277.2
	Rb (**4b**)	949	277.0
	Cs (**5c**)	953	276.7
$4\text{-}CH_3C_6H_4$	Li (**6b**)	1028	256.0
	Na (**7g**)	1015	256.0
	K (**3b**)	1015	256.1
	Rb (**4g**)	1008	256.1[c]
	Cs (**5f**)	1025	249.9[c]

[a] KBr. [b] CD_3OD. [c] DMSO-d_6.

Table 7. Reaction[a] of Alkali Metal Dithiocarboxylates $4\text{-}CH_3C_6H_4CSSM$, **3**−**7**, with Methyl Iodide

run	M	temp (°C)	yield of **9** (%)
1	Li (**6b**)	0	59
2	Na (**7g**)	0	86
3	K (**3b**)	0	92
4	Rb (**4g**)	0	29
5	Cs (**5f**)	0	22
6	Li (**6b**)	20	91
7	Na (**7g**)	20	97
8	K (**3b**)	20	94
9	Rb (**4g**)	20	35
10	Cs (**5f**)	20	22

[a] For 30 min.

Spectra. The ^{13}C NMR spectra of alkali metal dithiocarboxylates have not yet been described in the literature, although IR, electron, and ^{1}H NMR spectra have been reported.[6] The stretching frequencies and the carbon-13 chemical shifts of the dithiocarboxyl group of alkali metal 1-methylethane- and 4-methylbenzenecarbodithioates (**3**−**7**) are shown in Table 6. The dithiocarboxyl carbon signals are observed in the range δ 250−277. The alkali metal cations appeared to have very little influence on these signals.

Reaction. To our knowledge, there has been no systematic investigation concerning the reactivity of alkali metal dithiocarboxylates.[45] To compare the reactivities, the reactions of alkali metal 4-methylbenzenecarbodithioates with alkyl and organotin halides were carried out. The lithium **6**, sodium **7**, and potassium salts **3** readily reacted with methyl iodide at room temperature to give the corresponding methyl ester **9** in quantitative yields, while the reaction with rubidium **4** and cesium salts **5** resulted in low yields. At 0 °C, however, the reactivity of **6** to methyl iodide substantially decreased compared with those of the corresponding sodium **7** and potassium salts **3** (Table 7). The reaction with triorganotin chlorides at 20 °C led to high yields of the corresponding triorganotin dithioesters **10** (Scheme 4).

Summary. We have developed an alternative method for preparing heavier alkali metal dithiocarboxylates by reaction of dithiocarboxylic acid or its trimethylsilyl ester with the corresponding alkali metal fluorides. In the solid state, potassium, rubidium, and cesium 4-methylbenzenecarbodithioates have a dimeric structure in which the alkali metal cations are located on the upper and lower sides of the plane involving the two opposing dithiocarboxylate groups. Each of the rubidium and cesium cations is located in the center of the four sulfur

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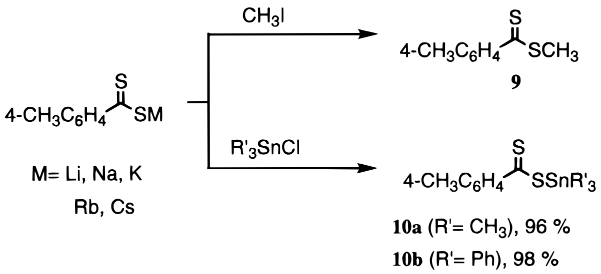
Table 8. ^{13}C NMR Spectral Data for Trimethylsilyl Dithiocarboxylates **1**, Dithiocarboxylic Acids **2**, Lithium Dithiocarboxylate **6b**, and Sodium Dithiocarboxylate **7g**

