ELSEVIER

Inorganica Chimica Acta 263 (1997) 201-207

Inorganica Chimica Acta

Synthesis and characterization of some Group 1 and 2 metal derivatives of the crowding terphenyl thiolate and selenolate ligands $-EC_6H_3$-2,6-$Trip_2$ ($E = S$ or Se; Trip = 2,4,6-i-$Pr_3C_6H_2^-$)

Mark Niemeyer, Philip P. Power *

Department of Chemistry, University of California, Davis, CA 95616, USA

Received 31 January 1997; accepted 27 March 1997

Abstract

The synthesis and characterization of the monomeric magnesium thiolate $Mg\{SC_6H_3$-2,6-$Trip_2\}_2$ (**1**) (Trip = 2,4,6-i-$Pr_3C_6H_2^-$), the new selenol $HSeC_6H_3$-2,6-$Trip_2$ (**2**), three of its alkali metal derivatives ($MSeC_6H_3$-2,6-$Trip_2$) (M = K, **3**·PhMe, **3**·Et_2O, Rb, **4**·PhMe) and the heterometallic thiolate $RbAlMe_2(SC_6H_3$-2,6-$Trip_2)_2$ (**5**) are described. Compound **1** was synthesized by the reaction of commercially available '$MgBu_2$' with 2 equiv. of HSC_6H_3-2,6-$Trip_2$. The new selenol **2** was obtained from the reaction of elemental selenium with LiC_6H_3-2,6-$Trip_2$. The potassium and rubidium derivatives **3** and **4** were isolated by direct reaction of the metals with the selenol whereas **5** is formed by an exchange reaction between the corresponding rubidium thiolate and $AlMe_3$. The compounds were characterized by ^1H, ^{13}C and ^{77}Se NMR and IR spectroscopy, and by X-ray crystallography. Compound **1** crystallizes as a unique monomer with an S–Mg–S angle of 166.8(2)°. Compounds **3**·PhMe and **4**·PhMe crystallize as isomorphous dimers with M_2Se_2 cores. In these compounds each potassium or rubidium interacts in a π-fashion with two *ortho* aryl groups as well as σ-bonding to the chalcogens. The π-interaction is retained even in the presence of donor solvents. Thus, the ether solvate **3**·Et_2O is obtained by recrystallization of **3**·PhMe from diethyl ether. Metal aryl interactions also are observed in the rubidium aluminate **5** which crystallizes with a planar $RbAlS_2$ core. Crystal data at 130 K are as follows: $Mg(SC_6H_3$-2,6-$Trip_2)_2$ (**1**), $a = 10.417(1)$, $b = 11.644(1)$, $c = 14.545(2)$ Å, $\alpha = 69.536(8)$, $\beta = 75.91(1)$, $\gamma = 80.26(1)°$, $V = 1596.2(3)$ Å^3, space group $P\bar{1}$, $Z = 1$, $R_1 = 0.043$; $(KSeC_6H_3$-2,6-$Trip_2)_2$·PhMe (**3**·PhMe), $a = 13.842(3)$, $b = 15.124(3)$, $c = 17.776(3)$ Å, $\alpha = 83.04(2)$, $\beta = 85.62(2)$, $\gamma = 89.64(2)°$, $V = 3683(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.090$; $(RbSeC_6H_3$-2,6-$Trip_2)_2$·PhMe (**4**·PhMe), $a = 13.959(2)$, $b = 15.179(1)$, $c = 17.713(2)$ Å, $\alpha = 97.636(7)$, $\beta = 93.320(8)$, $\gamma = 90.462(8)°$, $V = 3713.3(6)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.050$; $RbAlMe_2(SC_6H_3$-2,6-$Trip_2)_2 \cdot C_6H_{14}$ (**5**), $a = 26.610(5)$, $b = 13.142(1)$, $c = 21.575(5)$ Å, $\beta = 99.37(2)°$, $V = 7444(3)$ Å^3, space group $C2/c$, $Z = 4$, $R_1 = 0.047$. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Alkali metal compounds; Alkaline-earth metal compounds; Thiolate compounds; Selenolate compounds

1. Introduction

Alkali metal derivatives of chalcogenolate ligands, the majority of which are lithium salts, are usually crystallized as readily formed Lewis base adducts of donor molecules such as diethyl ether, THF or TMEDA [1]. Very few unsolvated species have been structurally characterized. The known examples are limited to the recently published thiolate derivatives having the crowding terphenyl sulfur substituents $-C_6H_2$-2,4,6-Ph_3, $-C_6H_3$-2,6-Mes_2 (Mes = 2,4,6-$Me_3C_6H_2^-$) or $-C_6H_3$-2,6-$Trip_2$ (Trip = 2,4,6-i-$Pr_3C_6H_2^-$) [2] and a small number of other chalcogenolate salts as in $[LiOSiMe_2(1\text{-naphthyl})]_6$ [3a] and $[LiTeSi(SiMe_3)_3]_6$ [3b]. No well-characterized unsolvated selenolate derivatives of the alkali metals have been reported although the structures of several solvated selenolate species e.g. $[Li(bipy)SePh]_2$ [4a], $[Li(glyme)SeSi(SiMe_3)_3]_2$ [4b], $Li(THF)_3SeMes^*$ [4c,d] and $[Li(THF)SeMes^*]_3$ [4e] (Mes* = 2,4,6-t-$Bu_3C_6H_2^-$) have been determined. In a similar vein, unsolvated chalcogenolate derivatives of the neighboring alkaline earth metals are also quite rare and are limited to magnesium derivatives as exemplified by compounds $[Mg(OC_6H_3$-2,6-t-$Bu_2)_2]_2$ [5a], $[Mg(OC_6H_2$-2,6-t-Bu_2-4-$Me)_2]_2$ [5a], $Mg\{SC_6H_3$-2,6-$Mes_2\}_2$ [5b], $[Mg(SMes^*)_2]_2$ [5c], $\{Mg(SC_6H_2$-2,4,6-$Ph_3)\}_2$ [5c] and $[Mg\{ESi(SiMe_3)_3\}_2]_2$ (E = Se or Te) [5d]. Of these, the two aryloxides and $\{Mg(SC_6H_2$-2,4,6-$Ph_3)_2\}_2$ have been shown to be dimeric in the solid by X-ray crystallography. The compound $Mg\{SC_6H_3$-2,6-$Mes_2\}_2$ [5b] is believed to be monomeric, and solution NMR studies of the selenolate

---

* Corresponding author.

