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Formation of separated *versus* contact ion pairs in alkali metal thiolates and selenolates

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The solvation and ligation tendencies of alkali metal thiolates and selenolates in relation to metal and donors were investigated by synthesizing a family of target compounds, and analysing their structural features in solution and the solid state. The target compounds were synthesized utilizing hydrogen elimination, involving treatment of the chalcogenol with either sodium or potassium hydride in the presence of various donors. The separated ions were [Na(18-crown-6)(THF)$_2$][SMes*] **1**, (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), [K(18-crown-6)(THF)$_2$][SMes*] **3**, and [K(18-crown-6)(THF)$_2$][SeMes*] **4**, and K(dibenzo-18-crown-6)(SMes*)·THF **2**, displayed potassium–sulfur contacts. Compounds **1**–**4** were characterized using X-ray crystallography, NMR and IR spectroscopy. Cyclic voltammetry studies were carried out on **1**–**3**, Na(dibenzo-18-crown-6)(SMes*) **5** and K(dibenzo-18-crown-6)(STrip)·THF **6** (Trip = 2,4,6-iPr$_3$C$_6$H$_2$). A concentration dependent equilibrium reaction, which leads to an increase in free thiolate at higher concentrations, was observed for all complexes. NMR experiments using solutions of **5** (8.5 and 0.085 mM, THF-d$_8$) and trimethyl phosphate confirmed the presence of free thiolate at higher concentration.

Introduction

The concept of contact and separated ions was introduced as early as 1958 by Winstein and Robinson.[1] Since then numerous studies have been carried out, investigating the influence of cation, anion, solvent, and donors on the formation of these species. The majority of these studies focused on the investigation of organometallic compounds in conjunction with light alkali metals.[2] Many of the well studied species exhibit extended, delocalized π-systems, effectively stabilizing the negative charge residing on the carbon atom. In contrast, little work has been carried out to explore the structural chemistry of heteroatomic species, specifically those bearing a chalcogen atom.[3]

Since the ion association of the target compounds dictates the physical properties of the candidate molecules, the investigation of structural parameters in relation to metal, ligand, and donor is warranted. Critical factors in the formation of separated or contact ions are the Lewis base strength, size, and hapticity of the donor, the steric demand of the ligand, and its capacity for charge delocalization, in addition to the charge density of the metal center. The reduced capacity of simple, monodentate, heteroatomic ligands to delocalize electron density efficiently results in a reduced propensity to form separated species. Accordingly, only a small number of separated heteroatomic derivatives have been reported. Among those, pnicogen derivatives are most common, while chalcogen derivatives are more scarce.[3] To the best of our knowledge, only two structurally characterized alkali metal chalcogen derivatives have been reported [Li(12-crown-4)$_2$][SMes*][4] (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) and [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$],[5] where crown ether was utilized to effect the cation–anion separation.

Our interest in the coordination chemistry of alkali metal chalcogenolates stems from their central role in organic and inorganic synthetic chemistry. One goal of our research program is to identify parameters affecting solution and solid state structural chemistry in families of alkali metal thiolates and selenolates. We report here a systematic study where the permutation of the metal and donor sheds light on the propensity of alkali metal centers to form contact or separated ions in the solid state. Described are the separated species [Na(18-crown-6)(THF)$_2$][SMes*] **1**, [K(18-crown-6)(THF)$_2$][SMes*] **3**, and [K(18-crown-6)(THF)$_2$][SeMes*] **4**, as well as K(dibenzo-18-crown-6)(SMes*)·THF **2**, displaying a bond between potassium and sulfur. Electrochemical studies were carried out to investigate whether contact or separated ions could be detected in solution since separated thiolates are expected to oxidize at lower potentials than those that form close contacts with alkali metals.

Results

Synthesis

Acid/base chemistry involving the reaction of sodium or potassium hydride with arene-thiol or -selenol was utilized for the synthesis of compounds **1**–**4** eqn. (1) where (A = Na or K; E = S

$$\mathrm{AH + HER} + n\mathrm{D} \longrightarrow \mathrm{A(ER)D}_n + \mathrm{H_2} \qquad (1)$$

or Se; D = 18-crown-6, dibenzo-18-crown-6 or THF; R = 2,4,6-tBu$_3$C$_6$H$_2$ or 2,4,6-iPr$_3$C$_6$H$_2$). Hydrogen elimination reactions have been used successfully to prepare a variety of sodium and potassium chalcogenolates.[4–7] Generally, the reaction proceeds smoothly if the solubility of the alkali metal hydride is ensured by addition of a Lewis donor.