no.	compd	^{13}C NMR^a (δ)
1a	$CH_3CSSSiMe_3$	4.5 (CH_3Si), 44.3 (CH_3), 238.3 (C=S)
1b	$C_2H_5CSSSiMe_3$	4.1 (CH_3Si), 20.8 (CH_3), 49.3 (CH_2), 245.3 (C=S)
1c	i-$C_3H_7CSSSiMe_3$	4.2 (CH_3Si), 24.0 (CH_3), 53.6 (CH), 252.0 (C=S)
1d	c-$C_6H_{11}CSSSiMe_3$	4.3 (CH_3), 25.6 (CH_2), 26.0 (CH_2), 34.5 (CH_2), 64.1 (CH), 250.7 (C=S)
2a	CH_3CSSH	40.1 (CH_3), 230.6 (C=S)
2b	C_2H_5CSSH	14.6 (CH_3), 46.6 (CH_2), 239.7 (C=S)
2c	i-C_3H_7CSSH	23.9 (CH_3), 50.8 (CH), 246.1 (C=S)
2d	c-$C_6H_{11}CSSH$	26.8, 27.2, 36.1, 68.9 (CH, CH_2), 274.0 (C=S)
2e	C_6H_5CSSH	126.8, 128.6, 133.2 (Ar), 225.4 (C=S)
2f	2-$CH_3C_6H_4CSSH$	21.5 (CH_3), 113.4, 113.7, 127.9, 128.5, 129.4, 136.7 (Ar), 221.9 (C=S)
2g	4-$CH_3C_6H_4CSSH$	20.7 (CH_3), 126.8, 127.0, 129.1, 140.0, 144.7 (Ar), 224.6 (C=S)
2h	4-$CH_3OC_6H_4CSSH$	55.7 (CH_3O), 113.5, 129.4, 136.6, 164.4 (Ar), 222.3 (C=S)
2i	4-ClC_6H_4CSSH	128.1, 128.6, 140.0, 141.4 (Ar), 223.1 (C=S)
2j	2,4,6-$(CH_3)_3C_6H_2CSSH$	19.1 (CH_3), 21.0 (o-CH_3), 128.6, 131.2, 138.1, 146.2 (Ar), 246.0 (C=S)
6b	4-$CH_3C_6H_4CSSLi^b$	21.3 (CH_3), 127.8, 128.2, 140.5, 151.9 (Ar), 256.0 (C=S)
7g	4-$CH_3C_6H_4CSSNa^b$	21.2 (CH_3), 127.9, 128.2, 140.7, 151.8 (Ar), 256.0 (C=S)

^{a} $CDCl_3$. ^{b} CD_3OD.

Scheme 4



atoms of the two dithiocarboxylate groups. In contrast to these heavier alkali metal salts, the geometry of the corresponding aromatic sodium dithiocarboxylate is significantly different, fundamentally a monomer. The coordination sphere of the cations of the K, Rb, and Cs salts is completed by two chelating dithiocarboxylate ligands and by one or two aromatic rings in which the ipso and ortho carbons are close to the cation, indicating the presence of nonbonding interaction. The C−S distances of the dithiocarboxylate group in the sodium and potassium salts are different, which seems to indicate some electronic localization on the dithiocarboxyl group. On the other hand, the C−S distances of the rubidium and cesium salts are equal, indicating a high degree of electronic delocalization on the dithiocarboxylate group.

Experimental Section

The details regarding the generic instruments given in ref 8b apply as well to this study.

Materials. Dithiocarboxylic acids **2** were prepared by acidolysis of the corresponding piperidinium dithiocarboxylates[38,39] with concentrated hydrogen chloride. Trimethylsilyl dithiocarboxylates **1**[46] and lithium **6**[6b] and sodium dithiocarboxylates **7**[6a] were prepared by the method described in the literature. Additional spectral data of **1**, **2**, and the lithium **6b** and sodium dithioates **7g** are shown in Table 8. 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 °C before use. The following solvents were purified under argon 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. Ethanol was refluxed and distilled on magnesium flakes. All manipulations were carried out under argon.

X-ray Measurements. The measurement was carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). A Rigaku XR-TCS-2-050 temperature controller was used for low-temperature measurement. All of the structures were solved and refined using the teXsan crystallographic software package on an IRIS Indigo computer. The crystals of **3b**, **4g**, **5f**, **7g**, **8e**, and **8f** were cut from the grown needles. The crystals were mounted on a glass fiber. 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 no decay was detected. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections (DIFABS[47]) were also applied. The structures was solved by direct methods using SHELXS86[48] for **3b**, **4g**, **5f**, **8e**, and **8f** and SAPI 91[49] for the Na salt **7g** and expanded using DIRDIF92.[50] Scattering factors for neutral atoms were from Cromer and Waber,[51] and anomalous dispersion[52] was used. The function minimized was $\sum w(|F_o| - |F_c|)^2$, 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 for **3b**, **4g**, **5f**, **8e**, and **8f**. For **7g**, non-hydrogen atoms except for the sodium atom were refined anisotropically. 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 Growth for X-ray Diffraction. Solvents: $EtOH/Et_2O$ = 0.3 mL/1.5 mL for **3b** and **4g**, $EtOH/Et_2O$ = 0.3 mL/1.0 mL for **5f**, $MeOH/Et_2O$ = 0.3 mL/1.0 mL for **7g**, $EtOH/Et_2O$ = 0.2 mL/1.0 mL for **8e** and CH_3CN/hexane/ether = 0.3 mL/0.8 mL/0.1 mL for **8f**. The diethyl ether (1−2 mL) was layered on the top of the alcohols or acetonitrile solution containing the salts. The single crystals of these salts were grown for 0.5−2 days at −20 °C.