PII S0020-1693(97)05657-0

and tellurolate derivatives indicate that they are dimeric in that phase and, presumably, in the solid as well [5d].

In this paper the synthesis and characterization of the new selenol HSeC$_6$H$_3$-2,6-Trip$_2$ (**2**) and its potassium and rubidium salts **3** and **4** are reported. In addition, the synthesis and characterization of the unique monomeric magnesium thiolate Mg(SAr)$_2$ (**1**) and the rubidium aluminate RbAlMe$_2$(SAr)$_2$ (**5**) are described.

2. Experimental

All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N$_2$ or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under N$_2$ from a Na/K alloy and degassed twice before use. The compounds Li(OEt$_2$)C$_6$H$_3$-2,6-Trip$_2$ [6] and HSC$_6$H$_3$-2,6-Trip$_2$ [2] were synthesized as previously described. 'MgBu$_2$' (1:1 mixture of n- and *sec*-Bu isomers, 1.0 M in heptane), Al$_2$Me$_6$ in PhMe (2M), HBF$_4$ and the alkali-metals were purchased from commercial suppliers and used as received. NMR spectra were recorded in C$_6$D$_6$ solution by using a General Electric QE-300 spectrometer. IR spectra (Nujol mull, CsI plates) were obtained in the range 4000–200 cm^{-1} with a Perkin-Elmer 1420 spectrometer.

2.1. Syntheses

2.1.1. Mg(SC$_6$H$_3$-2,6-Trip$_2$)$_2$ (1)

HSC$_6$H$_3$-2,6-Trip$_2$ (0.58 g, 1.13 mmol) was dissolved in toluene (~ 15 ml) and treated dropwise with a solution of MgBu$_2$ (0.55 ml heptane solution, 0.55 mmol). The reaction was allowed to stir overnight whereupon the solvent was removed under reduced pressure. The remaining solid was redissolved in n-hexane (~5 ml). Cooling in a −30°C freezer for 24 h afforded colorless crystals of **1** which were suitable for X-ray crystallographic studies. Yield: 0.37 g (63%). M.p.: 185–188°C. ^{1}H NMR (C$_6$D$_6$): δ 1.10 (d, *o*/*p*-CH(C*H*$_3$)$_2$, 1.29 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.39 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 2.93 (m, *o*+*p*-C*H*(CH$_3$)$_2$), 6.80–7.24 (m, aryl-*H*). ^{13}C NMR (C$_6$D$_6$): δ 24.0 (*o*-CH(*C*H$_3$)$_2$), 24.2 (*o*-CH(CH$_3$)$_2$), 24.6 (*p*-CH(*C*H$_3$)$_2$, 30.9 (*o*-*C*H(CH$_3$)$_2$), 34.1 (*p*-*C*H(CH$_3$)$_2$), 120.7 (*p*-Ph), 123.0 (*m*-Trip), 128.1 (*m*-Ph), 138.5 (i-Trip), 140.9 (*o*-Ph), 144.1 (i-Ph), 146.4 (*o*-Trip), 149.5 (*p*-Trip). IR (Nujol, cm^{-1}): 1601ms, 1562m, 1390ms, 1358s, 1332vw, 1360m, 1255w, 1233vw, 1165w, 1145vw, 1095w, 1065w, 1045m, 938m, 915vw, 873s, 842vw, 793s, 770w, 739ms, 730sh, 714sh, 645w, 521w, 480w.

2.1.2. HSeC$_6$H$_3$-2,6-Trip$_2$ (2)

Selenium powder (0.39 g, 5 mmol) was added via a solids-addition tube to a solution of Li(OEt$_2$)C$_6$H$_3$-2,6-Trip$_2$ (2.59 g, 5 mmol) in ~20 ml THF. The solution was stirred overnight at ambient temperature. The volatile materials were removed under reduced pressure and the residue was redissolved in toluene. HBF$_4$ (54% in diethyl ether, 2 ml) was added dropwise via syringe, and the resulting yellow solution was stirred for a further 30 min. The contents of the flask were allowed to settle, and the supernatant liquid was decanted via cannula. The volume was reduced to incipient crystallization, and cooled in a −30°C freezer to afford **2** as pale yellow crystals. Yield: 1.80 g (64%). M.p.: 221–223°C. ^{77}Se NMR (C$_6$D$_6$): δ 108 (d, ^1J(Se–H) = 65 Hz). ^{1}H NMR (C$_6$D$_6$): δ 1.17 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.25 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.42 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 2.90 (m, *o*+*p*-C*H*(CH$_3$)$_2$), 3.56 (s, Se*H*), 7.04–7.24 (m, aryl-*H*). ^{13}C NMR (C$_6$D$_6$): δ 24.1 (*o*-CH(*C*H$_3$)$_2$), 24.3 (*o*-CH(*C*H$_3$)$_2$), 25.1 (*p*-CH(*C*H$_3$)$_2$), 31.2 (*o*-*C*H(CH$_3$)$_2$), 34.8 (*p*-*C*H(CH$_3$)$_2$), 121.5 (*m*-Trip), 125.0 (*p*-Ph), 129.1 (*m*-Ph), 137.3 (i-Ph), 137.5 (i-Trip), 141.1 (*o*-Ph), 147.0 (*o*-Trip), 149.3 (*p*-Trip). IR (Nujol, cm^{-1}): 2301w, 1602ms, 1563ms, 1359s, 1334w, 1312m, 1252vw, 1236w, 1168m, 1150w, 1100m, 1068w, 1049w, 1030vw, 940m, 874s, 793s, 774w, 738ms, 648m, 490w.