Crystallographic studies

Pertinent bond distances and angles for all compounds are given in Table 1, while Figs. 1–3 illustrate the structural principles displayed in compounds **1**–**4**. In each complex, geometrical data for the respective crown ether molecule and thiolate anion (bond distances and angles) were unexceptional

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Table 1 Selected bond distances (Å) and angles (°) for compounds **1**–**4**

[Na(18-crown-6)(THF)$_2$][SMes*] **1**					
Na(1)–O(1)	2.907(3)	Na(1)–O(4)	2.756(3)	Na(1)–O(7)	2.349(3)
Na(1)–O(2)	2.951(3)	Na(1)–O(5)	2.583(3)	Na(1)–O(8)	2.356(3)
Na(1)–O(3)	2.688(3)	Na(1)–O(6)	2.574(3)	S(1)–C(1)	1.761(3)
O(7)–Na(1)–O(8)	178.75(14)				
K(dibenzo-18-crown-6)(SMes*)·THF **2**					
K(1)–S(1)	3.174(2)	K(1)–O(3)	2.767(4)	K(1)–O(6)	2.786(4)
K(1)–O(1)	2.815(4)	K(1)–O(4)	2.812(4)	S(1)–C(1)	1.773(5)
K(1)–O(2)	2.821(4)	K(1)–O(5)	2.826(4)		
K(1)–S(1)–C(1)	97.3(2)	S(1)–K(1)–O(4)	107.68(1)		
S(1)–K(1)–O(1)	96.00(1)	S(1)–K(1)–O(5)	93.64(1)		
S(1)–K(1)–O(2)	113.98(11)	S(1)–K(1)–O(6)	85.41(1)		
S(1)–K(1)–O(3)	116.46(1)				
[K(18-crown-6)(THF)$_2$][SMes*] **3**					
K(1)–O(1)	2.819(5)	K(1)–O(4)	2.843(5)	K(1)–O(7)	2.744(8)
K(1)–O(2)	2.835(5)	K(1)–O(5)	2.740(5)	K(1)–O(8)	2.742(7)
K(1)–O(3)	2.730(6)	K(1)–O(6)	2.704(6)	S(1)–C(1)	1.742(7)
O(7)–K(1)–O(8)	172.1(3)				
[K(18-crown-6)(THF)$_2$][SeMes*] **4**					
K(1)–O(1)	2.841(4)	K(1)–O(4)	2.852(3)	K(1)–O(7)	2.746(6)
K(1)–O(2)	2.837(4)	K(1)–O(5)	2.750(3)	K(1)–O(8)	2.763(5)
K(1)–O(3)	2.740(4)	K(1)–O(6)	2.717(4)	Se(1)–C(1)	1.930(4)
O(7)–K(1)–O(8)	172.8(2)				

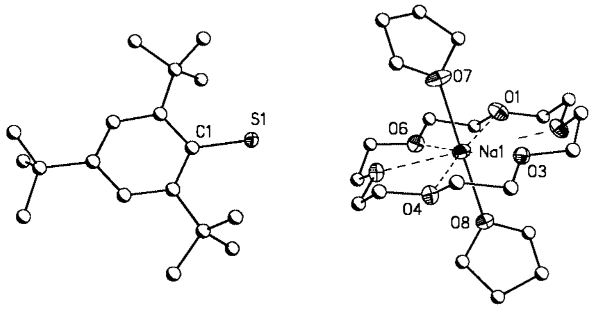

Fig. 1 Computer generated plot of compound **1** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

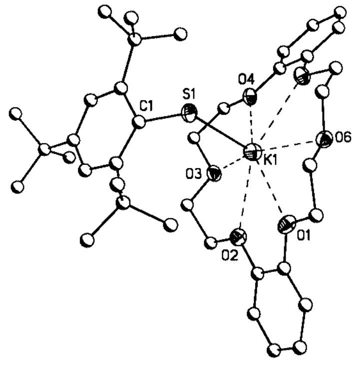

Fig. 2 Computer generated plot of compound **2**. Details as in Fig. 1.

and can be found in greater detail in the deposited crystal structure data.

[Na(18-crown-6)(THF)$_2$][SMes*] 1. Compound **1** crystallizes with separated anions and cations, as illustrated in Fig. 1. The cation and anion are formally separated by a distance greater than 5.0 Å. Na(1) is eight-coordinate with six crown ether oxygen interactions and two coordinating THF molecules, oriented *trans* to one another, as evidenced by the O(7)–Na(1)–O(8) bond angle of 178.75(14)°. The Na(1)–O(crown) contacts are observed between 2.574(3) and 2.951(3) Å. The closest Na(1)–O bonding is seen for the coordinating THF molecules with values of 2.349(3) and 2.356(3) Å. In the thiolate anion the S(1)–C(1) bond length is observed at 1.761(3) Å.