Synthesis of Potassium 3, Rubidium 4, and Cesium Dithiocarboxylates 5. The preparations of rubidium 1-methylethanecarbodithioate **(4c)** (method A), rubidium benzenecarbodithioate (**4e)** (method B), cesium 1-methylethanecarbodithioate (**5c)** (method A), and cesium benzenecarbodithioate (**5e**) (method B) are described in detail as typical

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procedures. Their yields are shown in Table 1. The structures of **3**−**5** were confirmed by comparison of spectral data with those of authentic samples. The IR spectra were exactly consistent with those of authentic samples prepared by the reactions of the dithiocarboxylic acids with the corresponding metal hydrides or acetates.[4]

Potassium 1-Methylethanecarbodithioate (3a). Method A: yellow plates. Mp: 178−180 °C dec. IR (KBr): 949 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.24 (d, 6H, CH$_3$), 3.59 (sept, 1H, CH). ^{13}C NMR (CD$_3$OD): δ 21.3 (CH$_3$), 58.0 (CH$_2$), 277.2 (C=S).

Potassium 4-Methylbenzenecarbodithioate (3b). Method B: dark red crystals, 0.298 g (44%). Mp: 210−211 °C dec. IR (KBr): 1015 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 2.31 (s, 3H, CH$_3$), 7.02−8.11 (m, 4H, Ar). ^{13}C NMR (CD$_3$OD): δ 21.3, 127.2, 128.2, 140.6, 151.7 (Ar), 256.1 (C=S).

Rubidium Dithioacetate (4a). Method A: yellow plates, 0.304 g (72%). Mp 201−203 °C dec. IR (KBr): 873 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.04 (s, 3H, CH$_3$). ^{13}C NMR (CD$_3$OD): δ 50.1 (CH$_3$), 264.0 (C=S).

Rubidium Dithiopropanoate (4b). Method A: yellow plates [recrystallization from ethanol/ether (1:3)]. Mp 186−188 °C dec. IR (KBr): 934 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.35 (t, 3H, CH$_3$), 3.14 (q, 2H, CH$_2$). ^{13}C NMR (CD$_3$OD): δ 17.3 (CH$_3$), 55.7 (CH$_2$), 274.0 (C=S).

Rubidium 1-Methylethanecarbodithioate (4c). Method A. A solution of trimethylsilyl 1-methylethanecarbodithioate (2.00 g, 10.4 mmol) in ether (5 mL) was added to rubidium fluoride (0.728 g, 6.97 mmol), and the mixture was stirred for 2 h at 20 °C. The resulting precipitates were filtered out and washed with ether (3 × 3 mL). The precipitates were dissolved in acetonitrile (5 mL), and the insoluble part was filtered out. Evaporation of the acetonitrile under reduced pressure and recrystallization from a mixed solvent (8 mL) of ethanol and ether (1:3) at −20 °C for 17 h gave rubidium 1-methylethanecarbodithioate (**4c**) as yellow plates: 1.22 g (85%). Mp 189−191 °C dec. IR (KBr): 949 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.24 (d, 6H, CH$_3$), 3.59 (sept, 1H, CH). ^{13}C NMR (CD$_3$OD): δ 25.3 (CH$_3$), 58.1 (CH$_2$), 270.0 (C=S). UV/vis (EtOH): 340, 459 nm. Anal. Calcd for C$_4$H$_7$S$_2$Rb (204.69): C, 23.47; H, 3.45. Found: C, 23.47; H, 3.56.

Method B: yellow plates [recrystallization from ethanol/ether (1:3) at −20 °C, for 18 h]; 77%.