2.1.3. (KSeC$_6$H$_3$-2,6-Trip$_2$)$_2$·PhMe (3·PhMe) and (KSeC$_6$H$_3$-2,6-Trip$_2$)$_2$·Et$_2$O (3·Et$_2$O)

Potassium (0.08 g, 2.1 mmol) was added via a solids-addition tube to a solution of HSeC$_6$H$_3$-2,6-Trip$_2$ (0.60 g, 1.07 mmol) in toluene (~ 15 ml). The mixture was warmed to ~50°C and stirred overnight. The supernatant liquid was separated from the excess alkali metal via a cannula. The volume was reduced to incipient crystallization and the solution was cooled for 2 days in a 0°C freezer to give **3**·PhMe as colorless crystals. Further reduction of the solvent afforded further quantities of the product to give an almost quantitative overall yield. M.p.: 246–248°C (> 180°C desolvation). ^{77}Se NMR (C$_6$D$_6$): δ 178. ^{1}H NMR (C$_6$D$_6$): δ 1.15 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.29 (d, *o*/*p*-C*H*(CH$_3$)$_2$), 1.33 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 2.10 (s, C$_7$*H*$_8$), 2.87 (sep, *p*-C*H*(CH$_3$)$_2$), 3.10 (m, *o*-C*H*(CH$_3$)$_2$), 6.93–7.13 (m, aryl-*H*). ^{13}C NMR (C$_6$D$_6$): δ 24.4 (*p*-CH(*C*H$_3$)$_2$), 24.7 (*o*-CH(C*H*$_3$)$_2$), 24.8 (*o*-CH(C*H*$_3$)$_2$), 30.9 (*o*-*C*H(CH$_3$)$_2$), 34.6 (*p*-*C*H(CH$_3$)$_2$), 120.1 (*p*-Ph), 119.8 (*m*-Trip), 127.2 (*m*-Ph), 143.9 (*o*-Ph), 145.3 (i-Trip), 146.5 (*p*-Trip), 148.4 (*o*-Trip), 149.4 (i-Ph). IR (Nujol, cm^{-1}): 1592w, 1558m, 1353s, 1333sh, 1312m, 1250w, 1230vw, 1163w, 1147vw, 1101w, 1074w, 1063vw, 1045vw, 1031m, 939w, 914vw, 874s, 845vw, 791vw, 789w, 772w, 752w, 730m, 648w. Crystals of compound **3**·Et$_2$O were obtained by recrystallization of **3**·PhMe from diethyl ether.

2.1.4. Rb(SeC$_6$H$_3$-2,6-Trip$_2$)$_2$·PhMe (4·PhMe)

The synthesis was accomplished in a similar manner to the preparation of **3**·PhMe with use of HSeC$_6$H$_3$-2,6-Trip$_2$ (0.60 g, 1.07 mmol) and rubidium (0.14 g, 1.6 mmol) to afford the product **4**·PhMe in nearly quantitative yield. M.p.: 252–254°C (> 170°C desolvation). ^{77}Se NMR (C$_6$D$_6$, 50°C): δ 216. ^{1}H NMR (C$_6$D$_6$): δ 1.15 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.26 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.33 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 2.10 (s, C$_7$*H*$_8$), 2.82 (sep, *p*-C*H*(CH$_3$)$_2$), 3.13 (sep, *o*-C*H*(CH$_3$)$_2$), 6.90–

7.05 (m, aryl–*H*). ^{13}C NMR (C_6D_6): δ24.4 (*p*-CH(*C*H$_3$)$_2$), 24.7 (*o*-CH(*C*H$_3$)$_2$), 24.8 (*o*-CH(*C*H$_3$)$_2$), 30.9 (*o*-*C*H(CH$_3$)$_2$), 34.6 (*p*-*C*H(CH$_3$)$_2$), 120.0 (*p*-Ph), 120.0 (*m*-Trip), 127.4 (*m*-Ph), 144.2 (*o*-Ph), 145.7 (i-Trip), 146.4 (*p*-Trip), 148.5 (*o*-Trip, 149.9 (i-Ph). IR (Nujol, cm^{-1}): 1597ms, 1358s, 1335w, 1313m, 1251m, 1231sh, 1164w, 1149vw, 1102m, 1077m, 1066sh, 1045sh, 1031m, 936w, 915vw, 877s, 845vw, 792w, 782m, 775m, 752w, 731ms, 650m.