K(dibenzo-18-crown-6)(SMes*)·THF 2. Compound **2**, depicted in Fig. 2, crystallizes as a contact pair. K(1) is formally seven-coordinate with six crown ether contacts and one thiolato bond. The K(1)–S(1) bond distance is 3.174(2) Å, while the K(1)–O contacts range over 2.767(4)–2.826(4) Å. A narrow K(1)–S(1)–C(1) bond angle of 97.3(2)° leads to a subtle but marked orientation of the crown ether with respect to the thiolate. The S(1)–K(1)–O(3) bond angle is the widest (116.46(1)°), while the S(1)–K(1)–O(6) angle is accordingly compressed at 85.41(1)°. In the thiolate anion the S(1)–C(1) bond length is 1.773(5) Å.

[K(18-crown-6)(THF)$_2$][SMes*] 3. Compound **3** crystallizes as a separated ion pair. The overall structural motif of **3** is very similar to that of the sodium analog **1**. In compound **3** the cation and anion are clearly non-interacting with a cation–anion separation of over 5.0 Å. K(1) is formally eight-coordinate with six crown ether contacts and two THF molecules, occupying *trans*-related axial coordination sites, with a O(7)–K(1)–O(8) bond angle of 172.1(3)°. The K(1)–O(crown) contacts fall in the range of 2.704(6)–2.843(5) Å, while the THF ligands interact with K(1) at 2.742(7) and 2.744(8) Å. In the arenethiolate, the S(1)–C(1) bond distance is observed at 1.742(7) Å.

[K(18-crown-6)(THF)$_2$][SeMes*] 4. Compound **4** is shown in Fig. 3. The overall structural features of **4** are very similar to those observed in **1** and **3**, with a cation and anion separation of more than 5.0 Å. About the eight coordinate K(1), crown ether contacts range over 2.717(4)–2.852(3) Å, and the THF molecules interact at 2.746(6) and 2.763(5) Å. The *trans* orientation of the THF ligands is evidenced by the O(7)–K(1)–O(8) bond angle of 172.8(2)°. In the selenolate anion the Se(1)–C(1) bond distance is 1.930(4) Å.

Table 2 X-Ray ion-pairing and electrochemical parameters

Compound	X-Ray ion-pairing	Redox process (V)[a] I	II	III
1 [Na(18C6)(THF)$_2$][SMes*]	Separated	[b]	+0.24	[b]
2 [K(DB18C6)][SMes*]	Contact	−0.14	+0.25	+0.47[c]
3 [K(18C6)(THF)$_2$][SMes*]	Separated	−0.13	+0.32	[d]
5 [NaDB18C6)][SMes*]	Contact	−0.17	+0.25	+0.39[e]
6 [K(DB18C6)][STrip]	Contact	−0.07	+0.35	+0.46[f]

18C6 = 18-crown-6, DB = dibenzo. [a] Potential *vs.* Ag–AgCl. [b] Not measured. [c] $\Delta_{i_{pa}-i_{pc}}$ = 66 mV. [d] At higher concentrations no peak was observed. [e] $\Delta_{i_{pa}-i_{pc}}$ = 144 mV. [f] Irreversible.

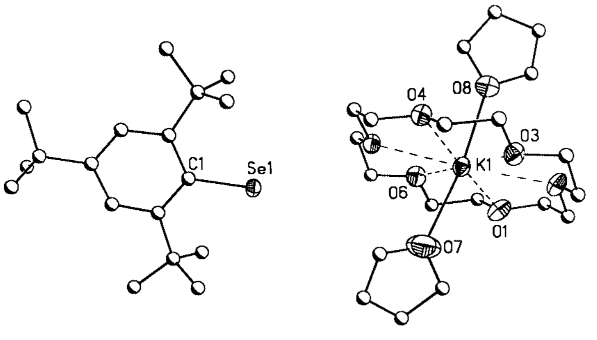

Fig. 3 Computer generated plot of compound **4**. Details as in Fig. 1.

Cyclic voltammetry

The cyclic voltammograms of compounds **1**–**3**, Na(dibenzo-18-crown-6)(SMes*) **5**,[8] and K(dibenzo-18-crown-6)(STrip)·THF, **6** (Trip = 2,4,6-iPr$_3$C$_6$H$_2$)[6g] were studied using a polished platinum working electrode, a platinum wire auxiliary electrode, and a Ag–AgCl reference electrode (BAS M1520: 0.194 V *vs.* NHE) in THF with 0.25 M NBu$_4$PF$_6$ as supporting electrolyte. The redox data are summarized in Table 2.