Rubidium Cyclohexanecarbodithioate (4d). Method A: yellow plates [recrystallization from ethanol/ether (1:3)], 1.09 g (90%). Mp 195−196 °C dec. IR (KBr): 967 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.18−1.19 (m, 10H, CH$_2$), 3.24 (m, 1H, CH). ^{13}C NMR (CD$_3$OD): δ 26.8, 27.2, 36.1, 68.9 (CH, CH$_2$), 274.0 (C=S).

Rubidium Benzenecarbodithioate (4e). Method B: A solution of benzenecarbodithioic acid (0.99 g, 4.14 mmol) in ether (5 mL) was added to rubidium fluoride (0.207 g, 1.98 mmol), and the mixture was stirred for 2 h at 20 °C. The resulting precipitates were filtered out and washed with ether (3 × 3 mL). The precipitates were dissolved in ethanol (8 mL), and the insoluble part was filtered out. The ethanol was evaporated under reduced pressure. The residue was dissolved in ethanol (3 mL), ether (6 mL) was slowly added, and the mixture was allowed to stand at −20 °C for 17 h. Filtration of the resulting crystals gave 0.231 g (49%) of rubidium benzenecarbodithioate (**4e**) as dark red needles: mp 200−202 °C dec. IR (KBr): 1201 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 7.18−8.13 (m, 5H, Ar). ^{13}C NMR (CD$_3$OD): δ 127.5 (*p*-C), 127.7 (*m*-C), 130.2 (*o*-C), (*ipso*-C), 276.6 (C=S). Anal. Calcd for C$_7$H$_5$S$_2$Rb (238.70): C, 35.22; H, 2.11. Found: C, 34.93; H, 2.09.

Rubidium 2-Methylbenzenecarbodithioate (4f). Method B: brown crystals [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 237−239 °C dec. IR (KBr): 1023 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 2.42 (s, 3H, CH$_3$), 7.00−7.14 (m, 4H, Ar). ^{13}C NMR (CD$_3$OD): δ 19.5 (CH$_3$), 125,1, 126.0, 126.5, 130.8, 159.9 (Ar), 256.1 (C=S). Anal. Calcd for C$_8$H$_7$S$_2$Rb (252.72): C, 38.02; H, 2.79. Found: C, 37.76; H, 2.89.

Rubidium 4-Methylbenzenecarbodithioate (4g) Method B: red brown crystals [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 223−225 °C. IR (KBr): 1008 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 2.30 (s, 3H, CH$_3$), 7.03 (d, 2H, Ar), 8.13 (d, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 21.3 (CH$_3$), 127.8 (*p*-C), 128.3 (*m*-C), 140.9 (*o*-C), 151.6 (*ipso*-C), 256.1 (C=S). Anal. Calcd for C$_8$H$_7$S$_2$Rb (252.72): C, 38.02; H, 2.79. Found: C, 37.73; H, 3.04.

Rubidium 4-Methoxybenzenecarbodithioate (4h). Method B: red crystals [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 193−194 °C dec. IR (KBr): 1018 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.30 (s, 3H, CH$_3$), 6.76 (d, 2H, Ar), 8.35 (d, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 55.8 (CH$_3$O), 112.6 (*p*-C), 129.9 (*m*-C), 146.5 (*o*-C), 163.0 (*ipso*-C), 254.0 (C=S). Anal. Calcd for C$_8$H$_7$OS$_2$Rb (268.73): C, 37.76; H, 2.63. Found: C, 37.77; H, 2.81.

Rubidium 4-Chlorobenzenecarbodithioate (4i). Method B: red brown crystals [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 225−226 °C dec. IR (KBr): 1008 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 7.19 (d, 2H, Ar), 8.18 (d, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 127.6 (*p*-C), 129.1 (*m*-C), 136.3 (*o*-C), 152.7 (*ipso*-C), 254.2 (C=S). Anal. Calcd for C$_7$H$_4$S$_2$ClRb (273.14): C, 30.44; H, 1.48. Found: C, 30.43; H, 1.47.

Rubidium 2,4,6-Trimethylbenzenecarbodithioate (4j). Method B: reddish orange crystals [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 200−202 °C dec. IR (KBr): 1013 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 2.20 (s, 6H, 2,6-CH$_3$), 2.35 (s, 3H, 4-CH$_3$), 6.73 (s, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 18.4 (2,6-CH$_3$), 19.4 (4-CH$_3$), 128.8 (*p*-C), 130.2 (*m*-C), 134.8 (*o*-C), 156.8 (*ipso*-C), 263.8 (C=S).