2.1.5. *RbAlMe$_2$(SC$_6$H$_3$-2,6-Trip$_2$)$_2$ · n-hexane (5 · n-hexane)*

A 2 M solution of $AlMe_3$ (0.5 ml, 1.00 mmol) in PhMe was added with stirring at room temperature to $RbSC_6H_3$-2,6-Trip$_2$ (0.50 g, 0.83 mmol) in ~15 ml of n-hexane. Stirring was immediately discontinued and the solution was allowed to stand at ambient temperature for 24 h which afforded the product **5** · n-hexane as colorless crystals which were suitable for X-ray crystallographic studies. The product was contaminated with small amounts of $RbAlMe_4$. This was removed as a suspension in the supernatant liquid via cannula. The remaining colorless crystals of **5** · n-hexane were dried by pumping at ~0.02 torr (~2.66 Pa) for 2 h. This resulted in the loss of n-hexane and transformation of the crystals to a white powder, compound **5**. Yield: 0.38 g (78%). M.p.: 255–260°C (decomp.). ^{1}H NMR (C_6D_6): δ −0.99 (AlMe$_2$), 1.09 (d, C*H*$_3$, ^3J(CH) = 7.7 Hz), 1.28 (m, C*H*$_3$), 1.42 (d, C*H*$_3$, ^3J(CH) = 6.7 Hz), 2.80 (m, *p*-CH), 3.00 (m, *o*-CH), 7.15–7.02 (m, aryl–H). ^{13}C NMR (C_6D_6): δ −5.4 (AlMe$_2$), 26.1–24.1 (CH$_3$), 34.7 (*p*-CH), 30.9 (*o*-CH), 147.8–120.8 (aryl–C). IR (Nujol, cm^{-1}): 1598m, 1562m, 1544sh, 1357s, 1332w, 1312ms, 1244sh, 1235w, 1170ms, 1145s, 1098m, 1076w, 1055w, 1046m, 1000vw, 953vw, 939m, 920w, 880ms, 870ms, 846w, 799ms, 788sh, 773m, 748s, 725vs, 672sh, 662s, 603vw, 553m, 412w, 342w, 288m.

2.2. *X-ray crystallography*

X-ray quality crystals were obtained as described in Section 2. Crystals were removed from the Schlenk tube and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature N_2-stream, as previously described [7]. All data were collected at 130 K with Cu Kα radiation using either a Syntex *P*2$_1$ (**1**, **3** · Et$_2$O) or a Siemens *P*4/RA (**3** · PhMe, **4** · PhMe, **5** · n-hexane) diffractometer. Crystal data are given in Table 1. Calculations were carried out with the SHELXTL-PLUS and SHELXL-93 [8a] program system installed on a UNIX workstation or PC's. Scattering factors and the correction for anomalous scattering were taken from common sources [8b]. The structures were solved by direct methods and refined by full matrix least-squares refinement. An absorption correction was applied by using the program XABS2 [8c]. Anisotropic thermal parameters were refined for all non-hydrogen atoms, excluding several C atoms in **3** · Et$_2$O and one disordered C atom in **5**. H atoms were included and refined by use of a riding model, with fixed C–H distances, and either refined or fixed isotropic thermal parameters equal to 1.2 or 1.5 times that of the bonded

Table 1
Crystallographic data [a] for compounds **1**, **3** · PhMe, **4** and **5** · n-hexane

	1	**3** · PhMe	**4** · PhMe	**5** · n-hexane
Empirical formula	$C_{36}H_{49}Mg_{0.5}S_1$	$C_{79}H_{106}K_2Se_2$	$C_{79}H_{106}Rb_2Se_2$	$C_{40}H_{59}Al_{0.50}Rb_{0.5}S$
Formula weight	525.97	1291.8	1384.5	626.14
Color, habit	colorless, plate	colorless, needle	colorless, block	colorless, block
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.417(1)	13.842(3)	13.959(2)	26.610(5)
b (Å)	11.644(1)	15.124(3)	15.179(1)	13.142(2)
c (Å)	14.545(2)	17.776(3)	17.713(2)	21.575(5)
α (°)	69.536(8)	83.04(2)	97.636(7)	
β (°)	75.91(1)	85.62(2)	93.320(8)	99.37(2)
γ (°)	80.26(1)	89.64(2)	90.462(8)	
V (Å^3)	1596.2(3)	3683(1)	3713.3(6)	7444(3)
Z	2	2	2	8
D (g cm^{-3})	1.094	1.165	1.238	1.117
Crystal dimensions (mm)	0.52×0.40×0.08	0.23×0.04×0.03	0.48×0.24×0.16	0.20×0.07×0.06
μ (cm^{-1})	11.33	25.51	31.12	18.39
No. unique data	7149	9319	9668	4846
No. data with $I > 2\sigma(I)$	4338	6080	7381	3612
No. parameters	404	867	879	472
R_1 ($I > 2\sigma(I)$)	0.043	0.090	0.050	0.047
wR_2 (all data)	0.110	0.267	0.129	0.097

[a] All data were collected at 130 K using Cu Kα (λ = 1.54178 Å) radiation.

[b] Crystal data at 130 K for 2(KSeC$_6$H$_3$-2,6-Trip$_2$)$_2$ · Et$_2$O (**3** · Et$_2$O), a = 14.982(4), b = 19.041(5), c = 24.972(6) Å, β = 93.71(2)°, V = 7109(3) Å^3, space group *Pn*, Z = 2, R_1 = 0.085. Compound **3** · Et$_2$O crystallizes with two independent (KSeAr)$_2$ dimers and one diethyl ether solvate molecule per asymmetric unit. The structural features are very similar to compound **3** · PhMe.