Cyclic voltammetry (CV) experiments showed a dramatic effect of alkali metal thiolate concentration on the oxidation processes observed. This is illustrated in Fig. 4 for compound **2**, where CV trace (a) is for a solution that is approximately ten times more concentrated than that of trace (b) (*ca.* 3 and 0.3 mM respectively). At lower concentration only a single irreversible oxidation process occurs at *ca.* +0.2 V. At higher concentration two additional redox processes appear; an irreversible wave at *ca.* −0.15 V and a reversible or quasireversible wave at *ca.* +0.5 V (I and III respectively in Fig. 4a). The redox process I grows in at the expense of II as the concentration increases up to 5 mM. Above 5 mM no change in peak I occurs and the reaction can fully be reversed by diluting the solution with electrolyte. All of the complexes studied showed peaks corresponding to I at higher concentrations, but III was observed only for the dibenzo-18-crown-6 complexes.

Discussion

Over the last decade a small, but growing number of well characterized alkali metal chalcogenolates[4–12] has appeared in the literature. Importantly, all but two compounds have been shown by X-ray crystallography to exhibit interactions between the alkali metal cation and the Group VIB anion, namely [Li(12-crown-4)$_2$][SMes*][4] and [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$],[5] where the combination of sterically demanding ligands and multidentate donor affected the cation–anion separation. Even though only limited structural work has been done, it is evident that ion separation commonly exists, specifically if bulky ligands are used in combination with multidentate donors, such as crown ethers.[13] Significantly, the formation of separated ions is often accompanied by drastic changes of physical properties, such as solubility or volatility, which can be utilized favorably in various applications.

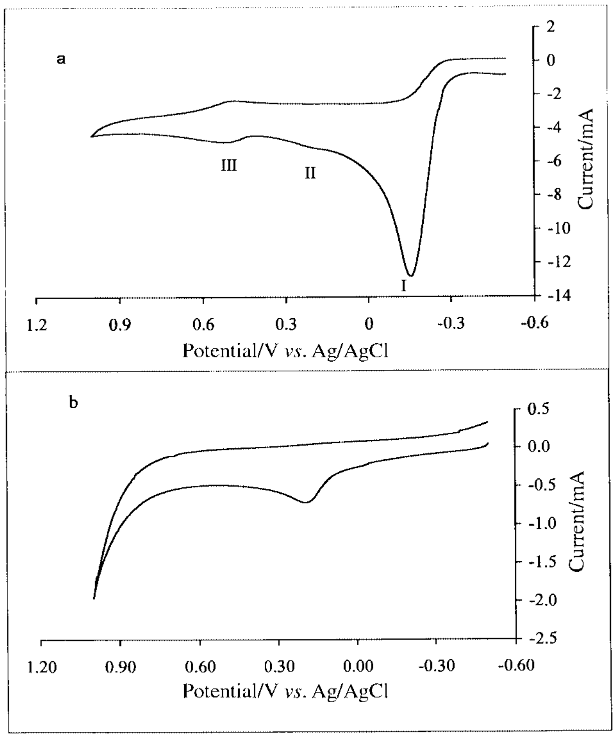

Fig. 4 Cyclic voltammograms of compound **2** at (a) 3.0 mM and at (b) 0.03 mM in 0.25 M NBu$_4$PF$_6$ in dry THF, using a 0.75 mm^2 platinum working electrode, platinum wire auxiliary electrode and a Ag–AgCl reference electrode with a scan rate of 0.1 V s^{-1}.

Lithium thiolates have been intensively investigated.[6b,10] In contrast, much less is known about either (1) the heavy chalcogen congeners,[7b,11,12] or (2) the heavy alkali derivatives.[6] Remarkably, all but two of the structurally characterized alkali chalcogenolates display cation–anion interactions. In marked contrast, compounds **1**, **3** and **4** are the first structurally characterized sodium and potassium thiolates and selenolates displaying separated anions and cations. Moreover, compound **4** is a rare example of a well characterized heavy alkali metal selenolate.

The combination of a sterically encumbered thiolate or selenolate ligand with crown ether leads to contact or separated alkali-metal thiolates or selenolates. The cation–anion interaction in K(dibenzo-18-crown-6)(SMes*)·THF **2** is a result of the cup-shaped crown ether conformation in the solid state, facilitating the approach of the thiolate anion to the cation (see Fig. 2). A similar structural motif was observed in K(dibenzo-18-crown-6)(STrip)·THF **6**.[6g] Again, the cup shape of the crown ether allowed a close approach of the anion. The K–S bond length in **2** (3.174(2) Å) compares favorably with those of related potassium thiolates, such as the eight coordinate K(dibenzo-18-crown-6)(HMPA)SCPh$_3$ (3.216 Å)[6f] (HMPA = hexamethylphosphoramide), K(dibenzo-18-crown-6)(THF)-(STrip) (3.202 Å),[6g] or the pseudo eight-coordinate K(dibenzo-18-crown-6)(C$_6$H$_6$)(SCPh$_3$) (3.135 Å, CN = 7 + arene), where a weak arene–metal interaction is filling the coordination void in the cup-shaped face of the crown ether.[6f]