Cesium Dithioacetate (5a). Method B: orange plates [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 201−203 °C dec. IR (KBr): 875 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.03 (s, 3H, CH$_3$). ^{13}C NMR (CD$_3$OD): δ 50.3 (CH$_3$), 263.9 (C=S).

Cesium Dithiopropanoate (5b). Method A: orange plates [recrystallization from ethanol/ether (1:2) at −20 °C]. Mp: 169−171 °C dec. IR (KBr): 934 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.13 (t, 3H, CH$_3$), 3.13 (q, 2H, CH$_2$). ^{13}C NMR (CD$_3$OD): δ 17.3 (CH$_3$), 55.7 (CH$_2$), 274.0 (C=S).

Cesium 1-Methylethanecarbodithioate (5c). Method A. A solution of trimethylsilyl 1-methylethanecarbodithioate (2.28 g, 11.8 mmol) in ether (5 mL) was added to cesium fluoride (1.020 g, 6.70 mmol), and the mixture was stirred for 2 h at 20 °C. The resulting precipitates were filtered out and washed with ether (3 × 3 mL). The precipitates were dissolved in acetone (5 mL), and the insoluble part was filtered out. Evaporation of the acetonitrile under reduced pressure and recrystallization from a mixed solvent (4.5 mL) of ethanol and ether (1:2) at −20 °C for 15 h gave cesium 1-methylethanecarbodithioate (**5c**) as yellow plates: 1.55 g (92%). Mp: 155−159 °C dec. IR (KBr): 953 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.24 (d, 6H, CH$_3$), 3.58 (sept, 1H, CH). ^{13}C NMR (CD$_3$OD): δ 25.3 (CH$_3$), 58.1 (CH), 276.6 (C=S).

Method B: yellow plates [recrystallization from ethanol/ether (1:2) at −20 °C, for 20 h]; 77%.

Cesium Cyclohexanecarbodithioate (5d). Method A: yellow plates [recrystallization from ethanol/ether (1:3)]. Mp: 195−196 °C dec. IR (KBr): 986 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.27−1.91 (m, 10H, CH$_2$), 3.23 (m, 1H, CH). ^{13}C NMR (CD$_3$OD) δ 27.1, 27.5, 36. 3 (CH$_2$), 69.4 (CH), 275.0 (C=S).

Cesium Benzenecarbodithioate (5e). Method B. A solution of benzenecarbodithioic acid (0.87 g, 4.18 mmol) in ether (5 mL) was added to cesium fluoride (0.292 g, 1.92 mmol), and the mixture was stirred for 3 h at 20 °C. The resulting precipitates were filtered out and washed with ether (3 × 3 mL). The precipitates were dissolved in ethanol (15 mL), and the insoluble part was filtered out. The ethanol was removed under reduced pressure. The residue was dissolved in ethanol (20 mL), then ether (20 mL) was added, and the mixture was allowed to stand at −20 °C for 15 h. Filtration of the resulting crystals gave 0.395 g (72%) of cesium benzenecarbodithioate (**5e**) as dark red granulates. IR (KBr): 1201 (νCSS) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.15−8.14 (m, 5H, Ar). ^{13}C (CD$_3$OD): δ 126.0 (*p*-C), 126.2 (*m*-C), 127.8 (*o*-C), 152.8 (*ipso*-C), 250.5 (C=S).

Cesium 4-Methylbenzenecarbodithioate (5f). Method B: red brown granulated crystals [recrystallization from ethanol/ether (1:1) at −20 °C overnight]. Mp: 244−246 °C dec. IR (KBr): 1025 (νCSS) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.30 (s, 3H, CH$_3$), 7.01 (d, 2H, Ar), 8.09 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6): δ 20.7 (CH$_3$), 126.4 (*p*-C), 126.6 (*m*-C), 137.5 (*o*-C), 149.9 (*ipso*-C), 249.9 (C=S).

Cesium 4-Methoxybenzenecarbodithioate (5g). Method B: red granulated crystals [recrystallization from ethanol/ether (1:1) at −20 °C overnight]. Mp: 232−234 °C dec. IR (KBr): 1026 (νCSS) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.75 (s, 3H, OCH$_3$), 6.70 (d, 2H, Ar), 8.33 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6): δ 55.8 (CH$_3$O), 111.0 (*p*-C), 128.2 (*m*-C), 145.0 (*o*-C), 160.2 (*ipso*-C), 248.0 (C═S).