Table 2
Selected bond distances (Å) and angles (°) for **1**, **3**·PhMe, **4** and **5**·n-hexane. X = centroid of the aromatic plane defined by positions C23 to C28 (**5**·n-hexane). X1, X2, X3 and X4 = centroids of the aromatic planes defined by positions C7 to C12, C22 to C27, C43 to C48 and C58 to C63 (**1**, **3**·PhMe, **4**)

Compound 1			
Mg–S	2.3277(13)	S–Mg–S′	166.8(2)
Mg–C(7)	2.691(4)	Mg–S′–C(1)′	119.22(12)
Mg–C(12)	2.789(4)	Mg–S–C(1)	106.43(12)
S–C(1)	1.766(2)	C(2)–C(1)–C(6)	118.7(2)
C(1)–C(2)	1.410(3)	S–C(1)–C(2)	124.6(2)
C(1)–C(6)	1.411(3)	S–C(1)–C(6)	116.7(2)
Compound 3 · PhMe			
K(1)–Se(1)	3.131(2)	K(2)···C(48)	3.710(9)
K(1)–Se(2)	3.171(2)	K(2)···C(45)	3.270(8)
K(2)–Se(1)	3.141(2)	K(2)···C(46)	3.440(8)
K(2)–Se(2)	3.232(2)	K(2)···C(47)	3.610(9)
K–Se(av.)	3.169	K(1)···X(1)	3.101
K(1)···C(7)	3.496(9)	K(1)···X(4)	3.061
K(1)···C(8)	3.515(8)	K(2)···X(2)	3.235
K(1)···C(9)	3.431(8)	K(2)···X(3)	3.199
K(1)···C(10)	3.312(8)	K(1)···K(2)	5.391(3)
K(1)···C(11)	3.261(8)	Se(1)–C(1)	1.914(8)
K(1)···C(12)	3.376(8)	Se(2)–C(37)	1.867(8)
K(1)···C(58)	3.482(8)		
K(1)···C(59)	3.409(9)	Se(1)–K(1)–Se(2)	63.69(5)
K(1)···C(60)	3.292(9)	Se(1)–K(2)–Se(2)	62.89(5)
K(1)···C(61)	3.280(9)	K(1)–Se(1)–K(2)	118.56(6)
K(1)···C(62)	3.307(9)	K(1)–Se(2)–K(2)	114.68(6)
K(1)···C(63)	3.423(9)	K(1)–Se(1)–C(1)	118.6(3)
K(2)···C(22)	3.622(8)	K(2)–Se(1)–C(1)	122.7(3)
K(2)···C(23)	3.674(9)	K(1)–Se(2)–C(37)	119.7(3)
K(2)···C(24)	3.573(8)	K(2)–Se(2)–C(37)	114.3(2)
K(2)···C(25)	3.455(8)	C(2)–C(1)–C(6)	119.5(7)
K(2)···C(26)	3.352(9)	Se(1)–C(1)–C(2)	120.8(6)
K(2)···C(27)	3.460(9)	Se(1)–C(1)–C(6)	119.6(6)
K(2)···C(43)	3.550(8)	Se(2)–C(37)–C(38)	123.3(6)
K(2)···C(44)	3.340(8)	Se(2)–C(37)–C(42)	120.4(6)
Compound 4			
Rb(1)–Se(1)	3.2352(8)	Rb(2)···C(44)	3.423(4)
Rb(1)–Se(2)	3.2586(8)	Rb(2)···C(45)	3.342(5)
Rb(2)–Se(1)	3.2389(8)	Rb(2)···C(46)	3.435(5)
Rb(2)–Se(2)	3.3068(8)	Rb(2)···C(47)	3.593(5)
Rb–Se(av.)	3.2599	Rb(2)···C(48)	3.700(5)
Rb(1)···C(7)	3.588(4)	Rb(1)···X(1)	3.174
Rb(1)···C(8)	3.605(5)	Rb(1)···X(4)	3.150
Rb(1)···C(9)	3.501(5)	Rb(2)···X(2)	3.250
Rb(1)···C(10)	3.360(5)	Rb(2)···X(3)	3.229
Rb(1)···C(11)	3.314(4)	Rb(1)···Rb(2)	5.568(1)
Rb(1)···C(12)	3.434(4)	Se(1)–C(1)	1.901(4)
Rb(1)···C(58)	3.581(4)	Se(2)–C(37)	1.896(5)
Rb(1)···C(59)	3.475(5)	Se(1)–Rb(1)–Se(2)	62.92(2)
Rb(1)···C(60)	3.349(5)	Se(1)–Rb(2)–Se(2)	62.36(2)
Rb(1)···C(61)	3.338(5)	Rb(1)–Se(1)–Rb(2)	118.64(2)
Rb(1)···C(62)	3.391(5)	Rb(1)–Se(2)–Rb(2)	116.00(2)
Rb(1)···C(63)	3.533(5)	Rb(1)–Se(1)–C(1)	119.04(14)
Rb(2)···C(22)	3.663(4)	Rb(2)–Se(1)–C(1)	122.32(14)
Rb(2)···C(23)	3.650(4)	Rb(1)–Se(2)–C(37)	120.56(14)
Rb(2)···C(24)	3.535(4)	Rb(2)–Se(2)–C(37)	115.77(14)
Rb(2)···C(25)	3.442(5)	Se(1)–C(1)–C(6)	120.2(4)
Rb(2)···C(26)	3.405(5)	Se(1)–C(1)–C(2)	120.8(3)
Rb(2)···C(27)	3.518(5)	Se(2)–C(37)–C(38)	121.5(4)
Rb(2)···C(43)	3.614(4)	Se(2)–C(37)–C(42)	120.4(3)
Compound 5 · n-hexane			
Al(1)–S(1)	2.342(2)	C(1)–Al(1)–C(1)′	120.5(2)
Al(1)–C(1)	1.963(4)	S(1)–Al(1)–C(1)′	108.20(12)
Rb(1)–S(1)	3.1967(11)	S(1)–Al(1)–C(1)	112.21(12)
Rb(1)···C(23)	3.537(3)	S(1)–Al(1)–S(1)′	91.80(7)
Rb(1)···C(24)	3.642(4)	S(1)–Rb(1)–S(1)′	63.50(4)
Rb(1)···C(25)	3.546(4)	C(2)–S(1)–Al(1)	114.43(12)
Rb(1)···C(26)	3.395(4)	Rb(1)–S(1)–C(2)	123.25(12)
Rb(1)···C(27)	3.286(4)	Al(1)–S(1)–Rb(1)	102.35(4)
Rb(1)···C(28)	3.373(3)	S(1)–C(2)–C(3)	121.7(3)
Rb(1)···X	3.171	S(1)–C(2)–C(7)	119.1(3)
Rb(1)···Al(1)	4.348(1)		
S(1)–C(2)	1.776(4)		

carbon. The Mg atom in **1** is equally disordered over two symmetry equivalent positions. Final *R* factors are listed in Table 1. Important bond distances and angles are given in Table 2. Further details are provided in Section 4.