The structural outcome changes dramatically if 18-crown-6 is employed, and the separated derivatives **1**, **3** and **4** are observed. The three compounds are structurally very similar, featuring eight-coordinate sodium (**1**) or potassium (**3**, **4**) cations with 18-crown-6 in the equatorial plane and two THF molecules in axial positions in addition to a separated thiolate (**1**, **3**) or selenolate (**4**) anion. The coordination of THF and 18-crown-6 about sodium or potassium has been recognized earlier as favorable for these metals.[14]

In contrast to the contact pair **2**, the almost planar solid-state conformation of 18-crown-6 prohibits the approach of the sterically demanding EMes* ligand (E = S or Se) to the cation, favoring the coordination of two THF donors. This result may be compared to that of K(18-crown-6)(TeTrip), displaying a cation–anion interaction of 3.499(1) Å.[7a] Apparently, the increased size of tellurium, as compared to sulfur or selenium, results in decreased effective ligand bulk, and the approach of the sterically encumbered tellurolate ligand becomes possible, despite the in-plane orientation of the crown ether. This result may also be compared with those for two magnesium thiolates, where the steric bulk of the ligand affected the formation of either contact or separated ions.[13c] Use of the sterically demanding SMes* in combination with 15-crown-5 and THF yielded the separated [Mg(15-crown-5)(THF)$_2$][SMes*]$_2$, while the smaller SCPh$_3$ anion forms bonds with magnesium, as observed in Mg(15-crown-5)(SCPh$_3$)$_2$.

Cyclic voltammetry experiments and thiolate trapping studies

Cyclic voltammetry experiments were conducted on compounds **1**–**3**, **5**, and **6** to determine if a correlation exists between the oxidation potential of alkali metal thiolates and the nature of the solid state metal–sulfur interaction as revealed by crystallographic studies. Free thiolates, such as PhS$^-$, undergo oxidation near 0 V (*vs.* SCE), followed by a very fast dimerization step, with rate constants in the range of 2×10^8 to 2×10^{10} M^{-1} s^{-1}.[15,16] In contrast, thiolates bonded to metals usually oxidize at higher potentials and are thus 'protected' by coordination to a metal. For example, in linear phosphine gold(I) thiolate complexes an irreversible sulfur-based oxidation process is observed at potentials above +0.5 V (*vs.* SCE)[17] and a magnesium complex with bridging thiolates, Mg(py)$_3$(μ-SPh)$_3$-Mg(μ-SPh)$_3$Mg(py)$_3$, shows only an irreversible oxidation at +0.975 mV (*vs.* Ag–AgCl).[18]

As noted in the Results section, the concentration dependence of the cyclic voltammetry experiments is striking. Although this precludes making conclusions about a correlation between peak potential and the degree of ion pairing, it reveals a dynamic and complex process occurring in solution.[19] At low concentrations (0.1–0.3 mM) a single, irreversible wave is observed for all compounds studied. Although minor differences were observed in wave shape and potential, Fig. 4b (complex **2**) is representative of the data set. To consider what type of oxidation process is involved in wave II, it is useful to recognize that **2** is composed of three parts: (a) dibenzo-18-crown-6, (b) K$^+$, and (c) [SMes*]$^-$. The oxidation of free dibenzo-18-crown-6 and alkali metal–dibenzo-18-crown-6 compounds has electrochemically been investigated by cyclic voltammetry.[20] No oxidation process is observed if the potential is kept below +1.5 V (*vs.* SCE).[16] These observations strongly suggest that peak II has a significant contribution from the SMes* ligand connected to the alkali metal cation. In comparison to Au(PPh$_3$)-(SC$_6$H$_4$CH$_3$-*p*), which oxidizes at +0.56 V (*vs.* SCE), **2** oxidizes at *ca.* +0.2 (*vs.* Ag–AgCl).[17] This is reasonable since the more covalently bound gold thiolate is expected better to 'protect' the thiolate ligand from oxidation.

At higher concentrations (0.5–17 mM) a significant change is observed in the wave shapes for all compounds studied. In Fig. 4a (complex **2**) a new irreversible oxidation process appears, labeled I. Savéant and co-workers investigated the potentials for the oxidation of *para*-substituted arenethiolates and found a linear correlation between oxidation potential and the Hammett σ coefficient of the *para* substituent group.[15] Extrapolation of their data,[21] using Hammett σ coefficients from Jaffé,[22] leads to an estimation of the oxidation potentials for [SMes*]$^-$ and [STrip]$^-$ as −0.16 and −0.11 V (*vs.* SCE), respectively.[21,22] For all of the SMes* compounds studied, peak I occurred in the narrow range of -0.17 ± 0.03 V (*vs.* Ag–AgCl), suggesting that it represents the oxidation of "free" thiolate ligands in solution. Consistent with this are CV experiments on concentrated solutions of **6**, containing *i*-Pr rather than *t*-Bu substituents on the thiolate. These show peak I occurring at −0.07 V, *ca.* 80 mV more positive than peak I for **2**.