Cesium 4-Chlorobenzenecarbodithioate (5h). Method B: red brown crystals [recrystallization from ethanol/ether (1:2) at −20 °C for 15 h]. Mp 246−248 °C dec. IR (KBr): 1032 (νCSS) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.19 (d, 2H, Ar), 8.20 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6): δ 126.0 (*p*-C), 128.0 (*m*-C), 133.2 (*o*-C), 150.9 (*ipso*-C), 247.7 (C═S).

Cesium 2,4,6-Trimethylbenzenecarbodithioate (5i). Method B: reddish orange granulated crystals [recrystallization from ethanol/ether (1:2) at −20 °C overnight]. Mp: 233−234 °C dec. IR (KBr): 1034 (νCSS) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.16 (s, 6H, 2,6-CH$_3$), 2.17 (s, 3H, 4-CH$_3$), 7.19 (d, 2H, Ar), 8.20 (d, 2H, Ar). ^{13}C (CD$_3$OD): δ 18.8 (CH$_3$), 18.9 (CH$_3$), 127.2 (*p*-C), 128.4, 131.3 (*o*-C), 156.1 (*ipso*-C), 258.7 (C═S).

Reaction of Dithiocarboxylic Acids with Alkali and Alkali Earth Metal Chlorides, Bromides, and Iodides or with Lithium and Sodium Fluorides. General Procedures. 1-Methylethanecarbodithioic 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. By filtration of the insoluble part and washing with ether (3 × 3 mL), the alkali metal except for KF and alkali earth metal halogenides were recovered in quantitative yield, respectively.

Tetramethylammonium Dithiocarboxylates. The preparation of tetramethylammonium 4-methylbenzenecarbodithioate (**8e**) is shown in detail as a typical procedure.

Tetramethylammonium Dithiopropanoate (8a): orange yellow needles [recrystallization from acetonitrile/ether (1:2) at −20 °C], 0.276 g (64%). Mp: 145−150 dec. IR (KBr): 949, 778 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.34 (t, J = 7.5 Hz, 3H, CH$_3$), 3.12 (q, J = 7.5 Hz, 2H, CH$_2$), 3.27 (s, 12 Hz, NMe). ^{13}C NMR (CD$_3$OD): δ 17.3 (CH$_3$), 55.8 (CH$_2$), 56.0 (NMe), 269.8 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 291 (4.08), 340 (4.27), 469 (2.81), 641 (2.77).

Tetramethylammonium 1-Methyldithiobutanoate (8b): orange yellow needle crystals [recrystallization from acetonitrile/ether (1:1) at −20 °C], 0.409 g (76%). Mp: 168−173 °C dec. IR (KBr): 949, 867 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 1.21(d, J = 6.8 Hz, 6H, CCH$_3$), 3.23 (s, 12 Hz, NMe) 3.57 (sept, J = 6.8 Hz, 1H, CH). ^{13}C NMR (CD$_3$OD): δ 25.3 (CH$_3$), 56.0 (NMe), 58.1 (CH), 275.4 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 271 (3.85), 340 (4.29), 469 (2.84), 640 (2.81). Anal. Calcd for C$_8$H$_{19}$NS$_2$ (193.36): C, 49.64; H, 9.84. Found: C, 49.69; H, 9.90.

Tetramethylammonium Benzenecarbodithioate (8c): reddish orange crystals [recrystallization from acetonitrile/ether (5:6) at −20 °C], 0.295 g (38%). Mp: 160−165 °C dec. IR (KBr): 1014 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.12 (s, 12H, NMe), 7.20 (t, J = 7.6 Hz, 1H, Ar), 7.22 (t, J = 7.6 Hz, 2H, Ar), 8.13 (d, J = 7.6 Hz, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 55.9 (NCH$_3$), 127.6, 127.8, 130.2, 154.8 (Ar), 256.0 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 276 (4.28), 361 (3.91), 502 (2.33).