3. Results and discussion

The magnesium dithiolate compound **1** was synthesized in good yield by the simple reaction of commercial 'MgBu$_2$' and 2 equiv. of the thiol HSC$_6$H$_3$-2,6-Trip$_2$. The most interesting feature of this compound is its monomeric structure which stands in contrast to other very sterically hindered magnesium thiolates. The latter are normally dimeric and become monomeric only when complexed to Lewis bases. Thus, both [Mg(SC$_6$H$_2$-2,4,6-Ph$_3$)$_2$]$_2$ and [Mg(SMes*)$_2$]$_2$ [5c] are dimers in the solid whereas the latter species only becomes monomeric in the complex (Et$_2$O)$_2$Mg(SMes*)$_2$ where magnesium is also coordinated to two ethers [5c]. The monomeric structure of **1** also tends to support the monomeric formulation (by ^{1}H NMR) of the related compound Mg(SC$_6$H$_3$-2,6-Mes$_2$)$_2$ [5b] in solution.

Compound **1** crystallizes as centrosymmetric monomers, however, the magnesium is disordered over two positions of equal occupancy, only one of which is shown in Fig. 1. The structural parameters of **1** may be compared to those of related magnesium thiolates. the Mg–S distance 2.3277(13) Å is just marginally shorter than the terminal Mg–S distances,

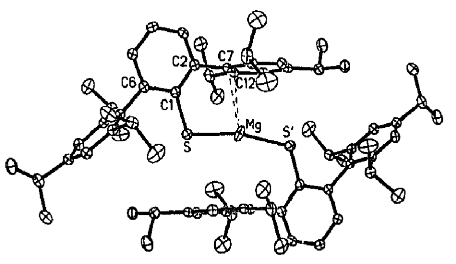

Fig. 1. Structure of **1**, showing 40% thermal ellipsoids and the atom labeling scheme. H atoms have been omitted for clarity. Only one position of the disordered Mg atom is shown.

2.349(5) Å in $[Mg(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_2]_2$ [5c] and the Mg–S distances, 2.382(2) and 2.392(2) Å in $(Et_2O)_2$-$Mg(SMes^*)_2$ [5c] in which the magnesium are three- and four-coordinated, respectively. The S–Mg–S angle in **1**, 166.8(2)°, shows a significant deviation from strict linearity. This angle may be compared to those observed in the other monomeric magnesium species, $Mg[C(SiMe_3)_3]_2$ (C–Mg–C = 180°) [9a], $Mg(Mes^*)_2$ (C–Mg–C = 158.2(2)°) [9b], $Mg[N(SiMePh_2)_2]_2$ (N–Mg–N = 162.8,(3)°) [9c], which are two-coordinate in the solid state. The structures of the bent compounds $Mg(Mes^*)_2$ and $Mg[N(SiMePh_2)_2]_2$ are characterized by relatively close secondary interactions between the metal and the ligand which may play a role in the bending [9b,c]. In a similar manner in **1** there are close contacts (involving C(7) (2.691(4) Å) and C(12) (2.789(4) Å) between the magnesium and one of the *ortho*-aryl rings. It is noteworthy that these lengths are also close to the Mg···C contacts (2.555–2.797 Å) observed in the dimer $[Mg(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_2]_2$ [5c].

The structures of the alkali metal selenolate salts **3**·PhMe, **3**·Et_2O and **4**·PhMe may be conveniently discussed together. The compounds **3**·PhMe and **4**·PhMe are isomorphous both to each other and to the closely related thiolate salt $(KSC_6H_3\text{-}2,6\text{-}Trip_2)_2$·PhMe [2]. They crystallize as dimers with K_2Se_2 or Rb_2Se_2 cores as shown in Figs. 2 and 3. The structural parameters of the two potassium salts **3**·PhMe and **3**·Et_2O are very similar and only the former species is included in the discussion and illustration. The dimeric structures of **3**·PhMe and **4**·PhMe have no crystallographically imposed symmetry. The M_2Se_2 cores in each case are almost planar with slight fold angles of 174.3 and 176.0° along the K···K and Rb···Rb axes. In compound **3** the average internal angles at K and Se are 63.3(4) and 116.6(1.9)° whereas in **4** the corresponding numbers are 62.6(3) and 117.3(1.1)°. The average K–Se and Rb–Se distances are 3.17(3) and 3.27(3) Å which may be compared to the average K–S and Rb–S distance of 3.055(8) and 3.166(8) Å in the corresponding sulfur derivatives [2]. The M–Se distances are thus slightly less than those expected from the difference (~0.15 Å) in covalent radii between sulfur (1.02 Å) and selenium (1.17 Å) [10]. In addition, the K–Se distances in **3** are far shorter than the ~3.4 Å K–Se bond length observed in the compound $[K\{Ph_2P(Se)NSiMe_3\}\cdot THF]_2$ [11a] or $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2EtOH$ [11b]. The structures of compound **3** and **4** are characterized by two different coordination geometries at the seleniums. In each compound one selenium has essentially trigonal planar coordination whereas the other selenium has a flattened pyramidal geometry; Σ° Se(2) in **3** = 348.7(3) and Σ° Se(2) in **4** = 352.3(1). The difference in geometry resembles that found for the two sulfurs in $(KSC_6H_3\text{-}2,6\text{-}Trip_2)_2$ [2]. The coordination of both the potassium and rubidium ions in **3** and **4** is characterized by interactions of each metal with two Trip substituents. In **3**, the K(1) ion interacts essentially equally with both Trip rings with K(1)–C(ring) distances in the relatively narrow range 3.261(8)–3.515(8) Å with an average value of 3.38(5) Å. In the case of K(2) the range of K(2)–C(ring) distances is greater, 3.270(8)–3.710(9) Å and the average K(2)–C(ring) distance, 3.50(6) Å, is longer than the corresponding K(1)–C average. Both values are, nonetheless, quite near the average K–C interaction, 3.42(2) Å, found in the corresponding thiolate derivative. For the rubidium derivative **4** the average Rb(1)—C(ring) distance is 3.46(5) Å with a range of 3.314(4)–3.605(5) Å and for Rb(2) the corresponding values are 3.44(6) and 3.353(5)–3.700(5) Å.