Further verification that separated thiolate forms at higher concentration was provided by thiolate trapping experiments using trimethyl phosphate.[23a] This reagent is rapidly demethylated by nucleophilic thiolates according to eqn. (2). An 8.5 mM

$$\mathrm{SR^- + (CH_3O)_3PO \longrightarrow CH_3SR + [(CH_3O)_2PO_2]^-} \quad (2)$$

solution of compound **5** in THF-d$_8$ was treated with approximately 1 molar equivalent of (CH$_3$O)$_3$PO. The ^{1}H NMR spectrum, recorded within 4 minutes, showed a new peak at δ 2.1 which is assigned to the SCH$_3$ resonance, CH$_3$SMes*.[23b] In contrast, a 0.085 mM solution of Na(dibenzo-18-crown-6)(SMes*) does not react with an excess of (CH$_3$O)$_3$PO after 5 hours. These experiments are consistent with the cyclic voltammetry studies which suggest that separated thiolate is formed at higher concentrations.

A possible explanation for the unusual formation of separated ions at higher concentration [in contrast to the well established behavior of electrolytes where dissociation decreases as concentration increases] involves either additional solvation of the alkali metal crown ether thiolate compounds, or the establishment of an equilibrium where as the concentration is increased two or more complexes react with release of free thiolate. The mechanistic details are unknown at this time. However, at higher concentration most of the oxidation current originates in I and only a trace of process II is observed. (The peak current for I in Fig. 4a is about 20 times greater than II in Fig. 4b.) Thus, as the concentration is increased formation of separated thiolate is fairly complete by 5 mM.

Fig. 4(a) also shows a reversible or quasi-reversible redox couple labeled III at *ca.* +0.5 V. This couple appears in cyclic voltammograms of alkali metal thiolate compounds containing dibenzo-18-crown-6 ethers, but not for the 18-crown-6 compound tested (**3**), suggesting that III forms as a result of the redox reactivity of the dibenzo moiety.[20,24]

Observations and conclusions

The synthesis and characterization of a family of sodium and potassium thiolates and selenolates shows that small changes (use of 18-crown-6 instead of dibenzo-18-crown-6) affects the ion pairing in the solid state. The arguments seem to be mainly based on steric reasons: dibenzo-18-crown-6 adopts a cup-shaped arrangement, allowing the approach of the sterically demanding ligand. In contrast, 18-crown-6 exhibits an almost planar orientation, with consequent steric repulsion between the ligand and the crown ether, and ion separation with formation of [A(18-crown-6)(THF)$_2$][EMes*] (A = Na or K; E = S or Se). Cyclic voltammetry experiments indicate that some degree of ion pairing occurs for all complexes in solution at low concentration. At higher concentrations, separated thiolate forms as a result of solvation processes or the establishment of an equilibrium where two or more complexes react with formation of free thiolate. The release of thiolate was confirmed for **5** by treating concentrated solutions of the alkali metal thiolate with (CH$_3$O)$_3$PO, a thiolate trapping reagent.

Experimental

General procedures

All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and/or a dry box. n-Hexane and tetrahydrofuran (THF) for synthetic purposes were distilled prior to use from a Na/K alloy followed by two freeze–pump–thaw cycles. THF for electrochemical studies was distilled over sodium–benzophenone. Trimethyl phosphate, $(CH_3O)_3PO$, was purchased from Aldrich and used as received. Commercially available 18-crown-6 was dissolved in freshly distilled diethyl ether and stirred with finely cut sodium metal for one day. After filtration from the metal, the crown was recrystallized at -20 °C and used as isolated. Dibenzo-18-crown-6 was kept at 50 °C in vacuum for several hours. Mineral oil suspensions of NaH and KH were each washed repeatedly with freshly distilled hexane and dried under vacuum. HSMes* and HSeMes* were prepared utilizing literature procedures.[11f,25,26] Commercially available (98%) tetrabutylammonium hexafluorophosphate was used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-300 and Varian Gemini 300 spectrometers, infrared spectra as Nujol mulls between KBr plates on a Perkin-Elmer PE 1600 FT-IR spectrometer. Elemental analysis was precluded by the high moisture sensitivity of the compounds reported. In addition, thiolates tend to give notoriously unreliable elemental analyses due to the formation of non-volatile metal sulfides.