Tetramethylammonium 2,4,6-Trimethylbenzenecarbodithioate (8d): dark red crystals [recrystallization from acetonitrile/ether (1:1) at −20 °C], 0.142 g (63%). Mp 190−192 °C. IR (KBr): 950, 880 (νCSS) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.20 (s, 3H, *p*-CH$_3$Ar), 2.35 (s, 6H, *o*-CH$_3$Ar), 3.19 (s, 12H, NMe), 6.73 (s, 2H, Ar). ^{13}C NMR (CDCl$_3$): δ 19.4 (CH$_3$), 21.0 (CH$_3$), 55.9 (NCH$_3$), 128.8, 130.2, 134.7, 156.8 (*ipso*-C, Ar), 271.3 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 252 (3.95), 343 (4.35), 475 (2.29), 641 (2.94).

Tetramethylammonium 4-Methylbenzenecarbodithioate (8e). Sodium 4-methylbenzencarbodithioate (0.339 g, 1.78 mmol) and tetramethylammonium chloride (0.19 g, 1.8 mmol) were stirred in acetonitrile (15 mL) at 20 °C for 2 h. Removal of sodium chloride by filtration and then evaporation of the filtrate under reduced pressure gave a red pink solid as microcrystals. The solid was dissolved in acetonitrile (5 mL), and then the mixture was filtered. Ether (8 mL) was slowly added at 0 °C, and the mixture was allowed to stand at −20 °C. Removal of the resulting crystals by filtration gave 0.298 g (69%) of tetramethylammonium 4-methylbenzenecarbodithioate (**8e)** as dark needles. Mp: 182−190 °C dec. IR (KBr): 1172 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 2.30 (s, 3H, CH$_3$Ar), 3.12 (s, 12H, CH$_3$N), 7.04 (d, J = 8.2 Hz, 2H, Ar), 8.14 (d, J = 8.2 Hz, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 21.2 (*p*-CH$_3$), 55.9 (NCH$_3$), 128.4, 128.9, 140.8, 151.8 (*ipso*-C), 255.3 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 291 (4.08), 364 (3.84), 508 (2.18), 637 (0.76). Anal. Calcd for C$_{12}$H$_{19}$NS$_2$ (241.41): C, 59.70; H, 7.93. Found: C, 59.70; H, 7.84.

Tetramethylammonium 2-Methoxybenzenecarbodithioate (8f): red crystals [recrystallization from acetonitrile/ether (2:1) at −20 °C]: 0.835 g (68%). Mp: 164−165 °C dec. IR (KBr): 1182, 1165 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.17 (s, 3H, NMe), 3.79 (s, 3H, CH$_3$O), 6.8−6.9 (m, 2H, Ar), 7.1−7.2 (m, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 56.0 (NCH$_3$), 56.4 (CH$_3$O), 112.9, 121.0, 127.1, 128.0, 152.0, 155.7 (Ar), 257.8 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 343 (3.34), 475 (2.95), 642 (2.94).

Tetramethylammonium 4-Methoxybenzenecarbodithioate (8g): reddish orange crystals [recrystallization from acetonitrile/ether (1:1) at −20 °C], 0.455 g (71%). Mp: 143−144 °C dec. IR (KBr): 1185, 1162 (νCSS) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 3.13 (s, 3H, NMe), 3.81 (s, 3H, CH$_3$O), 6.76 (d, J = 8.8 Hz, 2H, Ar), 8.35 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (CD$_3$OD): δ 55.9 (NCH$_3$), 55.9 (CH$_3$O), 112.7, 130.0, 146.7, 163.1 (Ar), 253.4 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 234 (3.71), 320 (3.93), 489 (2.37), 620 (1.97) 645 (1.96).

Tetramethylammonium 4-Chlorobenzenecarbodithioate (8h): reddish orange crystals [recrystallization from acetonitrile/ether (1:1) at −20 °C], 0.745 g (39%). Mp: 165−170 °C dec. IR (KBr): 1157 (νCSS) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.14 (s, 12H, NMe), 7.20 (d, J = 8.4 Hz, 2H, Ar), 8.18 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$): δ 55.9 (NCH$_3$), 127.7, 129.0, 136.2, 153.0 (Ar), 253.2 (C═S). UV/vis (EtOH): λ_{max} [nm] (log ϵ) 367 (3.84), 477 (2.99), 506 (2.52), 636 (2.94).