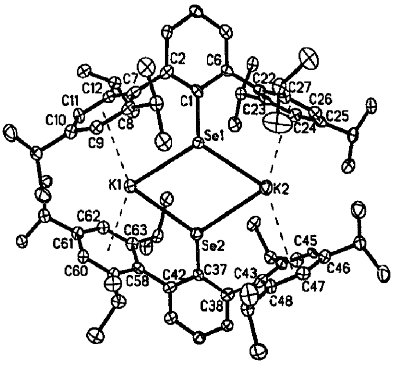

Fig. 2. Structure of **3**·PhMe, showing 30% thermal ellipsoids and the atom labeling scheme. H atoms have been omitted for clarity.

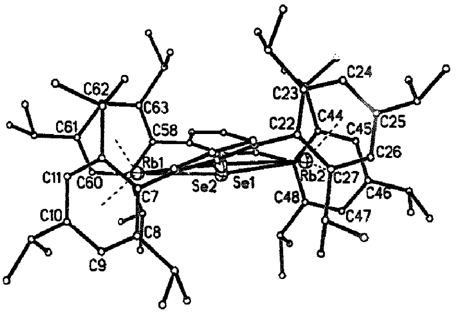

Fig. 3. Structure of **4**·PhMe, showing 30% thermal ellipsoids and the atom labeling scheme. H atoms have been omitted and C atoms are shown with arbitrary radius for clarity.

^{77}Se NMR spectroscopic data were also obtained for **2**, **3**·PhMe and **4**·PhMe. In the case of the selenol **2**, the ^{77}Se NMR chemical shift and coupling constant (δ = 108 ppm, $^1J(SeH)$ = 65 Hz) are in the expected range and relatively close to the values observed for Mes*SeH (δ = 139.9, $^1J(SeH)$ = 51.9 Hz) [12a]. The chemical shifts for the potassium and rubidium salt (δ = 178 and 216 ppm) are observed at a slightly lower field. This is surprising since alkali metal selenolate chemical shifts are intuitively expected to appear at higher field and this is what is usually observed [12b]. It is notable, however, that the arylselenolate $Li(THF)_3$-SeMes* also displays a downfield shift (δ = 128.5) in its

^{77}Se NMR spectrum [4d]. Thus, it is possible that alkali metal salts of aryl selenolates generally appear at a downfield chemical shift in contrast to their alkyl analogues. Further work will be required to confirm this hypothesis.

The compound **5** is derived from the reaction of 1 equiv. of $AlMe_3$ with $(RbSC_6H_3\text{-}2,6\text{-}Trip_2)_2$ the sulfur analogue of **4**. The hoped for product $RbSC_6H_3\text{-}2,6\text{-}Trip_2 \cdot AlMe_3$ did not materialize. Instead the product **5** was obtained according to the stoichiometry given by Eq. (1).

$$2AlMe_3 + 2RbSC_6H_3\text{-}2,6\text{-}Trip_2 \rightarrow RbAlMe_4 + \underset{\mathbf{5}}{RbAlMe_2SC_6H_3\text{-}2,6\text{-}Trip_2} \quad (1)$$

Structural data for organometallic compounds containing both aluminum and rubidium are quite rare and appear to be limited to a crystal structure of the azide RbN_3AlMe_3 [13a] and a powder diffraction study of $Rb[AlMe_4]$ [13b]. Crystals of **5** · n-hexane obtained from the reaction mixture include a n-hexane of crystallization. The structure of this compound is illustrated in Fig. 4. It consists of well-separated units of compound **5** in which the aluminum is bound to two methyl and two thiolate groups in a distorted tetrahedral fashion. The two thiolate groups form bridges to the rubidium ion, which also interacts with two Trip rings in a manner analogous to that seen in the structure of $(KSC_6H_3\text{-}2,6\text{-}Trip_2)_2$ [2] and compound **4**. There is a crystallographically imposed two-fold rotation axis along the Rb···Al vector. The Al–C and Al–S distances are 1.963(4) and 2.342(2) Å, respectively, and the Rb–S bond length is 3.197(1) Å. The Rb—C(ring) interactions are in the range 3.286(4)–3.642(4) Å with an average length of 3.66(1) Å. The coordination geometry at sulfur is much more pyramidal ($\Sigma°$ S(1) = 340°) than that in the rubidium thiolate $(RbSC_6H_3\text{-}2,6\text{-}Trip_2)_2$ [2]. Essentially, the structure of **5** demonstrates that the thiolate interaction with aluminum is significantly stronger than that with the rubidium. In fact the Rb–S distances in **5** are ~0.04 Å longer than those seen in $(RbSC_6H_3\text{-}2,6\text{-}Trip_2)_2$ whereas the Al–S distance is similar to those found in four-coordinate aluminum in a negatively charged moiety [14]. The short Al–S distance (in comparison to Rb–S) results in a very distorted geometry for the planar AlS_2Rb core and the pyramidal geometry observed for the sulfur is probably a consequence of the necessity to limit Rb–C(ring) and Rb–S distances to a certain range of values that can only be accommodated by a pyramidal rather than planar coordination at the sulfur center.