Procedure for the synthesis of compounds 1–4

A 100 mL Schlenk flask was charged with NaH or KH, crown ether and HSMes*. Approximately 25 mL of THF were added, resulting in the evolution of H_2. The homogeneous reaction mixture was stirred at room temperature for one hour then filtered through a Celite padded frit.

[Na(18-crown-6)(THF)$_2$][SMes*] 1. 0.03 g (1.0 mmol) NaH, 0.26 g (1.0 mmol) 18-crown-6, 0.28 g (1.0 mmol) of HSMes*, 25 mL THF, and 5 mL hexane. Cooling to 0 °C for several days yielded colorless crystals in 27% yield (0.19 g). The white powder decomposed to a brown oil above 200 °C. ^{1}H NMR (THF-d$_8$): δ 6.90 (s, 2 H), 3.55 (s, 24 H), 1.73 (s, 18 H) and 1.20 (s, 9 H). ^{13}C-{^{1}H} NMR (THF-d$_8$): δ 159.49, 149.70, 135.11, 119.79, 70.93, 39.36, 35.02, 32.69 and 31.75. IR (cm^{-1}) (Nujol): 2934s, 1463s, 1377s, 1352s, 1283m, 1244m, 1210w, 1186w, 1111s, 1059m, 1044m, 969s, 914m, 874w, 846m, 758w, 722w and 616w.

K(dibenzo-18-crown-6)(SMes*)·THF 2. 0.04 g (1.0 mmol) KH, 0.36 g (1.0 mmol) dibenzo-18-crown-6, 0.28 g (1.0 mmol) HSMes*, and 20 mL THF. Pale tan solution, stirring at room temperature for one hour, heated briefly to reflux, immediate filtration through a Celite padded frit. Colorless crystals after cooling to 0 °C in 61% yield (0.48 g). The white powder decomposed to a brown oil above 220 °C. ^{1}H NMR (THF-d$_8$): δ 7.02 (s, 2 H), 6.95–6.84 (doublet m, 8 H), 4.13 (broad d, 8 H), 4.02 (broad d, 8 H), 1.72 (s, 18 H) and 1.25 (s, 9 H). ^{13}C-{^{1}H} NMR (THF-d$_8$): δ 156.40, 150.16, 148.41, 136.52, 127.72, 120.06, 111.92, 69.72, 68.22, 39.13, 34.93, 32.48 and 31.64. IR (cm^{-1}) (NaCl, Nujol): 2915s, 1592m, 1504s, 1455s, 1377s, 1340w, 1321m, 1284w, 1247s, 1209s, 1124s, 1066s, 944s, 914m, 871w, 854w, 775m and 748s.

[K(18-crown-6)(THF)$_2$][SMes*] 3. 0.04 g (1.0 mmol) KH, 0.26 g (1.0 mmol) 18-crown-6, 0.28 g (1.0 mmol) of HSMes*, and 20 mL of THF. Formation of a clear, pale tan mixture. Stirring for one hour at room temperature, brief heating, filtration through a Celite padded frit. Addition of 5 mL hexane, reduction of volume to 5 mL under vacuum. Cooling to 0 °C for several days yielded colorless crystals in 63% yield (0.46 g). The white powder decomposed to a light brown solid above 255 °C. ^{1}H NMR (THF-d$_8$): δ 6.95 (s, 2 H), 3.60 (s, 24 H), 1.76 (s, 18 H) and 1.22 (s, 9 H). ^{13}C-{^{1}H} NMR (THF-d$_8$): δ 157.50, 149.55, 135.82, 119.80, 71.09, 39.15, 34.88, 32.47, 31.71. IR (cm^{-1}) (Nujol): 2857s, 1591w, 1463s, 1376s, 1350s, 1283m, 1247m, 1155m, 1107s, 1045s, 965s, 838m, 722w, 618w, 530w and 492w.

[K(18-crown-6)(THF)$_2$][SeMes*] 4. 0.04 g (1.0 mmol) KH, 0.26 g (1.0 mmol) 18-crown-6, 0.33 g (1.0 mmol) freshly prepared HSeMes*, 20 mL THF, homogeneous yellow solution. Addition of 10 mL of hexane, reduction of volume under vacuum. Cooling to 0 °C, clear crystals within several days in 43% yield (0.33 g). The yellow powder decomposed to a brown solid above 230 °C. ^{1}H NMR (THF-d$_8$): δ 6.94 (s, 2 H), 3.55 (s, 24 H), 1.77 (s, 18 H) and 1.19 (s, 9 H). ^{13}C-{^{1}H} NMR (THF-d$_8$): δ 152.19, 146.58, 140.31, 119.91, 71.12, 40.12, 35.03, 32.47 and 32.25. IR (cm^{-1}) (Nujol): 3040w, 1585w, 1524w, 1462s, 1379s, 1344s, 1282s, 1248s, 1213m, 1110s, 1006s, 951s, 875m, 834s, 738s, 627w, 572w, 531w and 476w.