Reaction of Alkali Metal Dithiocarboxylates with Methyl Iodide. Typical Procedures. Rubidium 4-methylbenzenecarbodithioate (**4g**) (0.270 g, 1.07 mmol) and methyl iodide (5.0 mL, 80.3 mmol) were stirred at room temperature for 30 min. Filtration and evaporation of the excess of methyl iodide under reduced pressure gave methyl 4-methylbenzenecarbodithioate (**9**) as a red oil. The IR and ^{1}H and ^{13}C NMR spectra were exactly consistent with those of an authentic sample prepared by the reaction of cesium 4-methylbenzenecarbodithioate (**5f**) with methyl iodide: red oil, 35% (0.069 g). IR (neat): 1245 (νCSS) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.36 (s, 3H, CH$_3$), 2.75 (s, 3H, SCH$_3$), 7.20 (d, J = 8.4 Hz, Ar), 7.93 (d, J = 8.4 Hz, Ar). ^{13}C NMR (CDCl$_3$): δ 20.5 (SCH$_3$), 21.5 (CH$_3$), 126.8, 129.0, 142.6, 142.3 (Ar), 228.6 (C═S). MS (CIDI) *m*/*z* (relative intensity, %): 183 [+] (100).

Reaction of Alkali Metal Dithiocarboxylates with Triorganotin Chloride. Typical Procedures. The IR and ^{1}H and ^{13}C NMR spectra of the tin esters **10a** and **10b** were exactly consistent with those of authentic samples prepared by the reaction of piperidinium 4-methylbenzenecarbodithioate with trimethyltin and triphenyltin chlorides, respectively.[53,54]

Trimethyltin 4-Methylbenzenecarbodithioate (10a):[53] dark red oil, 96%. ^{1}H NMR (CDCl$_3$): δ 0.69 (s, 9H, SnCH$_3$, $^{2}J_{^{1}\mathrm{H}-^{117}\mathrm{Sn}}$ = 54 Hz, $^{2}J_{^{1}\mathrm{H}-^{119}\mathrm{Sn}}$ = 57 Hz), 2.33 (s, 3H, CH$_3$), 7.10 (d, J = 8.4 Hz, 2H, Ar), 8.19 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$): δ −2.75 (CH$_3$, $^{1}J_{^{1}\mathrm{H}-^{117}\mathrm{Sn}}$ = 359 Hz, $^{1}J_{^{1}\mathrm{H}-^{119}\mathrm{Sn}}$ = 374 Hz), 21.5 (SCH$_3$), 127.3, 128.4, 143.0, 143.4 (Ar), 235.0 (C═S). ^{119}Sn NMR (CDCl$_3$): δ 51.2, $^{1}J_{^{13}\mathrm{C}-^{119}\mathrm{Sn}}$= 376 Hz. UV/vis (CH$_2Cl_2$): λ_{max} [nm] (log ϵ) 314 (4.17), 525 (1.99).

Triphenyltin 4-Methylbenzenecarbodithioate (10b).[54] Cesium 4-methylbenzenecarbodithioate (**5f**) (0.159 g, 0.53 mmol) and triphenyltin chloride (0.183 g, 0.47 mmol) were stirred in dichloromethane (3 mL) at 20 °C for 30 min. The insoluble part (excess **5f** and CsCl) was filtered out, and the solvent was evaporated, under reduced pressure. Crystallization of the resulting red oil with ether (3 mL) and hexane (3 mL) gave 0.237 g (98%) of triphenyltin 4-methylbenzenecarbodithioate

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(**10b**) as red brown crystals. The IR and ^{1}H NMR spectra were consistent with those of an authentic sample prepared by the reaction of piperidinium 4-methylbenzenecarbodithioate with triphenyltin chloride. Mp 119 °C. IR (KBr): 1221 (C═S) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.28 (s, 3H, CH$_3$), 7.40 (m, 19H, Ar). ^{13}C NMR (CDCl$_3$): δ 21.5 (CH$_3$), 127.6, 128.0, 128.8, 129.6, 130.7, 139.5, 141.4, 144.2 (Ar), 232.1 (C═S). ^{119}Sn NMR (CDCl$_3$): δ −138.8 ($^{1}J_{^{13}\mathrm{C}-^{119}\mathrm{Sn}} = 594$ Hz). UV/vis (CH$_2$Cl$_2$): $\lambda_{\max}$ [nm] (log ϵ) 328 (4.51), 504 (2.39).

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Supporting Information Available: X-ray structural information for the compounds **3b**, **4g**, **5f**, **7g**, **8e**, and **8f** in Table 3 including atomic coordinates, isotropic thermal parameters, and complete bond distances and angles. This material is availabe free of charge via the Internet at http://pubs.acs.org.

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