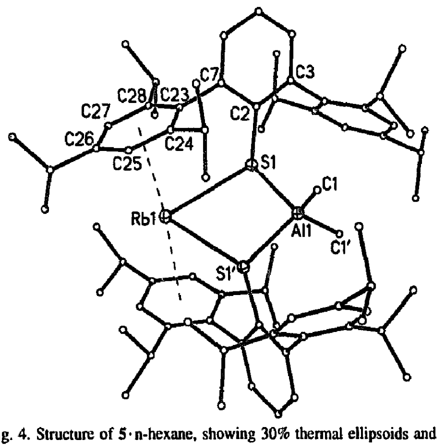

Fig. 4. Structure of **5** · n-hexane, showing 30% thermal ellipsoids and the atom labeling scheme. H atoms have been omitted and C atoms are shown with arbitrary radius for clarity.

4. Supplementary material

Further details of the crystal structures of **1**, **3** · PhMe, **3** · Et_2O, **4** · PhMe and **5** · n-hexane may be obtained from the authors upon request.

Acknowledgements

We thank the Donors of the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation for financial suport.

References

[1] (a) M.A. Beswick and D.S. Wright, *Comprehensive Organometallic Chemistry II*, Vol. 1, Pergamon, New York, 1995, Ch. 1; (b) F. Pauer and P.P. Power in A.M. Sapse and P.v.R. Schleyer (eds.), *Lithium Chemistry: A Theoretical and Experimental Overview*, Wiley, New York, 1995, Ch. 9.

[2] M. Niemeyer and P.P. Power, *Inorg. Chem.*, *35* (1996) 7264.

[3] (a) T.A. Bazhenova, R.M. Lobkovskaya, R.P. Shibaeva, A.E. Shilov and A.K. Shilova, *J. Organomet. Chem.*, *330* (1987) 9; (b) G. Becker, K.W. Klinkhammer and W.Z. Massa, *Z. Anorg. Allg. Chem.*, *619* (1992) 628.

[4] (a) D.V. Khasnis, M. Buretea, T.J. Emge and J.G. Brennan, *J. Chem. Soc., Dalton Trans.*, (1995) 45; (b) K.E. Flick, P.J. Bonasia, D.E. Gindelberger, J.E.B. Katari and D. Schwartz, *Acta Crystallogr. Sect. C*, *50* (1994) 674; (c) K. Ruhlandt-Senge and P.P. Power, *Inorg. Chem.*, *30* (1991) 3683; (d) W.-W. du Mont, S. Kubiniok, L. Lange, S. Pohl, W. Saak and I. Wagner, *Chem. Ber.*, *124* (1991) 1315; (e) K. Ruhlandt-Senge and P.P. Power, *Inorg. Chem.*, *32* (1993) 4505.

[5] (a) J. Calabrese, M.A. Cushing and S.D. Ittel, *Inorg. Chem.*, *27* (1988) 867; (b) J.J. Ellison and P.P. Power, *Inorg. Chem.*, *33* (1994) 4231; (c) K. Ruhlandt-Senge, *Inorg. Chem.*, *34* (1995) 3499; (d) D.E. Gindelberger and J. Arnold, *Inorg. Chem.*, *33* (1994) 6293.

[6] B. Schiemenz and P.P. Power, *Organometallics*, *15* (1995) 958.

[7] This method is described by: H. Hope in A.L. Wayda and M.Y. Darensbourg (eds.), *Experimental Organometallic Chemistry*, ACS Symposium Series, Vol. 357, American Chemical Society, Washington, DC, 1987, Ch. 10.

[8] (a) G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Göttingen, Germany, 1993; (b) *International Tables for Crystallography*, Vol. C, Reidel, Dordrecht, Netherlands, 1993; (c) S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, *28* (1995) 53.

[9] (a) S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, C.A. McGeary and J.D. Smith, *J. Chem. Soc., Chem. Commun.*, (1989) 273; (b) R.J.

Wehmschulte and P.P. Power, *Organometallics*, *14* (1995) 3264; (c) R.A. Bartlett, M.M. Olmstead and P.P Power, *Inorg. Chem.*, *33* (1994) 4800.

[10] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr., Sect. B*, *25* (1969) 925.

[11] (a) T. Chivers, M. Parvez and M.A. Seay, *Inorg. Chem.*, *33* (1994) 2147; (b) C.A. Marganian, N. Baidya, M.M. Olmstead and P.K. Mascharak, *Inorg. Chem.*, *31* (1992) 2992.

[12] (a) M. Bochmann, K. Webb, M. Harman and M.B. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 638; (b) H.C.E. McFarlane and W. McFarlane in P. Laszlo (ed.), *NMR of newly accessible nuclei*, Vol. 2, Academic Press, New York, 1983, Ch. 10.

[13] (a) R. Wolfrum, G. Sauermann and E. Weiss, *J. Organomet. Chem.*, *18* (1969) 27; (b) J.L. Atwood and J.M. Cummings, *J. Cryst. Mol. Struct.*, *7* (1977) 257.

[14] J.P. Oliver and R. Kumar, *Polyhedron*, *9* (1990) 409.