Electrochemical studies

In a VAC model HE-493 dry-box, 1 to 40 mg of crown ether metal thiolate was added to 6 mL of 0.25 M NBu_4PF_6 in THF. Cyclic voltammetry experiments were conducted on these solutions with an EG&G model 273 potentiostat/galvanostat interfaced with a Micron 75 MHz Powerstation using EG&G's m270 software. A 2 mm^2 platinum disc working electrode, polished with 1.0 μm water-soluble diamond suspension (Buehler) on a Buehler microcloth, with a 0.5 mm platinum wire coiled parallel to the working electrode at a distance of 4 mm and a Ag–AgCl reference electrode (BAS # MF 2063) were employed. The working electrode was polished between each experiment, and the other electrodes and the cell were rinsed thoroughly with distilled, dry THF. Cyclic voltammograms of ferrocene and the electrolyte solution were taken under the same conditions to assure that the cell was in working order.

Thiolate trapping studies

In the VAC model HE-493 dry-box, two solutions were prepared by dissolving 5 ± 1 mg (a) and a trace (b) of Na(dibenzo-18-crown-6)(SMes*), respectively, in 0.85 mL THF-d$_8$ (Aldrich 99.99% dry, sealed under nitrogen). The concentration of the first solution (a) was 8.5 mM. The concentration of the dilute solution (b) was estimated to be 0.085 mM on the basis of integration of the crown ether protons relative to an internal standard added to each tube. These solutions were transferred to 5 mm NMR tubes and sealed with rubber septa. In air, 10 μL trimethyl phosphate was diluted in 0.85 mL THF-d$_8$ to which 10 μL tetramethylsilane had been added. This resulted in a solution where 10 μL contained 1 μmol trimethyl phosphate (TMP). The tubes containing the crown ether complexes were removed from the dry-box and 60 and 10 μL of the TMP reagent solution were injected into the concentrated and dilute solutions, respectively. The ^{1}H NMR spectra were recorded within minutes.

X-Ray crystallographic studies

X-Ray quality crystals for all compounds were grown as described. The crystals were placed on the diffractometer as described earlier.[27] Data sets for compounds **2** and **4** were collected using a Rigaku AFC5S diffractometer equipped with a Molecular Structure Corporation low temperature device and graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Three standard reflections were measured every 150 and showed in both cases only statistical variation of the intensity (<1.5%). The intensities were corrected for Lorentz and polarization effects; extinction was disregarded. An absorption correction was applied using semi-empirical psi scans. The intensity data set for compound **1** was collected on a Siemens P4 diffractometer equipped with a locally modified Enraf Nonius low temperature device using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data for **3** were collected using a Siemens R3m/V rotating anode equipped with a locally modified Siemens LT 2 low temperature device, utilizing Ni-filtered Cu-Kα radiation ($\lambda = 1.54178$ Å). Absorption

Table 3 Crystallographic data for compounds **1**–**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{38}H_{69}NaO_8S$	$C_{42}H_{61}KO_7S$	$C_{38}H_{69}KO_8S$	$C_{38}H_{69}KO_8Se$
M	708.98	749.07	725.09	771.99
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2(1)/n$
a/Å	10.598(3)	10.029(2)	10.680(5)	10.778(2)
b/Å	16.124(6)	13.819(3)	16.110(1)	16.129(3)
c/Å	24.430(8)	15.207(3)	24.857(1)	25.169(5)
α/°		92.41(3)		
β/°	92.41(3)	91.39(3)	92.72(4)	93.60(3)
γ/°		106.17(3)		
V/Å^3	4171(2)	2021.0(7)	4272(4)	4366.7(14)
Z	4	2	4	4
μ/mm^{-1}	0.133	0.231	1.897	0.998
T/K	126	213	213	213
Independent reflections	7768	4973	4865	7674
Observed reflections ($>2\sigma$)	4511	2775	3214	4424
$R1$, $wR2$ (all data)	0.1277, 0.1687	0.1509, 0.1945	0.1471, 0.2788	0.1350, 0.1578
($>2\sigma$)	0.0654, 0.1332	0.0642, 0.1554	0.0999, 0.2416	0.0575, 0.1280

corrections for compounds **1** and **3** were performed with the program XABS2.[28] The crystal structures of all compounds were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXL).[29] Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was handled by including split positions for the affected groups, and included the refinement of the respective occupancies. A set of restraints was applied to aid in the modeling. Crystallographic parameters for compounds **1**–**4** are summarized in Table 3.

CCDC reference number 186/1966.

See http://www.rsc.org/suppdata/dt/b0/b000665n/ for crystallographic files in .cif format.

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